

KUNO KASAK

Greenhouse gas emissions and water
treatment efficiency in subsurface
flow filters using various substrates



DISSERTATIONES TECHNOLOGIAE CIRCUMIECTORUM
UNIVERSITATIS TARTUENSIS

24

KUNO KASAK

Greenhouse gas emissions and water
treatment efficiency in subsurface
flow filters using various substrates



Department of Geography, Institute of Ecology and Earth Sciences, Faculty of Science and Technology, University of Tartu, Estonia

This dissertation has been accepted for the commencement of the degree of *Doctor philosophiae* in Environmental Technology at the University of Tartu on April 25, 2016 by the Scientific Council on Environmental Technology, faculty of Science and Technology, University of Tartu.

Supervisors: Prof. Dr. Ülo Mander
Institute of Ecology and Earth Sciences
University of Tartu
Estonia

Senior Research Fellow Dr. Marika Truu
Institute of Ecology and Earth Sciences
University of Tartu
Estonia

Opponent: Assoc. Prof. Dr. Florent Chazarenc
Ecole des Mines de Nantes
France

Commencement: J.G. Granö auditorium (Room 327), 46 Vanemuise Street, Tartu, on 21 June 2016 at 10.15 a.m.

Publication of this thesis is granted by the Institute of Ecology and Earth Sciences, University of Tartu

ISSN 1736-3349
ISBN 978-9949-77-102-8 (print)
ISBN 978-9949-77-103-5 (pdf)

Copyright: Kuno Kasak, 2016
University of Tartu Press
www.tyk.ee

TABLE OF CONTENTS

ORIGINAL PUBLICATIONS	6
ABBREVIATIONS	7
ABSTRACT	8
1. INTRODUCTION.....	10
1.1. Subsurface flow filters for greywater and municipal wastewater treatment	10
1.2. Filter materials used in subsurface flow filters.....	12
1.3. Greenhouse gas emissions from subsurface flow filters.....	13
1.4. The aim of the thesis.....	14
2. MATERIALS AND METHODS	15
2.1. Greywater treatment system – first experiment.....	15
2.2. Municipal wastewater treatment systems	16
2.2.1. The mesocosm study - second experiment.....	16
2.2.2. The full-scale study - third experiment	16
2.3. Meta-analysis of the sand, gravel and LECA filled HSSF CWs and their GHG emissions.....	17
2.4. Sampling and statistical analyses	18
2.4.1. Water sampling	18
2.4.2. Gas flux measurements and calculations.....	18
2.4.3. Statistical analyses.....	19
3. RESULTS AND DISCUSSION	21
3.1. Greywater and municipal wastewater treatment.....	21
3.1.1. Changes in wastewater pH	21
3.1.2. Nitrogen removal.....	23
3.1.3. Reduction of COD and TOC values.....	25
3.1.4. Phosphorus removal	26
3.2. Effect of the filter material on greenhouse gas emissions from the HSSF filters	28
3.2.1. CO ₂ emission.....	29
3.2.2. CH ₄ emission.....	32
3.2.3. N ₂ O emission.....	35
4. CONCLUSIONS.....	39
5. REFERENCES.....	41
SUMMARY IN ESTONIAN	49
ACKNOWLEDGEMENTS	52
APPENDIX	53
PUBLICATIONS	55
CURRICULUM VITAE	119
ELULOOKIRJELDUS.....	123

ORIGINAL PUBLICATIONS

- I. Karabelnik, K., Kõiv, M., **Kasak, K.**, Jenssen, P.D., Mander, Ü. 2012. High strength greywater treatment in compact hybrid filter systems with alternative substrates. *Ecological Engineering*, 49, 84–92, j.ecoleng.2012.08.035.
- II. Mander, Ü., Dotro, G., Ebie, Y., Towprayoon, S., Chiemchaisri, C., Nogueira, S.F., Jamsranjav, B., **Kasak, K.**, Truu, J., Tournebize, J., Mitsch, W.J. 2014. Greenhouse gas emissions in constructed wetlands for wastewater treatment: a review. *Ecological Engineering*, 66, 19–35, j.ecoleng.2013.12.006.
- III. **Kasak, K.**, Mander, Ü., Truu, J., Truu, M., Järveoja, J., Maddison, M., Teemusk, A. 2015. Alternative filter material removes phosphorus and mitigates greenhouse gas emissions in horizontal subsurface flow filters for wastewater treatment. *Ecological Engineering*, 77, 242–249, jecoleng.2015.01.038.
- IV. **Kasak, K.**, Mõtlep, R., Truu, M., Truu, J., Kõiv-Vainik, M., Espenberg, M., Paiste, P., Kirsimäe, K., Mander, Ü. 201X. Hydrated oil shale ash mitigates greenhouse gas emissions from horizontal subsurface flow filters for wastewater treatment. (submitted)

Author's contribution

Publication I: Author was partly responsible for the fieldwork and data collection (about 50%), analyses (about 50%), and for writing the manuscript (about 40%).

Publication II: Author was partly responsible for the data collection (about 10%), analyses (about 40%), and for writing the manuscript (about 20%).

Publication III: Author designed the experiment unit and was responsible for the fieldworks and data collection (90%), analyses (about 90%), and for writing the manuscript (about 80%).

Publication IV: Author was responsible for the fieldwork and data collection (80%), analyses (about 90%), and for writing the manuscript (about 80%).

ABBREVIATIONS

CH₄ – methane
CO₂ – carbon dioxide
COD – chemical oxygen demand
CW – constructed wetland
H₂S – hydrogen sulfide
HLR – hydraulic loading rate
HOSA – hydrated oil shale ash
HS⁻ – bisulfide ion
HSSF – horizontal subsurface flow
LECA – light-weight expanded clay aggregate
N – nitrogen
N₂O – nitrous oxide
NH₃-N – ammonia nitrogen
NH₄-N – ammonium nitrogen
P – phosphorus
PE – purification efficiency
Q – discharge
SO₄²⁻ – sulfate ion
SRB – sulfur reducing bacteria
SSF – subsurface flow
TAN – total ammoniacal nitrogen
TN – total nitrogen
TOC – total organic carbon
TP – total phosphorus
VSSF – vertical subsurface flow

ABSTRACT

In this dissertation the performance and efficiency of various filter materials in order to remove nutrients and organic compounds from greywater and municipal wastewater and its impact on greenhouse gas emissions (GHG) are assessed.

In 2009–2011, a greywater treatment system was established to determine the performance of Filtralite[®], Filtralite-P[®] and hydrated oil shale ash (HOSA) in vertical- and horizontal subsurface flow filters in order to remove nutrients and organic compounds in different hydraulic loading regimes. In 2012–2013, a municipal wastewater treatment experiment was conducted to analyse the wastewater treatment efficiency and its impact on GHG emissions in horizontal subsurface flow (HSSF) filters that were filled with well mineralised peat, HOSA and combinations of peat and HOSA (Publication III). In 2013–2015, a full-scale experiment was performed to analyse GHG emissions from HOSA filled HSSF filters using different hydraulic loading regimes (Publication IV).

The water treatment efficiencies from greywater and municipal wastewater studies showed good results in order to reduce nutrient concentration. Total nitrogen (TN) removal from Filtralite[®] filled systems achieved a purification efficiency of up to 55%, specifically in the vertical subsurface flow (VSSF) filters, with a median effluent concentration between 5.5–6.5 mg N L⁻¹. In the HOSA filters, the TN removal was 46%, with a median effluent concentration of 6 mg N L⁻¹. Nitrogen removal from peat, HOSA, and peat/HOSA filters was rather low, achieving a purification efficiency of between 25–36%, with a median effluent concentration of 38.5–48.5 mg N L⁻¹. Total phosphorus (TP) removal by the HOSA filters was outstanding in both studies, with a median removal rate of 86–99%, compared to the 40–44% found in Filtralite[®] and peat filters. Surprisingly, the increased loading rate from 32.5 to 80 L d⁻¹ per treatment unit did not affect water treatment efficiency. The reduction of organic matter values in VSSF filters presented in the greywater treatment system was outstanding, achieving purification efficiency of up to 88% while in the HSSF filters the effectiveness was around 3–7%. Total organic carbon (TOC) removal in HOSA filters was also surprisingly high – up to 52%.

The greenhouse gas emission levels (CO₂, CH₄ and N₂O) measured in wastewater treatment systems showed a significantly lower level of emissions when compared to various widely used filter materials (e.g. sand, gravel, LECA etc.) that are commonly used in HSSF filters (Publication II). The lowest median CO₂ emissions (-6.3 to -7.9 mg CO₂-C m⁻² h⁻¹) were found in systems where HOSA was used. The highest emissions were registered in the HSSF filters where peat (Publication III), sand, gravel or LECA (Publication II) was used as the main filter media. CH₄ emissions were significantly lower in peat and HOSA filters, with a median value of 70 µg CH₄-C m⁻² h⁻¹, compared with the 6400 µg m⁻² h⁻¹, with sand, gravel and LECA filters. Surprisingly, filters with a peat/HOSA combination emitted a high amount of CH₄, probably due to the optimal pH. According to the N₂O emission, there were no significant

differences between peat and HOSA filters and with the sand, gravel and LECA filters. Median values were between 19.9 to 130 $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ in all cases.

Based on the results, this dissertation concludes that the most effective water treatment system can be combined with the use of crushed Filtralite® in VSSF filters and HOSA in HSSF flow filters. This kind of setup will result in effective nitrogen and organic matter removal in VSSF filters and high phosphorus removal in HSSF filters. In addition, the use of HOSA in HSSF filters will reduce the GHG emissions, substantially.

1. INTRODUCTION

1.1. Subsurface flow filters for greywater and municipal wastewater treatment

Constructed wetlands (CWs) are engineered systems designed to utilise natural processes in the treatment of wastewater. We have more than 50 years-worth of experience in the use of CWs for wastewater treatment but their technology has developed substantially over the past two decades (Vymazal, 2011a). The advancements made in this sustainable treatment technology during the past decades have allowed the construction of ecologically and economically constructive treatment systems that compete with or have even better purification efficiency ratings than the conventional wastewater treatment systems.

CWs can be categorised according to several design parameters; however the three main criteria are: hydrology (free water surface flow or subsurface flow) in the wetland unit, presence or absence of macrophytes, and flow path (horizontal and/or vertical) (Kadlec and Wallace, 2009; Vymazal, 2011a).

In horizontal subsurface flow (HSSF) CWs, the wastewater flows slowly through the water saturated filter material and often-emergent vegetation is planted on the filter. During the flow, the wastewater flows through different zones – aerobic, anaerobic and anoxic (Kadlec and Wallace, 2009; Vymazal, 2011a). However, in most parts of the HSSF filter bed, anaerobic conditions prevail due to the state of permanent water saturation. Aerobic conditions are presented only in the top layer of the filter bed, where the oxygen diffusion from air and leakage from plant roots and rhizomes occurs. In most cases, HSSF CWs are planted with various species of macrophytes, of which the common reed (*Phragmites australis*) and cattail (*Typha latifolia*) are the most common (Vymazal and Kröpfelová, 2009a). However, in cases where plants are not used, these systems are named as subsurface flow filters (SSF).

HSSF filters are commonly used in secondary wastewater treatment and have proven to be effective in the removal of organic matter, nitrogen, suspended solids, microbial pollution and heavy metals (Zurita et al., 2009). In HSSF filters, bacteria — under aerobic and anaerobic conditions — will degrade organic compounds. However, it has been shown that due to the insufficient amount of oxygen in the filter body, aerobic decomposition takes place only in the top layer of the filter system and anaerobic treatment processes play a key role in organic matter degradation in these systems (Kadlec and Wallace, 2009). Due to the lack of oxygen, the nitrification process is limited and anaerobic denitrification is the main N transformation process in HSSF filters (Kadlec and Wallace, 2009). Phosphorus (P) removal, however, is usually quite low and is therefore the most critical process in these filters (Vymazal, 2007). This problem is usually solved either by utilising a special filter material in the filters, or by implementing an additional treatment step (P saturation by aluminium or ferric based chemicals) to the process.

VSSF filters are not water saturated and thus perform aerobic purification processes. Wastewater is usually pumped intermittently on the filter surface which then flows down through the filter material and is collected by the drainage pipes at the bottom (Mander et al., 2011). As the system drains completely it allows more oxygen transfer to the filter bed and therefore supports the nitrification process. VSSF filters have a good ability to remove nitrogen, organic compounds and suspended solids (Vymazal & Kröpfelová, 2009b) as well as to oxidise ammonia. Some wastewater types — e.g. landfill leachate and food processing wastewater — can have ammonia level up to hundreds of milligrams per litre, and therefore aerobic nitrification in VSSF filters is an important part of water treatment (Kadlec and Wallace, 2009).

In France, the two stage vertical flow CW (also known as the French system) treating domestic wastewater is the most common design. However, the special feature of that system is that it accepts raw wastewater directly into the first stage of treatment process, allowing for easier sludge management in comparison to handling the primary treatment with a settling tank (Molle et al., 2005). Treatment system usually consists of two-stage filters which are both filled with different fractions of gravel and sand. The important difference with regular VSSF filters is that the primary stage unit is fed with full organic load during the feeding phase, which lasts several days, before being rested for twice the amount of loading days. These feeding and resting phases are elementary in regulating the growth of biomass on the filter media and maintaining aerobic conditions. The effluent of first stage is expressed to the second phase to complete the treatment process, especially nitrification (Boutin and Lienard, 2003; Molle et al., 2005). This system is excellent for organic matter removal and nitrogen reduction; however, its phosphorus removal is often insignificant.

HSSF CWs are mainly used for municipal wastewater treatment, but these systems have increased popularity in the treatment of greywater and landfill leachate, as well as in the purification of agricultural and industrial wastewaters. Numerous studies have been carried out to analyse the wastewater treatment capacity (Morari and Giardini, 2009; Sklarz et al., 2009; Pöldvere et al., 2010; Melian et al., 2010; Vymazal and Kröpfelová, 2011; Vymazal, 2011b; Amado et al., 2012; Vymazal, 2014) and the greywater purification capacity (Jenssen and Vråle, 2003; Li et al., 2009; Eriksson et al., 2009; Revitt et al., 2011; Leal et al., 2011; Kasak et al., 2011) of the HSSF filters.

Various types of CWs may be combined in order to achieve the higher treatment effects of the system, especially with regard to nitrogen and phosphorus removal (Vymazal, 2005). The combination of vertical and horizontal subsurface flow CWs are often named as hybrid CWs (Kadlec and Wallace, 2009). These combinations have proven to be powerful wastewater treatment systems, providing multiple treatment processes. Hybrid subsurface flow CWs have shown high potential especially for total nitrogen removal, since the nitrogen that enters into the system is nitrified in the first compartment (VSSF) and denitrified in the second compartment (HSSF) of the system (Melian et al., 2010).

1.2. Filter materials used in subsurface flow filters

The selection of a proper filter material for the SSF filters is one of the most crucial filter design issues. Numerous studies have been carried out to analyse the suitability of different natural filter materials such as sand, gravel, peat and mineral-apatite (Kõiv et al., 2006; Bellier et al., 2006; Kängsepp et al., 2008; Kadlec and Wallace, 2009) as well as various industrial products like expanded light-weight clay aggregates (LECA), Filtralite® and Filtralite-P® (Jenssen and Vråle, 2003; Jenssen et al., 2005; Noorvee et al., 2007; Põldvere et al., 2009; Põldvere et al., 2010; Karabelnik et al., 2012), and industrial by-products, such as different slags and ashes (Liira et al., 2009; Kõiv et al., 2010; Vohla et al., 2011; Klimeski et al., 2014) for the treatment of different types of wastewater.

Filtralite® and Filtralite-P® are industrially produced light-weight expanded clay aggregates, designed for wastewater treatment in SSF filters. Filtralite-P® is developed especially for the phosphorus removal that has high pH (10) and high content of Ca^{2+} and Mg^{2+} ions, which are important for phosphorus sorption (Jenssen and Vråle, 2003; Jenssen et al., 2005).

Several studies have shown the great potential of peat in wastewater and landfill leachate treatment (Ayaz and Akca, 2001; Öövel et al., 2005; Kõiv et al., 2006; Kõiv et al., 2009a). The filter filled with peat has shown effective removal of nitrogen, suspended solids and phosphorus from the wastewater, making it sustainable, environmentally friendly alternative filter material (Kõiv et al., 2006; Champagne, 2006).

Oil shale is a fossil fuel with a low energetic value, which is used in the Estonian thermal power plants. Oil shale is a highly calcareous material that leaves a large amount of ash (up to 48%) behind after its thermal combustion (Uibu et al., 2008). The produced ash is transported *via* hydro-transport to the ash plateaus where, after the reaction between lime, anhydrite and water, the ash sediments harden resulting in the formation of different reactive Ca-minerals such as ettringite, portlandite and calcite (Kaasik et al., 2008; Bitukova et al., 2010). Several studies have shown that hydrated oil shale ash (HOSA) has a high capacity for phosphorus removal from various types of wastewater (Vohla et al., 2005; Liira et al., 2009; Kõiv et al., 2009b; Kõiv et al., 2010; Vohla et al., 2011; Karabelnik et al., 2012; Kasak et al., 2015). P removal by ash sediments mostly takes place through Ca-phosphate precipitation and the formation of insoluble calcium phosphate complexes (Kõiv et al., 2010). In addition, HOSA has shown great ability to sequester CO_2 by mineral carbonation (Uibu et al., 2008; Uibu et al., 2009).

1.3. Greenhouse gas emissions from subsurface flow filters

Several gaseous compounds are produced in the SSF CWs during the purification processes. These gases include carbon dioxide (CO_2), ammonia (NH_3), hydrogen sulfide (H_2S), dinitrogen (N_2), nitrous oxide (N_2O) and methane (CH_4) (Kadlec and Wallace, 2009). When considering GHG, emission of CO_2 have been measured only in a few full-scale SSF filters (Teiter and Mander, 2005; Mander et al., 2005; Picek et al., 2007; Rosso and Stenström, 2008; Barbera et al., 2014) whereas several studies have focused on the CH_4 (Søvik et al., 2006; Chiemchaisri et al., 2009; Pangala et al., 2010; Mander et al., 2014) and N_2O emission (Mander et al., 2003; Søvik et al., 2006; Inamori et al., 2008; Liu et al., 2009; Huang, 2013; Jahangir et al., 2016).

In the SSF filters, N_2O is mainly produced by nitrification, denitrification, nitrifier denitrification and nitrate ammonification (Mander et al., 2014; Jahangir et al., 2016). The predominant process in HSSF filters is shown to be denitrification, which is the microbial reduction of $\text{NO}_3\text{-N}$ to $\text{NO}_2\text{-N}$ and henceforward to the gaseous NO , N_2O and N_2 (Reddy and DeLaune, 2008), although only in the case of nitrous oxide reductase producing microorganisms the harmless end-product (N_2) is possible (Thomson et al., 2012). However, several studies have shown that in well-aerated, moist conditions the emitted N_2O can originate from nitrification (Robertson and Tiedje, 1987). This process is carried out by ammonia-oxidizing bacteria (Arp and Stein, 2003) and archaea (Stieglmeier et al., 2014) that oxidize hydroxylamine (NH_2OH) to nitrite (NO_2^-). Alternatively, N_2O can be produced by autotrophic nitrifiers that reduce NO_2^- to N_2O under aerobic conditions by a process called nitrifier denitrification (Shaw et al., 2006).

HSSF filters receive organic carbon from the influent wastewater and from the photosynthetic macrophytes, which incorporate into the filter material as organic carbon (C). Therefore, organic C undergoes several biogeochemical processes that regulate C accumulation in filter media and microbial respiration, producing CO_2 (Picek et al., 2007; Jahangir et al., 2016). CH_4 emission mostly occurs in HSSF filters under the anaerobic mineralization of organic C by methanogenic archaea (Pangala et al., 2010). Methanogens, which are strict anaerobes, share a complex biochemistry of CH_4 synthesis as part of their energy metabolism (Garcia et al., 2000; Le Mer and Roger, 2001). Both CH_4 and N_2O have a strong negative impact on global warming. N_2O has a global warming potential of 298 relative to CO_2 over a 100-year time period and is responsible for about 6% of anticipated warming, while CH_4 has a global warming potential of 34 relative to CO_2 , and is responsible for about 20% of foreseen warming (IPCC, 2013).

1.4. The aim of the thesis

The main aim of this dissertation was to analyse the effect of different filter materials for greywater and municipal wastewater treatment in subsurface flow filters applying different hydraulic and organic loading regimes and its impact on greenhouse gas emissions.

The specific objectives were:

- To evaluate the effect of HOSA and Filtralite® filled vertical and horizontal subsurface flow filters to treat household greywater (Publication I, i.e. Karabelnik et al., 2012);
- To evaluate the effect of peat and HOSA and their proportion combinations in the HSSF filters on the municipal wastewater treatment and its impact on the greenhouse gas (CO_2 , CH_4 and N_2O) emissions (Publication III, i.e. Kasak et al., 2015);
- To analyse the impact of hydraulic loading regimes on the greenhouse gas emissions from full-scale HOSA filled HSSF filter (Publication IV, i.e. Kasak et al., 201X);
- To analyse the impact of C and N loading on greenhouse gas emissions in HSSF filters and to determine the CH_4 and N_2O emission factor values, as well as to evaluate the relationship between CH_4 and N_2O emission from the HSSF filters based on the results of the studies available in the literature (Publication II, i.e. Mander et al., 2014);
- And to compare different filter materials (widely adopted and alternative substrates) used in the HSSF filters from the aspect of filters' purification efficiencies and greenhouse gas emissions (Publications I, II, III and IV).

2. MATERIALS AND METHODS

Three water treatment experiments were conducted during this study at different scales and the data concerning the different HSSF filters — their properties and GHG emissions from these systems available in literature — were analysed and compared with the current case study results.

2.1. Greywater treatment system – first experiment

An indoor onsite mesocosm study for the treatment of greywater from a household containing five residents was carried out from November 2009 to July 2011 (Publication I). Greywater was collected from the showers, hand basins, laundry and kitchen using separated piping system to avoid black water (wastes from toilet) entering into the system.

The experimental pilot scale hybrid filter system (A,B,C,D; Fig. 1) consisted of three shallow ($h=20\text{cm}$) vertical flow filters (VSSF; 0.02 m^3 each) followed by water saturated horizontal flow filters (HSSF; 0.06 m^3 each). The filter materials used in the treatment systems were different fractions of Filtralite® (2–4 mm, 4–10 mm and 4–10 mm – cracked), Filtralite-P® (0–4 mm) and hydrated oil shale ash (5–20 mm).

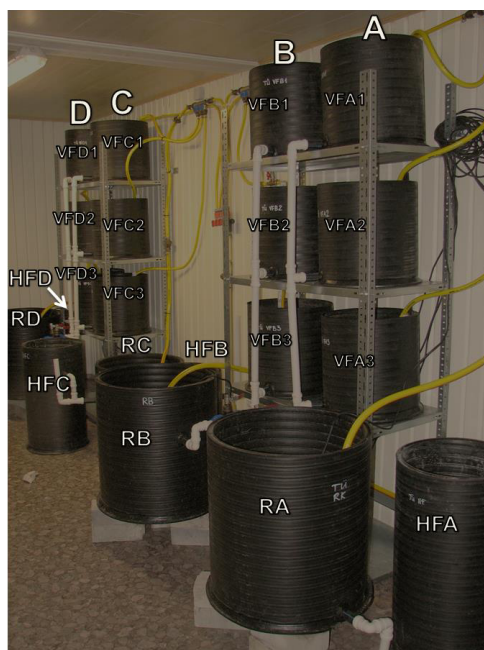


Figure 1. The layout of the experimental filter subsystems: A, B, C, and D. Each system consists of three VSSF filters (VF), followed by HSSF filter (HF) and a re-circulation well (R). The numbers (1, 2, 3) indicate the VF replicates of each subsystem.

The study was divided into two main periods, based on the greywater loading rate applied to the systems. The first period lasted from October 2009 to February 2010. The second period began in February 2010, when system C was switched off due to a significantly lower purification efficiency level compared to the other systems. Thereafter, the total hydraulic loading rate was raised from 32.5 L d^{-1} to 80 L d^{-1} per each parallel system ($100\text{--}250 \text{ mm d}^{-1}$), with an additional re-circulation rate of 300%. For re-circulation, a re-circulation well (R, 0.07 m^3 ; Fig. 1) was used. A detailed description of the system, filter materials and operational characteristics are given in Publication I.

2.2. Municipal wastewater treatment systems

Two municipal wastewater treatment studies were carried out at different times with experimental systems that used raw wastewater from the inlet of an activated sludge wastewater treatment plant, located in the village of Nõo, Tartu County in Southern Estonia. The treatment plant treats domestic wastewater, combined with the effluent from the local meat processing industries – with a loading rate up to 1000 personal equivalent and having a maximum flow rate of 750 m^3 per day.

2.2.1. The mesocosm study – second experiment

A hybrid constructed wetland system with different alternative filter materials was carried out from November 2011 to October 2012 (Publication III). Untreated wastewater was first pumped ($0.3 \text{ m}^3 \text{ d}^{-1}$) into a septic tank (2 m^3). From the tank, the wastewater flowed directly into the distribution well, and then the pre-treated wastewater was pumped into the VSSF filters (total area 3 m^2). In the VSSF, wastewater flowed by gravity through the filter body (filled with LECA 2–4 mm) and onward into the distribution box where it was equally divided into five parallel water saturated HSSFs (0.06 m^3 each). Each mesocosm had three sections separated by low walls that created one hydrological unit and was filled either with peat (HF1), HOSA (HF5) or different combinations of these materials (HF2–HF4). The combination of peat and HOSA in the filters HF2, HF3 and HF4 was divided as follows: HF2 (5/1), HF3 (3/1) and HF4 (1/1). The water level was constantly 5 cm below the surface. The detailed description and schematic layout of this experimental system is given in Publication III.

2.2.2. The full-scale study – third experiment

A full-scale experiment was conducted from September 2013 to December 2015 (Publication IV). The current study was carried out in an HSSF filter system, which was fed with raw wastewater pumped from the inlet of an activated

sludge treatment plant. The treatment system consists of a septic tank (2 m^3); followed by two VSSF LECA filters (with an area of 4 m^2 each). After pre-treatment by septic tank and VSSF filters, wastewater flows into two HSSF filters (NH1, NH2) with a volume of 8 m^3 each, filled with crushed HOSA rubble. Both filter systems had the same organic and hydraulic loading rate – 3.8 m^3 per week. However, the system NH1 had stable hydraulic loading, whereas the system NH2 had fluctuating loading regime, imitating the wastewater production of a typical household. For a schematic overview and the preliminary water treatment effectiveness of the systems, see Figure 2 and (Kõiv et al., 2015).

The data (filter type, filter material, wastewater type treated, loading rate, purification efficiencies and GHG emissions) for all types of filters analysed in this thesis is shown in the Supplementary Table 1.

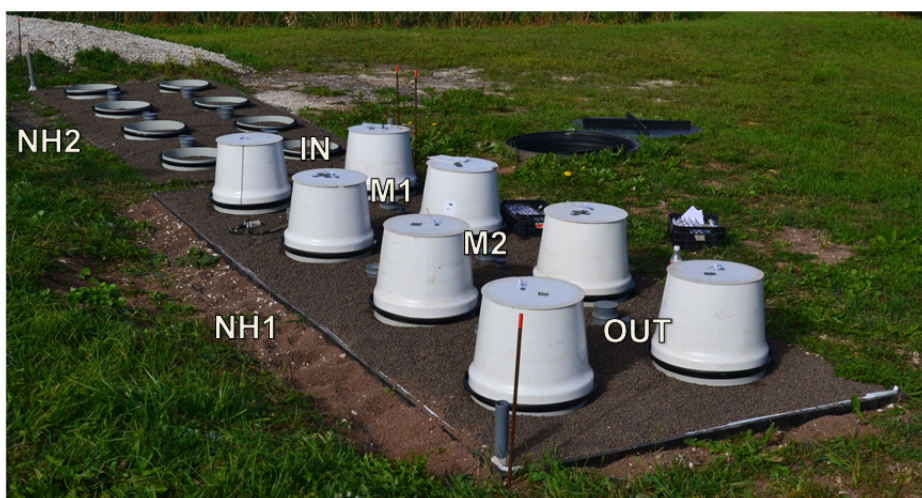


Figure 2. Greenhouse gas sampling points on the filter beds NH1 (with chambers) and NH2: inflow (IN), middle (M1 and M2) and outflow (OUT) areas.

2.3. Meta-analysis of the sand, gravel and LECA filled HSSF CWs and their GHG emissions

Results from 158 published studies analysing GHG emissions from different types of constructed wetlands – treating municipal or domestic wastewater with different hydraulic loadings – were integrated and analysed together in order to estimate the relationship between CH_4 and N_2O emission and C and N loading in the inflow of HSSF CW systems. In all cases, studies with widely used filter materials (e.g. sand, gravel, LECA etc.) were used excluding alternative materials (e.g. different slags, ashes) to avoid specific parameters presented in some materials (high pH, high content of specific ions, etc.). All GHG emission data

used in the meta-analysis were collected using the static chamber/gas-chromatograph technique (Hutchinson and Livingston, 1993). The detailed description of the analysis is given in the review paper (Publication II).

2.4. Sampling and statistical analyses

2.4.1. Water sampling

In the greywater treatment system – water samples from a septic tank, a collection well and from the outflow of VSSF and HSSF filters were taken at least once a month during the experimental period from November 2009 to June 2011. A total of 14 and 13 samples from the outflow of the VSSF and HSSF filters from all subsystems were taken during 1st and 2nd period, respectively (Publication I). During the second study, water samples were taken quarterly (n=4) from the inflow and outflow of each filter system (Publication III). BOD₇, COD_{Cr} and pH as well as TN, NH₄-N, NO₃-N, NO₂-N, TP, PO₄-P, SO₄²⁻, Ca²⁺, Mg²⁺ and TOC concentrations were determined in the water samples by a certified laboratory using standard methods (APHA-AWWA-WEF, 2005) (Publications I and III). During the third experiment, water samples from the inflow and outflow, as well as from each observation well (6 per treatment unit), were taken at each gas-sampling occasion (n=184). Polyethylene bottles with the water samples were stored in a thermal box before transported to the laboratory. The concentration of TN and TOC in the water were determined using Vario TOC cube (Elementar GmbH, Germany). The concentration of Ca²⁺, Mg²⁺, SO₄²⁻, NH₄⁺-N and NO₃⁻-N, and water pH values was determined in the certified laboratory using standard methods (APHA-AWWA-WEF, 2005) (Publication IV).

2.4.2. Gas flux measurements and calculations

Emission of CO₂, CH₄ and N₂O from the filters was measured using the static closed chamber method (Hutchinson and Livingston, 1993; Mander et al., 2003) (Publications III and IV). Measurements were conducted monthly, from January 2012 to October 2013, except for a short period of thick snow cover (Publication III), and from September 2013 to December 2015 (Publication IV). At each sampling location, a collar (Ø 50 cm) was permanently installed in such a way that the water filled ring for airtight sealing stayed on top of the filter material and the collar walls were inserted (10 cm) into the material. For measurements of gas fluxes (CO₂, CH₄ and N₂O) white PVC chambers (h = 40 cm, V = 65 L) were placed on the collars. At each sampling occasion gas samples were taken at the beginning, after 20 min, after 40 min and after 60 min from the enclosure of samplers using previously evacuated (0.3 mbar) glass bottles.

The CO₂, CH₄ and N₂O concentrations in the collected air were determined using a Shimadzu GC-2014 gas chromatograph (ECD, FID) in combination with a Loftfield's autosampler (Loftfield et al., 1997). The gas concentrations in

the chambers increased in a near-linear fashion and linear regression was applied for calculation of the fluxes. Flux measurements with a determination coefficient (R^2) of 0.95 or greater were used in further analyses (Publications III and IV).

For the calculation of the emission factor (EF) values, TOC_{in} and TN_{in} values in $mg\ m^{-2}\ h^{-1}$ were calculated based on the filter system area, hydraulic loading, and inflow TOC and TN concentration data (Eq. 1 and 2):

$$TOC_{in}(mg\ m^{-2}h^{-1}) = \frac{Q\ (l\ h^{-1}) \times TOC\ (mg\ l^{-1})}{area\ (m^2)} \quad (1)$$

$$TN_{in}(mg\ m^{-2}h^{-1}) = \frac{Q\ (l\ h^{-1}) \times TN\ (mg\ l^{-1})}{area\ (m^2)} \quad (2)$$

The EF% values for CH_4 (Eq. 3) and N_2O (Eq. 4) were calculated as follows:

$$EF_{CH_4} = \left(\frac{CH_4 - C\ (mg\ m^{-2}h^{-1})}{TOC_{in}(mg\ m^{-2}h^{-1})} \right) \times 100\ (\%) \quad (3)$$

$$EF_{N_2O} = \left(\frac{N_2O - N\ (mg\ m^{-2}h^{-1})}{TN_{in}(mg\ m^{-2}h^{-1})} \right) \times 100\ (\%) \quad (4)$$

2.4.3. Statistical analyses

In all studies (Publications I–IV) the normality of variables was checked using Kolmogorov-Smirnov, Shapiro-Wilk and Lilliefors tests. A Mann-Whitney *U*-test was used to compare the filter systems' performance according to the water purification efficiency parameters (Publication I) and GHG emission (Publication IV). A Wilcoxon Matched pairs test was carried out in order to compare the performance of filter systems for greywater treatment (Publication I) and for GHG emission from pilot studies (Publication III). A Kruskal–Wallis ANOVA test was applied to assess differences in the gas fluxes between mesocosms and between the inflow and outflow areas of a mesocosm (Publication III). Spearman's rank order correlation analysis was used to observe the correlations between measured greenhouse gas fluxes and the temperature in the mesocosm filter body (Publication III). The same analysis was used to analyse the relationships between different water parameters (Publication I). In order to find the functional relationships between gas emissions and the water's chemical parameters, the MINE (Maximal Information-based Nonparametric Exploration) application was used to calculate MIC (Maximal Information Coefficient) values (Reshef et al., 2011) (Publication IV). Post-hoc analyses for Friedman's test were used to analyse

spatial variation of GHG fluxes in filter systems in the third experiment (Publication IV).

All calculations and statistics were computed using the STATISTICA 7.1 and R (version 3.2.2) software's. The level of significance of $p < 0.05$ was accepted in all cases.

3. RESULTS AND DISCUSSION

3.1. Greywater and municipal wastewater treatment

According to Estonian regulations, target values for the effluent of wastewater treatment systems have been established for TP, TN, COD and pH according to the capacity of the treatment plant. TP concentration in the outflow of a wastewater treatment plant must be 2 mg L^{-1} or less, with a purification efficiency of at least 70%, for TN 60 mg L^{-1} and 45% and for COD 125 mg L^{-1} and 75%. Effluent pH values from the treatment plant must be between 6 and 9 (RT I, 13.06.2013, 13). However, there are no regulations specified for greywater, therefore the target values designated for municipal wastewater was implemented.

3.1.1. Changes in wastewater pH

The pH values of the pre-treated greywater and wastewater were quite stable and similar (6.9–7.1) in all conducted experiments. Median pH values to the inflow of greywater treatment systems (Publication I) and wastewater treatment systems (Publications III and IV) were 7.0 and 7.1, respectively. A clear effect of the filter material properties on the treated water pH was observable in all experiments. In addition, a rapid pH increase was seen in most of the filters, except the peat filled filter (HF1) from the second experiment.

The VSSF filters filled, with different fractions of Filtralite® (Publication I), had significantly increased pH values in the effluent of each parallel system, with a median pH value of between 8.1–8.2, and also showing, however, no significant difference between different fractions of filter material. The pH values from the outflow of the HSSF filters were significantly higher when compared with the VSSF filters, which was due to their longer residence time. The highest median pH values occurred in subsystem D – containing HOSA, which achieved a median effluent value of 9.2 due to the presence of portlandite, Ca(OH)_2 (Fig. 3). After the hydraulic loading rate was increased from 32.5 L d^{-1} (first period) to 80 L d^{-1} (second period) in the whole system, the effluent pH values dropped to almost the same level as was in the influent pH in most of the studied subsystems' HSSF filters, except the effluent of HOSA filled system D, where the median value stayed at pH 8.6. Since all the parallel systems had high initial pH (≥ 10 in Filtralite® filters and > 12 in HOSA filters) (Fig. 3), an increase in effluent pH values compared to the influent was predictable for all the subsystems.

A different combination of well mineralised peat and HOSA was used in HSSF filters for municipal wastewater treatment, to find out the pH buffering capability of well-mineralised peat in the presence of highly alkaline HOSA (Publication III). The water analyses showed that the effluent pH value varied in large extent between the subsystems and the lowest pH values (6.9–8.2) were found in the filter mesocosms HF1 and HF2, where well-mineralised peat was

used as the main component. The mesocosms HF3, HF4 and HF5 showed remarkably higher pH due to the high amount of HOSA (10.7, 12.3 and 12.1, respectively) (Fig. 3). Likewise the second study, significant pH raise was also observable in the third study where median pH value of the outflow of both filters was 12 (Fig. 3).

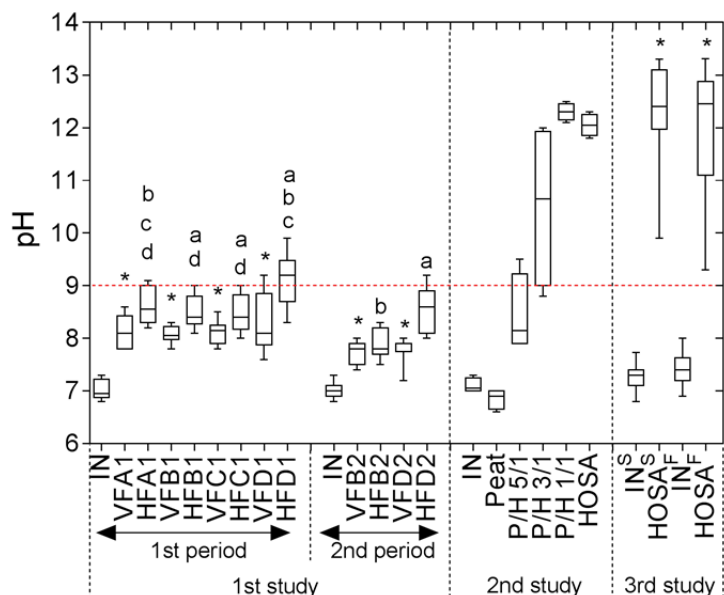


Figure 3. Influent and effluent pH values of the filters (mesocosms) studied in the greywater and municipal wastewater treatment experiments (first, second and third study, respectively). Box-whiskers plots show median, 25%–75% and min-max values. For the abbreviations of the filters, see Materials and Methods. The target value, according to Estonian regulations, is marked with a red line. Letters indicate the significant differences ($p < 0.05$) between different filter systems, and asterisks show the significant ($p < 0.05$) differences between inflow and outflow.

The wastewater pH increased in all highly alkaline HOSA filters of all studies, however, in the greywater treatment system the pH values dropped remarkably during the experiment. At the beginning of the experiment, the system D effluent values were between 9.5–9.9 and, after 1.5 years in operation, the median values were around 8.6. High hydraulic loading rate (Herrmann et al., 2013a; Herrmann et al., 2013b) and also more active biological processes related to the biofilm formation to the surface of the filter material (Nilsson et al., 2013) could have caused the decrease in the effluent pH.

The peat/HOSA HSSF filters (HF2, HF3) showed rather unstable effluent pH values that fluctuated between 7.9–9.5 and 8.8–12, respectively (Publication III). Well-mineralised peat used in these filters was able to buffer pH values at the

beginning of the experiment, however lost its neutralizing ability after four months of filter operation. The loss of buffering capacity can be related to the organic components that were flushed out of the peat during the experiment (Patterson, 2001; Kõiv et al., 2006). In the HF4 filter, where the peat and HOSA were used in equal portions (1/1), the peat had no pH buffering capability and the median pH value in the effluent of the filter was similar (12.3) to the HOSA filled filter (HF5).

In the third study, there was no significant difference in the effluent pH values in two hydraulic loading regimes. This clearly shows that in HSSF filters the high hydraulic loading regime will not decrease the high pH as rapidly as in VSSF filters.

3.1.2. Nitrogen removal

In the pre-treated municipal wastewater, most of the nitrogen was in the form of ammonium-nitrogen, the median $\text{NH}_4\text{-N}$ concentration was 40.5 mg L^{-1} , while the TN concentration was 60 mg L^{-1} (Publication III). In the greywater experiment, however about one quarter of the nitrogen entering the treatment system was in the form of $\text{NH}_4\text{-N}$ (median concentration of 3.2 mg L^{-1}) (Publication I).

The reduction of TN concentration within greywater treating VSSF filters was quite moderate, showing no significant difference between filter materials. The TN removal efficiency in the Filtralite[®] VSSF filters (subsystems A, B and C) was 48% to 60%, compared to a 54% presented in the HOSA filter (D). The median effluent TN concentration for Filtralite[®] VSSF filters was between 5.0 mg N L^{-1} and 14 mg N L^{-1} , while the effluent TN concentration in HOSA filter was 6 mg N L^{-1} (Fig. 4). TN removal in HSSF filters was unexpectedly low in all filters, being between 0–6%, which was probably due to the effective VSSF filters removing most of the nitrogen and organic compounds and therefore suppressing denitrification processes in HSSF filters.

Surprisingly, the results revealed that the ~2.5 times higher hydraulic loading rate in the second period of the first experiment did not affect nitrogen removal efficiency. This might be due to the higher microbial activity and larger biofilm formation because the high initial materials pH has dropped to the more suitable level (Liu et al., 2012; Wen et al., 2012). The effluent concentration of the TN stayed below target value in all filter systems (RT I, 13.06.2013, 13).

The median influent nitrogen concentration was 60 mg L^{-1} and was reduced remarkably in all filters in the second study (Publication III). Best results were achieved using the peat filter (HF1) and peat-HOSA combination in equal portions (HF4). The TN removal efficiency was 25% in HF1 and 36% in HF4, achieving a median effluent concentration of 38.5 and 48.5 mg N L^{-1} , respectively. In the filters with highest HOSA HF2, HF3 and HF5, the TN removal efficiency was rather low, being between 19–24%. The low TN removal can be explained by suppressed denitrification processes under unfavourably high pH conditions (Simek and Cooper, 2002; Ligi et al., 2014a).

In the third study the median influent TN concentration of 82 mg L⁻¹ was reduced significantly in both loading regimes and removal efficiency was in the same range as noted in first and second study where HOSA was used. Total nitrogen removal in NH1 and NH2 was 44% and 43%, achieving a median outflow concentration of 46 and 45 mg L⁻¹, respectively.

The decreased NH₄-N concentration in the effluent compared to the inflow was observable in all filters of all experiments. However, the significant reduction was only presented in the second period of the first study (Fig. 4). The removed amount of NH₄-N was moderate and it varied between 17–32%, achieving a median effluent concentration between 17–33.5 mg L⁻¹. Low removal rates were most probably caused by the high pH levels, which prevailed in all studies, especially in the filters where highly alkaline HOSA was used. High pH is one of the main inhibitors of nitrification and denitrification, which have been shown to be the principal NH₄-N transformation processes in HSSF CWs (Kadlec and Wallace, 2009). In most types of CWs, ammonia is predominantly presented in ionised (NH₄⁺) form. However, when pH values (>9.5) and temperature increases, the percentage of total ammonia presented in the un-ionised (NH₃) form increases rapidly and therefore the loss of NH₃ *via* volatilization can be a significant pathway for nitrogen removal (Middlebrooks and Pano, 1983).

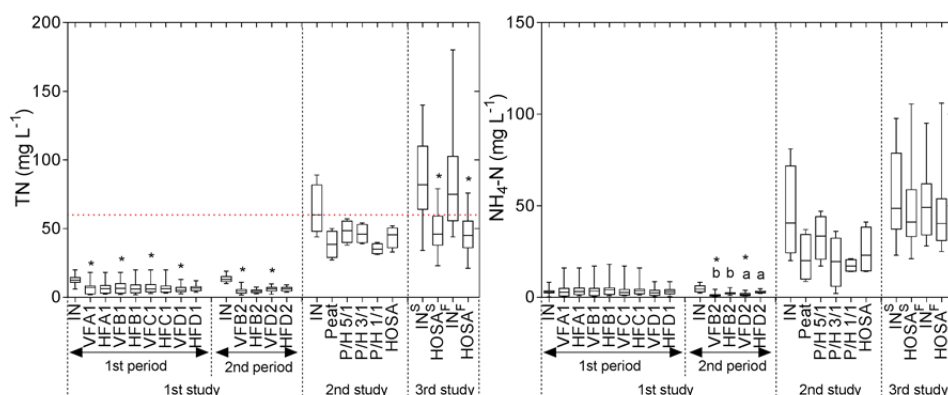


Figure 4. Total nitrogen (TN) and ammonium-nitrogen (NH₄-N) concentrations in the influent and effluent of the greywater and municipal wastewater treatment experiments (first, second, and third study, respectively). Box-whiskers plots with median, 25%–75% and min-max values are shown. For the abbreviation of filters, see Materials and Methods. Target concentration, according to Estonian regulations, is marked with a red line. Letters indicate significant differences ($p < 0.05$) between different filter systems, and asterisks show significant ($p < 0.05$) differences between inflow and outflow.

It has been reported that losses of NH₃ *via* volatilization from flooded soils and wetlands are insignificant if the pH value is below 7.5. At a pH value of 8.0,

about 95% of total ammoniacal nitrogen ($\text{TAN} = \text{NH}_3\text{-N} + \text{NH}_4\text{-N}$) is in form of NH_4^+ , whereas at pH 9.3 the ratio between NH_4^+ and NH_3^- ions is 1/1 and losses through volatilization can be remarkable (Middlebrooks and Pano, 1983; Reddy and Patric, 1984). In addition to the pH and TAN concentration in the wastewater, other parameters like temperature, pH buffering capacity, partial pressure of NH_3^- and plant canopy will influence the release into the atmosphere (Vymazal and Kröpfelova, 2008). Therefore, according to Miner (1974), not all of the NH_3^- produced in the system is released into the atmosphere and at wastewater temperature of 20°C and pH 8.0, the potential NH_3^- release is about 3% of total ammonia nitrogen, while in the pH value of 9.3, the release is rather stable and around 15% (Miner, 1974).

The concentration of NO_3^- -N and NO_2^- -N in the greywater treatment system was extremely low, achieving a median influent concentration of 0.021 and 0.003 mg L⁻¹, respectively, and the effluent of all filter systems stayed in the same range, showing no changes in concentrations. NO_3^- -N concentration in the raw wastewater was rather high, achieving a median concentration of 9.6 mg L⁻¹, while the median NO_2^- -N concentration was 1.7 mg L⁻¹. The highest NO_3^- -N removal efficiency was in the peat filter, followed by the peat/HOSA in 3/1 combination (HF3), achieving a purification rate of 53% and 48%, respectively. The removal of NO_3^- was 30% and 19% in the peat/HOSA 5/1 and 1/1 filters, respectively and 27% in the HOSA filter. The comparably high influent NO_2^- -N concentration (1.7 mg L⁻¹) was even increased to 2.0, 3.4, 2.9 and 5.2 mg L⁻¹ in the effluent of these mesocosms, respectively. This relatively high NO_2^- concentration was one of the unexpected results, because NO_2^- is an intermediate oxidation state of N between NH_3^+ and NO_3^- . Due to its intermediate energetic status, NO_2^- is not chemically stable in most wetlands and is often found in very low concentrations (Kadlec and Wallace, 2009) that were also observable in the cases of greywater treatment filters. However, it has been reported that in pH value 8–9; an elevated NO_2^- accumulation may occur (Bae et al., 2001). A high NO_2^- concentration in combination with a relatively high NH_4^+ content in the wastewater is a strong prerequisite for the presence of anammox bacteria in the filters (Zhu et al., 2011).

3.1.3. Reduction of COD and TOC values

The median influent COD value to the greywater treatment systems was 684 mg O₂ L⁻¹. The median reduction of COD in the VSSF filters was 81–85% for Filtralite® systems (A,B,C) and 75% for the HOSA subsystem (D), showing no significant difference between filter materials (Publication I). All of the Filtralite® VSSF subsystems performed slightly better than HOSA subsystem. The achieved COD effluent values in the VSSF filters were 91–100 mg O₂ L⁻¹ and 110 mg O₂ L⁻¹ (median values for Filtralite® systems and HOSA system, respectively) in the first experimental period while the effluent values in the second period were 95 mg O₂ L⁻¹ (B) and 140 mg O₂ L⁻¹ (D), respectively.

The outstanding COD removal efficiency (75–85%) in the shallow vertical filters with high organic loading rate was probably due to the effective aeration by high pressure pump and nozzles. The nozzles used for greywater distribution provided equal distribution of the wastewater and maximized contact surface between the filter material and small water particles. The positive impact of nozzles and high pressure pump application on the removal of organic compounds from the wastewater has also been reported by Heistad et al., (2006). Somewhat lower organic C removal efficiency in HOSA filter in the subsystem D was probably due to the high pH that probably inhibited certain microbial processes. It was also clear that the highest C removal processes occurred in the aerobic VSSF filters while under anaerobic conditions in the HSSF filters the removal efficiency was almost imperceptible, being around 3–7% (Publication II).

The median influent TOC concentration to the second experiment was 37 mg L⁻¹. The removal of TOC from the municipal wastewater in the second experiment was observable only in the HSSF mesocosms with HOSA (HF5, 57%), while in the mesocosms HF1-HF4, the effluent concentration was remarkably higher compared to the influent. The increased TOC concentration in the effluent of HSSF filters was probably caused by the washed out organic compounds, especially in case when peat and HOSA was in the same unit, probably due to the decompose of peat in alkaline conditions (Kõiv et al., 2006) (Publication III).

The median influent TOC concentration was 118 mg L⁻¹ in the third experiment (Publication IV). The TOC removal efficiency was slightly higher in the case of stable loading, achieving a purification efficiency of 52% (NH1) while under the fluctuating loading regime the organic C removal efficiency was 46% (NH2), however the difference was not significant. The TOC concentration in the effluent was 52.0 and 46.3 mg L⁻¹ for NH1 and NH2, respectively. Rather effective TOC removal was probably due to the anaerobic microbial sulfate reduction and methanogenesis (Kadlec and Wallace, 2009).

3.1.4. Phosphorus removal

The TP concentration was 5 mg P L⁻¹ (median value) in the pre-treated greywater and 20 mg P L⁻¹ in the pre-treated municipal wastewater (second experiment) (Publications I and III, respectively).

Regarding TP removal from greywater in the first period, the HOSA VSSF filter in subsystem D, outperformed Filtralite® VSSF filters (A,B,C) in achieving a removal efficiency of up to 81%, compared with 35–38% presented in the Filtralite® VSSF systems. The median effluent concentration from VSSF HOSA system was significantly lower, being 1.1 mg P L⁻¹, while in Filtralite® filters it was around 3.3 mg P L⁻¹, being slightly above the target (2 mg L⁻¹) value (RT I, 13.06.2013, 13) (Fig. 5). It was also observable that the Filtralite® and HOSA filters showed significantly different dynamics. After the loading rate was increased from 32.5 to 80 L d⁻¹, the TP removal efficiency dropped significantly

in Filtralite® filters (from 35–38% to 13%) and in HOSA VSSF filters (from 81% to 39%) (Fig. 5). The TP removal efficiency in the HSSF filters using Filtralite-P® was unexpectedly low, being only 5.7–13% in subsystems A, B and C, while in the subsystem D with HOSA, the removal efficiency stayed around 39% in the first period, which however increased to 55% in the second period. The significant increase of TP removal in the second period with higher hydraulic loading rate might be due to the low treatment efficiency presented in the VSSF filters. Probably the higher loading rate flushed more P through the VSSF filter.

The Filtralite® filters' low TP removal efficiency from the greywater study was rather unexpected, especially if to consider previous studies that reported >90% removal efficiency for this filter material (Jenssen et al., 2005; Heistad et al., 2006; Ádám et al., 2007). For example, Ádám et al., (2007) showed that the outflow pH value of the HSSF Filtralite® filter experiment was above 10.5, which dropped to 9–9.5 over 300 days of operation, while the TP removal rate was still around 91%. These results did not correspond with our investigation and therefore we conclude that the hydraulic loading regime might have been too high for these filters, because the pH values dropped remarkably after a few months in operation. Another important factor could have been the intensive formation of a biofilm on the surface of the filter material caused by the higher organic loading mainly composed by a kitchen wastewater. Due to the high organic matter and high concentration of P, several investigators have excluded kitchen wastes from greywater to achieve higher purification efficiency (Donner et al., 2010; Abu Ghunmi et al., 2011).

The removal efficiency of TP in the wastewater treatment system (Publication III) was outstanding in filters HF4 and HF5, where the removal rate was up to 99%, achieving a median outflow concentration of 0.2–0.3 mg P L⁻¹, compared with the median influent concentration of 20 mg P L⁻¹. During the experiment, it was observable that filters HF1, HF2 and HF3 lost their P removal efficiency gradually after 4 months of operation.

All of the analysed HOSA filters maintained their treatment capacity after more than one year in operations unlikely to Liira et al., (2009) who reported a significant decrease in purification efficiency in HSSF filters after five month period at a loading of 1.66 g P m⁻² d⁻¹ with residence time of 18h (Liira et al., 2009). However, in the current greywater treatment system, the loading rate was about 5 times higher (2.93 g P m⁻² d⁻¹) and the residence time was three times shorter (6h), but still maintaining P removal efficiency during the experiment (Publication I). In the case of the second experiment the P loading rate was even higher ~4.4 gP m⁻² d⁻¹, with a residence time about 48h (Publication III).

The outstanding TP removal efficiency of the HOSA filters has also been described by Liira et al. (2009) and Kõiv et al. (2010). Kaasik et al., (2008) reported that high phosphorus precipitation potential of HOSA is due to the high content of the reactive calcium mineral, of which portlandite (Ca(OH)₂) and ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂•26H₂O) are the most important. During

wastewater treatment, P is mostly bounded to the HOSA as a hydrated calcium phosphate $\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ (Eq. 5):



where the activity of Ca^{2+} and pH is controlled by the solubility of ettringite (Eq.6) and portlandite (Eq. 7) (Kaasik et al., 2008):

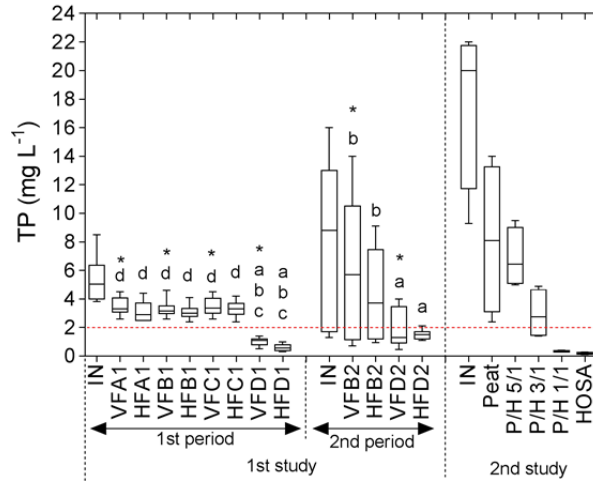
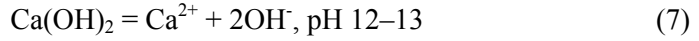
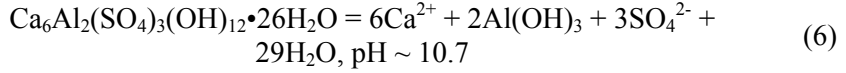


Figure 5. Total phosphorus (TP) concentration in the inflow and outflow of the filters studied in the first and second experiment. Box-whiskers plots show median, 25%–75% and min-max values. For the abbreviation of filters, see Materials and Methods. Target concentration, according to Estonian regulations, is marked with a red line. Letters indicate significant differences ($p < 0.05$) between different filter systems, and asterisks show significant ($p < 0.05$) differences between inflow and outflow.

3.2. Effect of the filter material on greenhouse gas emissions from the HSSF filters

The production of GHG in HSSF CWs is mostly dependent on the influent concentration of nutrients and organic compounds. As HSSF CWs are designed to remove pollutants in an anaerobic/suboxic environment, they change the C and N biogeochemistry and therefore contribute significantly to CH_4 and N_2O emission (Mander et al., 2008; Jahangir, 2016). Greenhouse gas measurements (CO_2 ,

CH₄ and N₂O) were carried out in the second (Publication III) and in the third experiment (Publication IV). In addition to the experiments, a meta-analysis was performed to analyse the GHG emissions from HSSF CWs treating municipal wastewater (Publication II).

3.2.1. CO₂ emission

The results from the mesocosm study (second experiment) showed that the peat and HOSA, and their combinations at different proportions, significantly affected CO₂ emissions from the HSSF filters during the municipal wastewater purification process (Publication III). The largest emissions occurred during summer and early autumn, when biological activity was highest in all filter types. However, it was only in the peat filter (HF1) that a link between seasonal dynamics and a positive exponential correlation between CO₂ emissions and soil temperature ($R^2=0.82$; $p<0.05$) could be found. In most filters, CO₂ emissions were slightly higher in the inflow part; however a significant difference ($p<0.05$) between these filters areas was observable in the case where equal portions of peat and HOSA (1/1) were used (HF4) and in the case of the HOSA filter (HF5). The lowest median values of CO₂ emissions (-6.1 to -7.9 mg CO₂-C m⁻² h⁻¹) were found in filters where HOSA was the main component. The highest CO₂ emission (up to 426 mg CO₂-C m⁻² h⁻¹) were measured from the well-mineralised peat filter (HF1; Fig. 6), probably due to the higher microbial activity (Kadlec and Wallace, 2009), therefore displaying effective organic carbon mineralisation.

CO₂ emissions from NH1 and NH2 filters, filled with HOSA, varied between -28.6 to 138.4 and -19.7 to 105.2 mg m⁻² h⁻¹ with a median value of -6.3 and 1.2 mg m⁻² h⁻¹, respectively (Publication IV). CO₂ emissions were significantly ($p<0.001$) higher in the NH2 with a fluctuating loading regime. Similarly to other studies (Teiter and Mander, 2005; Søvik et al., 2006), significantly higher levels of CO₂ fluxes were observable wherever temperature conditions were rising.

According to the literature, sand, gravel and LECA were the most widely used filter materials in HSSF CWs for wastewater treatment, and CO₂ emissions from these types of materials reached up to 567 mg CO₂ m⁻² h⁻¹, with a median value of 137 mg CO₂-C m⁻² h⁻¹ (Fig. 6) (Publication II).

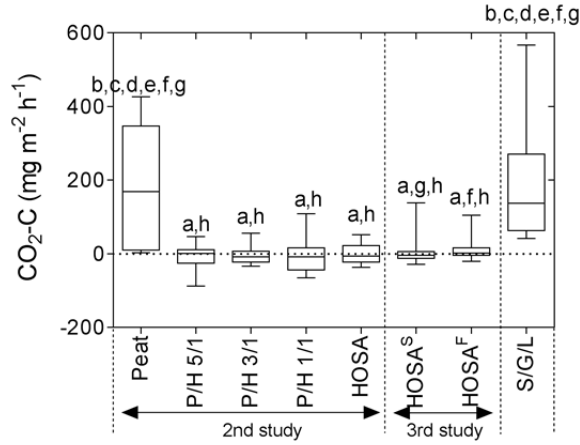
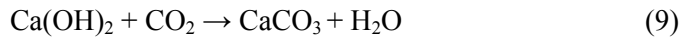
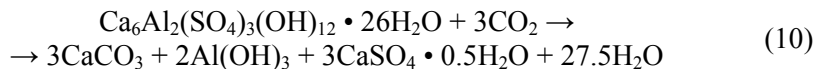


Figure 6. Median, 25%–75% and min-max values of CO₂ flux from the municipal wastewater treating HSSF filters filled with peat (HF1; n=14), HOSA (HF5; n=14) and their combinations (5/1, n=14; 3/1, n=14 and 1/1, n=14 of peat and HOSA in HF2, HF3 and HF4, respectively) in the case of the second experiment; from the full scale HOSA-filled HSSF filters that had stable and fluctuating loading regimes NH1 (n=224) and NH2 (n=216), respectively); and in the case of third experiment, from the sand, gravel, LECA (S/G/L) filters (n=11; review). Letters indicate significant differences (p<0.05) between different filter systems based on Kruskal-Wallis ANOVA.

Considering the case of the HOSA filters, the CO₂ emissions were closely dependent on several geochemical cycles, especially at the beginning of the experiments. Albeit no significant correlation between the filter's purification efficiencies and GHG emissions were revealed in any of the filters, a strong link between the produced CO₂ and the analysed filter material can be assumed as the CO₂ sequestration by reactive Ca-minerals, found abundantly in HOSA, can be significant (Mötlep et al., 2010). During the ash transportation from thermal power plants to the ash plateaus, the ash hydration process is governed by fast hydration of lime to portlandite and the process continues in plateau deposits (Eq. 8; Mötlep, 2010). The main reaction of carbon sequestration is portlandite (Ca(OH)₂) carbonation in aqueous medium (Eq. 9) (Garcia-Carmona et al., 2003a; Garcia-Carmona et al., 2003b; Rendek et al., 2006; Uibu et al., 2009; Uibu et al., 2010).



In addition, the second important carbonation reaction is ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂•26H₂O) dissolution and subsequent Ca-carbonate formation described by Eq. 10 (Mötlep, 2010).



The precipitation of secondary Ca-carbonate was evident in the second (Publication III) and third (Publication IV) experiment, where negative CO_2 fluxes were observable in HOSA filters. The massive authigenic calcite crystallisation of HOSA in NH1 and NH2 after 1.5 years of operation can be seen in Fig. 7. The formation of CaCO_3 in the presence of atmospheric CO_2 will reduce the availability of Ca from dissolution of Ca-rich phases (e.g. ettringite and portlandite) whose solubility controls the Ca reactivity in HOSA filters. The latter is important for P removal from wastewater and the formation of calcium phosphate (Liira et al., 2009; Publication IV). Some studies have also shown that the most intensive CO_2 capturing takes place in the top layer of the HOSA filter, while the binding in deeper layers is limited due to the inhibited CO_2 diffusion (Uibu et al., 2008).

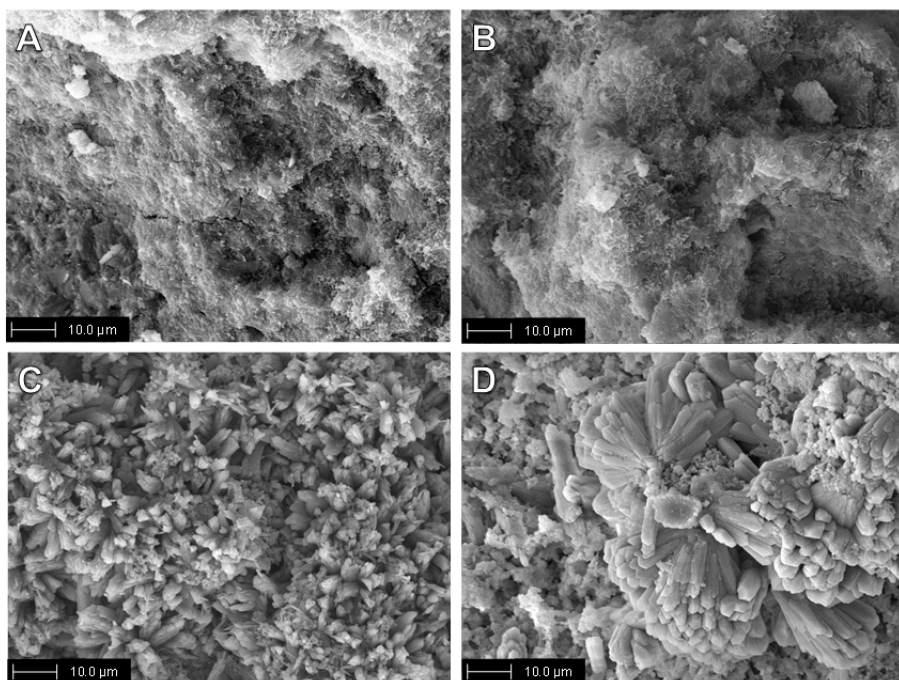


Figure 7. The amorphous Ca-silicates and Ca-carbonate (A, B) on the surface of the initially hydrated oil shale ash, and massive calcite (CaCO_3) crystals formed on the surface of the filter material (C and D for NH1 and NH2, respectively) after 1.5 years of the filter being in operation.

The results also affirm that the emission of CO₂ from HOSA filters depended significantly on the pH within the filter. Decreased pH values and concordant higher CO₂ emission, especially from the inflow part of each studied filter system was caused evidently by slow dissolution of portlandite and ettringite, which are primary pH controlling mineral phases in oil shale ash. Portlandite and ettringite have equilibrium conditions at pH values 13 and 10.7, respectively (Mötlep et al., 2007). Wastewater that was pumped into the filters had near neutral pH. It can be assumed that this wastewater degrades the buffering capacity of portlandite and ettringite bringing pH down and eventually depleting those mineral phases altogether. The solubility of these minerals provides Ca²⁺ for both Ca-phosphate precipitation and CO₂ binding by CaCO₃ precipitation (Mötlep, 2010). Understandably, the inflow area of the HOSA filter system is more influenced by wastewater induced portlandite dissolution reaction and we should observe faster pH drop and therefore CO₂ emission from negative to positive. This suggestion is supported by the measurement results obtained from the inflow area where significantly higher ($p < 0.05$) CO₂ emission compared to the outflow areas was obtained. As portlandite and ettringite buffering capacity progressively decreases we can see zonal decrease of pH and consequent reduction of CO₂ binding ability of HOSA from the inflow towards the outflow area of the filters. The significant loss of the material CO₂ binding capacity was observable in all studied HOSA filters. However, the CO₂ binding capacity decreased more intensively in HOSA filter where fluctuating loading regime (NH2) was used. NH2 filter has 5 day period of volumetrically lower waste water feeding rate and 2 day period of more intense feeding. This kind of pumping arrangement probably affects portlandite dissolution kinetics depleting its sources faster compared to filter system with stable feeding rate.

3.2.2. CH₄ emission

As was revealed from the median values of the CH₄ fluxes, the filter material significantly affected CH₄ flux from the municipal wastewater treating HSSF filters. The median CH₄ emission was in the range of 16.4–556.2 µg CH₄-C m⁻² h⁻¹ in the inflow parts and 11.0–237.3 µg CH₄-C m⁻² h⁻¹ in the outflow parts of all the studied filters (HF1-HF5). The fluxes were significantly different between the peat-filled filter (HF1) and between HF2 and HF4 with peat/HOSA combinations in both inflow and outflow sections (Publication III). The highest emissions (up to 17 311 µg CH₄-C m⁻² h⁻¹) were recorded from the filters HF2 and HF3 where peat was the main filter material component; however the HOSA layer (10 and 20 cm, respectively) also strongly influenced filter performance. From the peat filter (HF1) and filters with large proportions of HOSA (from HF4 and HF5), the maximum emission level was between 81–4080 µg CH₄-C m⁻² h⁻¹ (Publication III; Fig. 8).

CH₄ emissions from the full-scale HOSA-filled filters (NH1 and NH2) varied between -272.8 to 7071.9 and between -112.5 to 7018.4 µg m⁻² h⁻¹ with

median values of 64.9 and 70.1 $\mu\text{g m}^{-2} \text{h}^{-1}$, respectively. Although the emissions were slightly lower in case of the stable loading regime (NH1), a statistically significant difference between the two loading regimes could not be found. The temporal dynamics of the CH_4 fluxes showed remarkably higher emissions from these two filters during the summer months. A rapid increase in CH_4 fluxes was detected in the second year of the filters' operation and the fluxes stayed at a permanently high level from this point onward (Publication IV).

The CH_4 emission from the sand, gravel and LECA filled HSSF CWs ranged between 4.8–17 500 $\mu\text{g m}^{-2} \text{h}^{-1}$; with a median value of 6400 $\mu\text{g m}^{-2} \text{h}^{-1}$ (Publication II).

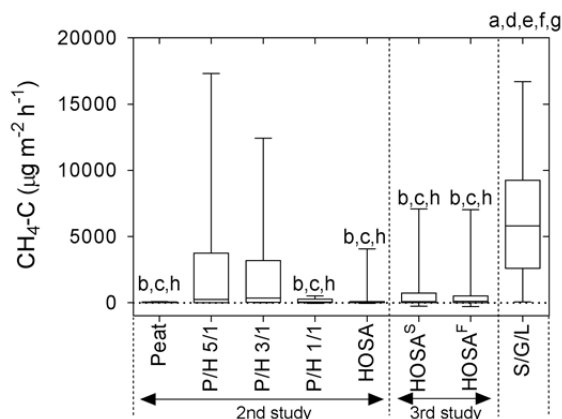


Figure 8. Median, 25%–75% and min-max values of CH_4 flux from the municipal wastewater treating HSSF filters filled with peat (HF1; $n=14$), HOSA (HF5; $n=14$) and their combinations (5/1, $n=14$; 3/1, $n=14$ and 1/1, $n=14$ of peat and HOSA in HF2, HF3 and HF4, respectively) in the case of second experiment; from the full scale HOSA-filled HSSF filters having stable and fluctuating loading regimes NH1 ($n=224$) and NH2 ($n=216$), respectively); and in the case of third experiment, from the sand, gravel, LECA (S/G/L) filters ($n=11$; review). Letters indicate significant differences ($p<0.05$) between different filter systems based on Kruskal-Wallis ANOVA.

The CH_4 emission factors of inflow TOC loading were relatively small in all studied filters. The EF% values calculated for the peat/HOSA filters were between 0.01–0.91% (Publication III) and between 0.67–0.97% for the full scale HOSA filters (Publication IV). These values were significantly lower compared to those (on average 4.5% and 16.8%) reported for sand, gravel and LECA HSSF CWs (Publication II and Jahangir et al., 2016, respectively). The TOC loading into these HSSF filters, analysed in Publication II, were significantly ($p<0.05$) lower compared to the full scale HOSA filled filters, however the CO_2 and CH_4 emissions from those HSSF filters were significantly ($p<0.05$) higher. This shows that widely used filter materials (e.g. sand, gravel and

LECA) with a neutral pH provide a more suitable environment for microbes and support organic carbon mineralisation, which results in a greater level of GHG fluxes from the filters.

The CH₄ emissions from all the studied filters were relatively low and stable. The highest median emissions originated from filters HF2 and HF3 in the second experiment (Publication III), where the Ca²⁺ content was lowest and pH values were between 6.9 and 8.2. According to several studies, the activity of methanogens is usually optimal at neutral pH or under slightly alkaline conditions (Garcia et al., 2000; Le Mer and Roger, 2001). Such conditions were also to be found in these two filters.

The significantly lower CH₄ emissions from the peat (HF1), and HOSA (HF4, HF5, NH1, NH2) filters, compared to the peat/HOSA combinations in HF2 (5/1), HF3 (3/1) and HSSF CWs with sand, gravel and LECA, can be attributed to a number of reasons. The most important factors might be the high pH (except HF1) and high concentration of Ca²⁺ and SO₄²⁻ ions, which probably mitigate the CH₄ emissions (van der Gon, 2001; Mander et al., 2012). The presence of sulfate ions can play a significant role in regulation of the methanogenesis intensity. Lovley and Klug (1983) suggested that the mechanism behind this mitigation could be a competition between methanogens and sulfate reducing bacteria (SRB) for the same substrate. Methanogenic archaea are anaerobic organisms that primarily use acetate (CH₃COO⁻) and H₂/CO₂ as substrates. However, in an anaerobic environment, methanogens have to compete with other microorganisms that can use the same substrates, but are able to use alternative electron acceptors, such as nitrate (NO₃⁻), ferric ion (Fe³⁺) or sulfate (SO₄²⁻) (van der Gon, 2001). Therefore, in the presence of SRB, the CH₄ production can be suppressed, but not completely outcompeted (van der Gon, 2001) — this possible reduction mechanism has been described by several other authors (Gauci et al., 2004; Pangala et al., 2010; Mander et al., 2012). However, this mechanism is predominant in neutral conditions where SRB has the highest activity (Reis et al., 1992) but is inhibited above pH 9 (Widdel, 1988). In highly alkaline conditions the SRB are not completely absent, but can be presented as an alkaliphilic (Zhilina and Zavarzin, 1994) or non-alkaliphilic consortium, protected in a biofilm where pH gradient can occur (Lee and Debeer, 1995). While being protected by a biofilm, the SRB are able to outcompete methanogens in the same consortium, which therefore results in lower CH₄ fluxes from these environments.

The high Ca²⁺ concentration in the environment may also inhibit CH₄ emissions, as demonstrated by Biasi et al. (2008). The link between CH₄ emissions, pH and availability of Ca²⁺ can be seen more precisely in the third experiment where the loss of portlandite and ettringite in the HOSA filters during the experiment has magnified CH₄ emission by two orders of magnitude (Publication IV). But emissions could also be affected by a clogging of the filter system, which is another important factor, escalating CH₄ emissions from HSSF filters (Picek et al., 2007). In the clogging occasion, the high pH is rapidly neutralised in the presence of neutral wastewater and therefore increasing microbial

activity. We were able to see quite a heavy level of clogging and biofilm formation in the HOSA-filled NH1 and NH2 filters after 1.5 years in operation, which then produces significantly higher CH₄ emissions, especially in the inflow part (Publication IV).

Some of the CH₄, which passes through the top-layer of the filter's system, enters an oxygen-containing zone where methanotrophic bacteria are able to convert a part of the CH₄ to CO₂ (Eq. 11). This process is referred to as CH₄ oxidation and can be described by an equation (Borjesson and Svensson, 1997; Oonk, 2010):



CH₄ oxidation is confirmed by a significant linear regression analysis between CO₂ emission and CH₄ EF% with widely used filter materials and in the third study with HOSA (Fig. 9). As can be seen in figure 9, the strongest relationship between CH₄ EF% and CO₂ emissions occurred in HSSF CWs, described in Publication II (A) and in NH2 (Publication IV; B). In the case of sand, gravel and LECA HSSF filters, high EF% values were obtained for these filters that had overloading and where clogging occurred most (Søvik et al., 2006; Picek et al., 2007).

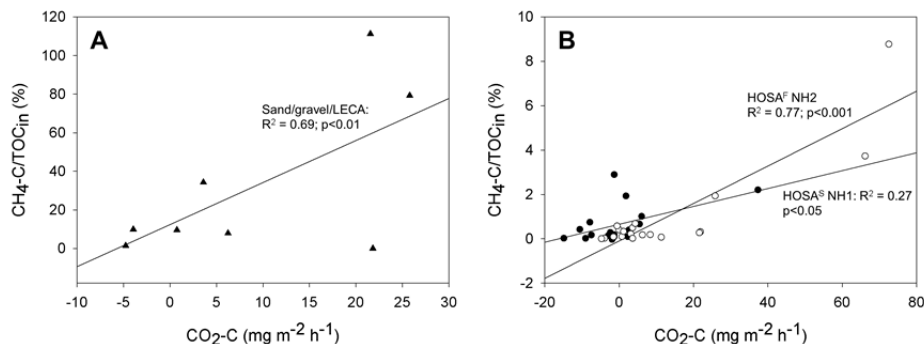


Figure 9. Regression analyses of CO₂-C emission and CH₄-C emissions factor (CH₄-C/TOC_{in}) for widely used filter materials (A; Publication II) and the HOSA filters (Publication IV) with two loading regimes (B); Black triangles – sand, gravel and LECA filters, black circles – filter with stable loading (HOSA^S), white circles – filter with fluctuating loading (HOSA^F).

3.2.3. N₂O emission

The median values of N₂O emission varied between 20.9 to 72.3 μg m⁻² h⁻¹ in the inflow part and between 19.9 to 40.2 μg m⁻² h⁻¹ in the outflow part of all mesocosm filled with peat, HOSA and their combinations (Publication III). The lowest emission occurred in peat/HOSA filters HF2 (5/1), HF4 (1/1) and HF5

(median values of 24.6, 40.9 and 18.9 $\mu\text{g m}^{-2} \text{h}^{-1}$, respectively). The highest fluxes were registered in the peat (maximum value 280 $\mu\text{g m}^{-2} \text{h}^{-1}$) and HOSA-filled (582 $\mu\text{g m}^{-2} \text{h}^{-1}$) filters (Publication III).

The N_2O emission from the full-scale HOSA filters varied between -28.2 to 783.5 and -42.8 to 606.4 $\mu\text{g m}^{-2} \text{h}^{-1}$ with median values of 5.7 and 8.6 $\mu\text{g m}^{-2} \text{h}^{-1}$, for stable loading and fluctuating loading respectively, being significantly lower ($p < 0.05$) in the case of stable hydraulic regime (Publication IV). Temporal variation in both filters showed clear seasonal dynamics and also revealed that the emissions were significantly higher ($p < 0.01$) in the second year (Fig. 10).

In the sand, gravel and LECA filled HSSF CWs, N_2O emission varied between 0–894 $\mu\text{g m}^{-2} \text{h}^{-1}$, with a median value of 130 $\mu\text{g m}^{-2} \text{h}^{-1}$ (Publication II). There was also a significant correlation between the N_2O emission and the inflow TN loading in these filters, which was not revealed in the HOSA filters.

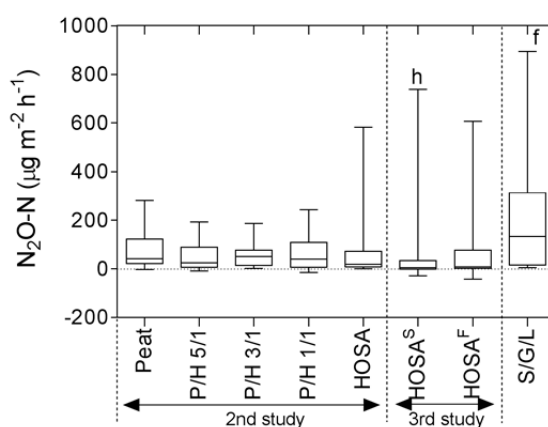


Figure 10. Median, 25%–75% and min-max values of N_2O flux from the municipal wastewater treating HSSF filters filled with peat (HF1; $n=14$), HOSA (HF5; $n=14$) and their combinations (5/1, $n=14$; 3/1, $n=14$ and 1/1, $n=14$ of peat and HOSA in HF2, HF3 and HF4, respectively) in the case of second experiment; from the full scale HOSA filled HSSF filters having stable and fluctuating loading regimes NH1 ($n=224$) and NH2 ($n=216$), respectively) in the case of third experiment; and from the sand, gravel, LECA (S/G/L) filters ($n=11$; review). Letters indicate significant differences ($p < 0.05$) between different filter systems based on Kruskal-Wallis ANOVA.

The N_2O emission factors of inflow TN loading were rather small for all the studied experimental filters (Publications III and IV). In the peat (HF1), peat/HOSA (HF2–HF4) and HOSA (HF5) filters EF% values were between 0.007 and 0.04%, while in the NH1 and NH2 the values were between 0.09 and 0.16%, respectively. These results were close to those reported in the sand, gravel and LECA filled HSSF CWs (0.79%) (Publication II) and 0.61% reported by Jahangir et al. (2016). EF% shows that only a small amount of TN entering to the HSSF filter systems is transformed to N_2O . There is also a possi-

bility that the denitrification process is complete and the nitrogen is emitted as N_2 . TN loadings varied in the higher range ($1.0\text{--}295\text{ mg m}^{-2}\text{ h}^{-1}$) within the sand, gravel and LECA HSSF filters analysed in Publication II, when compared to the HOSA filters ($4.3\text{--}23.3\text{ mg m}^{-2}\text{ h}^{-1}$) (Publication IV).

According to several other studies, the anaerobic denitrification activity is optimal around neutral pH (Thomas et al., 1994; Ligi et al., 2014; Ligi et al., 2015). The same phenomenon was also revealed in the analysed sand, gravel and LECA HSSF filters (Publication II). However, in the current experimental study, the highest N_2O emissions were detected from the peat (HF1), and especially in the highly alkaline peat/HOSA (HF4) and HOSA (HF5, NH1 and NH2) filters.

The spatial variation of N_2O emissions was observable in both experiments and higher fluxes were detected in the inflow sections of the filters (Publication III and IV). These results clearly indicate that higher nitrogen and organic matter concentrations in the inflow promoted higher emissions. In addition, the decreased pH levels in this area of the filter also provided a more suitable environment for denitrification. Similarly to the CH_4 emissions, higher N_2O fluxes (Fig. 11) were detected from the HOSA filter with the fluctuating loading regime after the filter clogged — probably due to the neutralised pH and more suitable environment for denitrifying bacteria.

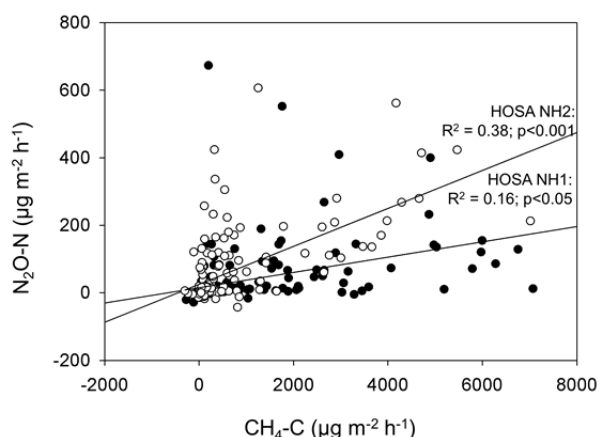


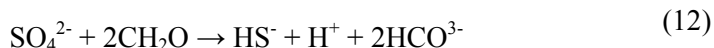
Figure. 11. Regression analyses of N_2O -N and CH_4 -C emission in filters NH1 (black dots) and NH2 (white dots).

Seasonal dynamics in N_2O emissions were not revealed in the peat (HF1), peat/HOSA (HF2-HF4) and HOSA (HF5) filters (Publication III); however, in the full scale HOSA filters (NH1 and NH2) the relationship between air temperature and N_2O emissions were substantial (Publication IV). A remarkable N_2O emission peak was observable in all filters when the air temperature increased rapidly from minus to plus degrees in April 2012 (second experiment) and February 2015 (third experiment), respectively. This phenomenon is well

known and studies have shown that freezing-thawing cycles can significantly increase N₂O emissions (Prieme and Christensen, 2001; Teepe et al., 2001; Song et al., 2010). In the HSSF CWs, freezing of the top layer of the filter system can expand N₂O production in deeper layers, as the microorganisms are isolated from oxygen diffusion through the surface and the denitrification process is expanded (Teepe et al., 2001). It is probably that the N₂O produced will congregate beneath the frozen surface since it is not able to diffuse through the frozen surface, as described by Burton and Beauchamp (1994).

The inflow SO₄²⁻ concentration was high in the third experiment, however in the effluent; a significant reduction of this compound was seen. The statistical analysis detected a significant negative correlation between N₂O emission and wastewater SO₄²⁻ concentration in both studied HOSA filters (Publication IV). An active sulfate reduction by SRB in these filters can be assumed from the rapid reduction of the high inflow SO₄²⁻ concentrations. This refers to the more favourable conditions for sulfate reduction than denitrification since these two anaerobic processes are known to prefer different redox conditions. Kadlec and Wallace, (2009), also showed that significantly lower N₂O emission in HSSF CWs was detected in sulfate reducing conditions. It is also known, that the sulfate reducers can use a wide range of alternative electron acceptors and donors, allowing them to occupy various environments (Pester et al., 2012). The sulfides can have both stimulatory and inhibitory effects on denitrification, since some autotrophic denitrifiers are able to use sulfides as an electron donor. On the other hand, the inhibitory effect of sulfide on nitrous oxide reductase may lead to the higher N₂O emission (Bowles et al., 2012). However, the activity of SRB can be lowered in highly alkaline conditions (Goeres et al., 1998).

In the HSSF CWs sulfate reduction is possibly activated by the presence of organic matter (Kadlec and Wallace, 2009). Usually, the pH stays around neutral in most types of constructed wetlands and some of the sulfate entering into the filter system will be released as highly toxic H₂S gas (van den Bosch et al., 2007). However, in the treatment systems where pH levels are high (>8) the bisulfide (HS⁻) formation can be dominant (Kadlec and Wallace, 2009). Similarly to the H₂S, bisulfide is also toxic compound for humans and the environment and is not a preferred end product in the treatment systems. Eq. 12 describes the formation of bisulfide in highly alkaline wastewater treatment systems, where CH₂O represents the organic substrate required by the microbes (Kadlec and Wallace, 2009).



In the HOSA filters, the environmental pH was suitable for the formation of a significant amount of HS⁻. However, microbes in the presence of organic matter produce bisulfide as well as H₂S. The amount of these toxic compounds can be reduced if the organic matter is removed before the wastewater enters the HOSA-filled filter.

4. CONCLUSIONS

Results of this study show that the wastewater treatment efficiency as well as greenhouse gas emissions from the subsurface flow constructed wetlands are highly dependent on the selection of suitable filter materials and the hydraulic loading regime.

The Filtralite® and HOSA filters used in greywater treatment showed rather good nutrient and organic carbon removal efficiency under different hydraulic loading regimes. The Filtralite® filled systems removed up to 55% of the TN entering to the system compared with 46% removed by HOSA. The highest TN removal occurred in VSSF filters and the most effective was the system where crushed Filtralite® with a fraction of 4–10 mm was used. Phosphorous removal efficiency from the greywater was greatly dependent on filter material properties. The HOSA outperformed other systems and achieved removal efficiency of up to 81%. The Filtralite® filters phosphorus removal efficiency was 35–38%. The results of the study show that a combination of crushed Filtralite® in VSSF filters followed by HOSA-filled HSSF filters could result in highly effective treatment system for nitrogen, organic carbon and phosphorus removal. The peat, HOSA and a combination of these two materials in the municipal wastewater treatment system strongly affected treatment efficiency of the system. The nitrogen removal was moderate in all these filters, achieving purification efficiency up to 36%. However the filters with highest amount of HOSA showed remarkable phosphorus removal efficiency, which was up to 99%. The combination of peat/HOSA with large amount of peat was not effective and resulted in remarkably lower purification rates. The high phosphorus removal efficiency of HOSA is related to the high content of reactive Ca minerals (most important are ettringite and portlandite) in this material that cause the precipitation of phosphorus in the form of Ca-phosphates. Reduction of organic matter in the greywater was outstanding in VSSF filters with a removal efficiency of up to 88% in Filtralite® filled systems. However, the organic matter removal efficiency of 78% in HOSA filters was also surprisingly high. HSSF filters were not effective for organic matter reduction, principally due to the anaerobic conditions. Highest organic matter removal efficiency was achieved in the third study, up to 52%. This rather good result was probably due to the anaerobic microbial sulfate reduction and methanogenesis.

In the cases of HOSA filters the target value (9) for the effluent pH established by the Estonian regulations was not achieved. The best pH reduction was evidently in filters with the highest amount of peat, however those filter systems lost their water treatment efficiency, especially phosphorus removal, after a few months of operation. Therefore, it is not reasonable to use peat and HOSA in the same treatment unit but instead, peat could be applied additionally after the treatment of HOSA filters, as a pH neutralizer. The results indicate that at high pH conditions and presence of sufficient amounts of organic matter, nitrogen and sulfur, large amounts of toxic sulfur compounds and NH_3^- can be produced in the HOSA filters. Thereafter it is recommendable to use HOSA filters for TP

removal as a tertiary treatment system when most of the organic and nitrogen compounds have already been removed from the wastewater.

HOSA had strong effect on GHG emissions from the wastewater treating HSSF filters. The CO_2 and CH_4 emissions were significantly lower from the filters where this material was used as a main filter material, compared with the filters, where peat or more widely used filter materials (sand, gravel and LECA) were used. The main mechanism behind the low CO_2 emissions from this material is the reaction between the highly reactive Ca ions and atmospheric CO_2 that results in the formation of calcium carbonate. However, this is not a permanent process and after the free Ca is used for calcite and phosphate precipitation, the filter starts to emit CO_2 during microbial activities. The results indicate that the highly alkaline and sulfate rich HOSA filter environment is not suitable for methanogenic archaea that are suppressed by the sulfate reducing bacteria. However, the clogging in the filter system can provide suitable environment for the methanogens and also nitrogen transforming organisms and extremely high CH_4 and N_2O fluxes can occur from the filters. This clearly indicates that the clogging of the filter system is one of the crucial problems, which will decrease water treatment efficiency and magnify GHG emissions. N_2O emissions, however, were in the close range as reported in the literature, showing no significant difference. It can be estimated, that denitrification process in HSSF filters is complete and most of the nitrogen is emitted as N_2 .

Based on the results of this thesis, it can be concluded that when establishing a wastewater treatment plant, the most effective treatment system for the nutrient removal and organic matter reduction from the wastewater could be VSSF filters filled with crushed Filtralite[®] for nitrogen and organic matter removal with re-circulation for higher removal efficiency, followed by the HOSA filled HSSF filter for phosphorus precipitation, with the last step being HSSF peat filter for pH neutralisation. That kind of setup should avoid excessive nitrogen and organic matter inflow to the HOSA filter and evade the formation of toxic elements like ammonia, hydrogen sulfide and bisulfide ions and in addition prevent high GHG emissions from the system.

Further research is needed to study the microbial processes taking place in the highly alkaline HOSA filters. In particularly, the microbial processes regulating GHG emissions in these kinds of hostile environments are still unclear and need more precise studies.

5. REFERENCES

- Abu Ghunmi, L., Zeeman, G., Fayyad, M. and van Lier, J.B. (2011) Grey Water Treatment Systems: A Review. *Critical Reviews in Environmental Science and Technology* 41(7), 657–698.
- Ádám, K., Krogstad, T., Vrale, L., Sovik, A.K., Jenssen, P.D. (2007) Phosphorus retention in the filter materials shellsand and Filtralite-P – Batch and column experiment with synthetic P solution and secondary wastewater. *Ecol. Eng.*, 29, 200–208.
- Amado, L., Albuquerque, A. and Santo, A.E. (2012) Influence of stormwater infiltration on the treatment capacity of a LECA-based horizontal subsurface flow constructed wetland. *Ecological Engineering* 39, 16–23.
- APHA-AWWA-WEF (2005) *Standard Methods for the Examination of Water and Wastewater*, 21th ed. American Public Health Organisation.
- Arp, D.J. and Stein, L.Y. (2003) Metabolism of inorganic N compounds by ammonia-oxidizing bacteria. *Critical Reviews in Biochemistry and Molecular Biology* 38(6), 471–495.
- Ayaz, S.C. and Akca, L. (2001) Treatment of wastewater by natural systems. *Environment International* 26(3), 189–195.
- Bae, W., Baek, S., Chung, J. and Lee, Y. (2001) Optimal operational factors for nitrite accumulation in batch reactors. *Biodegradation* 12(5), 359–366.
- Barbera, A.C., Borin, M., Ioppolo, A., Cirelli, G.L. and Maucieri, C. (2014) Carbon dioxide emissions from horizontal sub-surface constructed wetlands in the Mediterranean Basin. *Ecological Engineering* 64, 57–61.
- Bellier, N., Chazarenc, F. and Comeau, Y. (2006) Phosphorus removal from wastewater by mineral apatite. *Water Research* 40(15), 2965–2971.
- Biasi, C., Lind, S.E., Pekkarinen, N.M., Huttunen, J.T., Shurpali, N.J., Hyvonen, N.P., Repo, M.E. and Martikainen, P.J. (2008) Direct experimental evidence for the contribution of lime to CO₂ release from managed peat soil. *Soil Biology & Biochemistry* 40(10), 2660–2669.
- Bityukova, L., Mötlep, R. and Kirsimäe, K. (2010) Composition of Oil Shale Ashes from Pulverized Firing and Circulating Fluidized-Bed Boiler in Narva Thermal Power Plants, Estonia. *Oil Shale* 27(4), 339–353.
- Borjesson, G. and Svensson, B.H. (1997) Seasonal and diurnal methane emissions from a landfill and their regulation by methane oxidation. *Waste Management & Research* 15(1), 33–54.
- Boutin, C., Lienar, A. (2003) Constructed wetlands for wastewater treatment: the french experience. 1st International seminar on the use of aquatic macrophytes for wastewater treatment in constructed wetlands, May 2003, Lisbonne, Portugal. pp. 437–466.
- Bowles, M.W., Nigro, L.M., Teske, A.P. and Joye, S.B. (2012) Denitrification and environmental factors influencing nitrate removal in Guaymas Basin hydrothermally altered sediments. *Frontiers in Microbiology* 3.
- Burton, D.L. and Beauchamp, E.G. (1994) Profile Nitrous-Oxide and Carbon-Dioxide Concentrations in a Soil Subject to Freezing. *Soil Science Society of America Journal* 58(1), 115–122.
- Champagne, R.D., Khalekuzzaman, : (2006) A sequential aerated peat biofilter system for the treatment of landfill leachate. In: Martin-Duque, J.P., Brebbia, C.A., Emmanouloudis, D., Mander, Ü. (Eds), *Geo-Environment and Landscape Evolution II*. Wit press. 125–134.

- Chiemchaisri, C., Chiemchaisri, W., Junsod, J., Threedeach, S. and Wicranarachchi, P.N. (2009) Leachate treatment and greenhouse gas emission in subsurface horizontal flow constructed wetland. *Bioresource Technology* 100(16), 3808–3814.
- Donner, E., Eriksson, E., Revitt, D.M., Scholes, L., Lutzhoft, H.C.H. and Ledin, A. (2010) Presence and fate of priority substances in domestic greywater treatment and reuse systems. *Science of the Total Environment* 408(12), 2444–2451.
- Eriksson, E., Andersen, H.R., Madsen, T.S. and Ledin, A. (2009) Greywater pollution variability and loadings. *Ecological Engineering* 35(5), 661–669.
- Garcia, J.L., Patel, B.K.C. and Ollivier, B. (2000) Taxonomic phylogenetic and ecological diversity of methanogenic Archaea. *Anaerobe* 6(4), 205–226.
- Garcia-Carmona, J., Gomez-Morales, J., Fraile-Sainz, J. and Rodriguez-Clemente, R. (2003b) Morphological characteristics and aggregation of calcite crystals obtained by bubbling CO₂ through a Ca(OH)(2) suspension in the presence of additives. *Powder Technology* 130(1–3), 307–315.
- Garcia-Carmona, J., Morales, J.G. and Rodriguez-Clemente, R. (2003a) Morphological control of precipitated calcite obtained by adjusting the electrical conductivity in the Ca(OH)(2)-H₂O-CO₂ system. *Journal of Crystal Growth* 249(3–4), 561–571.
- Gauci, V., Fowler, D., Chapman, S.J. and Dise, N.B. (2004) Sulfate deposition and temperature controls on methane emission and sulfur forms in peat. *Biogeochemistry* 71(2), 141–162.
- Goeres, D.M., Nielsen, P.H., Smidt, H.D. and Frolund, B. (1998) The effect of alkaline pH conditions on a sulphate reducing consortium from a Danish district heating plant. *Biofouling* 12(4), 273–286.
- Heistad, A., Paruch, A.M., Vrale, L., Ádám, K., Jenssen, P.D. (2006). A high-performance compact filter system treating domestic wastewater. *Ecol. Eng.* 28, 374–379.
- Herrmann, I., Jourak, A., Gustafsson, J.P., Hedstrom, A., Lundstrom, T.S. and Viklander, M. (2013b) Modeling phosphate transport and removal in a compact bed filled with a mineral-based sorbent for domestic wastewater treatment. *Journal of Contaminant Hydrology* 154, 70–77.
- Herrmann, I., Jourak, A., Hedstrom, A., Lundstrom, T.S. and Viklander, M. (2013a) The Effect of Hydraulic Loading Rate and Influent Source on the Binding Capacity of Phosphorus Filters. *Plos One* 8(8).
- Huang, L., Gao, X., Guo, J., Ma, X., Liu, M. (2013) A review on the mechanisms and affecting factors of nitrous oxide emission in constructed wetlands. *Environmental Earth Sciences* 68, 2171–2180.
- Hutchinson, G.L. and Livingston, G.P. (1993) Use of Chamber Systems to Measure Trace Gas Fluxes. *Agricultural Ecosystem Effects on Trace Gases and Global Climate Change* 55, 63–78.
- Inamori, R., Wang, Y.H., Yamamoto, T., Zhang, J.X., Kong, H.N., Xu, K.Q. and Inamori, Y. (2008) Seasonal effect on N₂O formation in nitrification in constructed wetlands. *Chemosphere* 73(7), 1071–1077.
- IPCC (2013) The Physical, Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.
- Jahangir, M.M.R., Richards, K.G., Healy, M.G., Gill, M.G., Müller, C., Johnston, P., Fenton, O. (2016) Carbon and nitrogen dynamics and greenhouse gas emissions in constructed wetlands treating wastewater: a review. *Hydrology and Earth System Sciences* 20, 109–123.
- Jenssen, P.D., Maehlum, T., Krogstad, T. and Vrale, L. (2005) High performance constructed wetlands for cold climates. *Journal of Environmental Science and Health*

- Part a-Toxic/Hazardous Substances & Environmental Engineering 40(6–7), 1343–1353.
- Jenssen, P.D., Vråle, L. (2003) Greywater treatment in combined Biofilter/constructed Wetlands in Cold Climate. 875–881.
- Kaasik, A., Vohla, C., Mõtlep, R., Mander, Ü. and Kirsimäe, K. (2008) Hydrated calcareous oil-shale ash as potential filter media for phosphorus removal in constructed wetlands. *Water Research* 42(4–5), 1315–1323.
- Kadlec, R.H., Wallace, S.D. (2009) *Treatment Wetlands*. Second Edition. 1016p.
- Kängsepp, P., Kõiv, M., Kriipsalu, M. and Mander, Ü. (2008) Leachate Treatment in Newly Built Peat Filters: A Pilot-Scale Study. *Wastewater Treatment, Plant Dynamics and Management in Constructed and Natural Wetlands*, 89–98.
- Karabelnik, K., Kõiv, M., Kasak, K., Jenssen, P.D. and Mander, Ü. (2012) High-strength greywater treatment in compact hybrid filter systems with alternative substrates. *Ecological Engineering* 49, 84–92.
- Kasak, K., Karabelnik, K., Kõiv, M., Jenssen, P.D., Mander, Ü. (2011) Phosphorus removal from greywater in an experimental hybrid compact filter. In Brebbia, C.A., Popov, V (Eds), *Water Resources Management VI*, WIT Press, 649–657
- Kasak, K., Mander, Ü., Truu, J., Truu, M., Järveoja, J., Maddison, M. and Teemusk, A. (2015) Alternative filter material removes phosphorus and mitigates greenhouse gas emission in horizontal subsurface flow filters for wastewater treatment. *Ecological Engineering* 77, 242–249.
- Klimeski, A., Uusitalo, R. and Turtola, E. (2014) Screening of Ca- and Fe-rich materials for their applicability as phosphate-retaining filters. *Ecological Engineering* 68, 143–154.
- Kõiv, M., Kriipsalu, M. and Mander, Ü. (2006) After treatment of landfill leachate in peat filters. *Geo-Environment and Landscape Evolution II* 89, 93–103.
- Kõiv, M., Kriipsalu, M., Vohla, C. and Mander, Ü. (2009b) Hydrated Oil Shale Ash and Mineralized Peat as Alternative Filter Materials for Landfill Leachate Treatment in Vertical Flow Constructed Wetlands. *Fresenius Environmental Bulletin* 18(2), 189–195.
- Kõiv, M., Liira, M., Mander, Ü., Mõtlep, R., Vohla, C. and Kirsimäe, K. (2010) Phosphorus removal using Ca-rich hydrated oil shale ash as filter material – The effect of different phosphorus loadings and wastewater compositions. *Water Research* 44(18), 5232–5239.
- Kõiv, M., Mõtlep, R., Paiste, P., Kirsimäe, K. (2015) Reactive filtration of phosphorus in Ca-rich hydrated oil shale ash filters: effect of organic and hydraulic loading rate. In: Dotro G., Gagnon, V. (Eds): *6th International Symposium on Wetland Pollutant Dynamics and Control*, 166–167.
- Kõiv, M., Vohla, C., Mõtlep, R., Liira, M., Kirsimäe, K. and Mander, Ü. (2009a) The performance of peat-filled subsurface flow filters treating landfill leachate and municipal wastewater. *Ecological Engineering* 35(2), 204–212.
- Le Mer, J. and Roger, P. (2001) Production, oxidation, emission and consumption of methane by soils: A review. *European Journal of Soil Biology* 37(1), 25–50.
- Leal, L.H., Temmink, H., Zeeman, G. and Buisman, C.J.N. (2011) Characterization and anaerobic biodegradability of grey water. *Desalination* 270(1–3), 111–115.
- Lee, W.C. and Debeer, D. (1995) Oxygen and Ph Microprofiles above Corroding Mild-Steel Covered with a Biofilm. *Biofouling* 8(4), 273–280.

- Li, F.Y., Wichmann, K. and Otterpohl, R. (2009) Review of the technological approaches for grey water treatment and reuses. *Science of the Total Environment* 407(11), 3439–3449.
- Ligi, T., Oopkaup, K., Truu, M., Preem, J.K., Nölvak, H., Mitsch, W.J., Mander, Ü. and Truu, J. (2014a) Characterization of bacterial communities in soil and sediment of a created riverine wetland complex using high-throughput 16S rRNA amplicon sequencing. *Ecological Engineering* 72, 56–66.
- Ligi, T., Truu, M., Oopkaup, K., Nölvak, H., Mander, Ü., Mitsch, W.J. and Truu, J. (2015) The genetic potential of N-2 emission via denitrification and ANAMMOX from the soils and sediments of a created riverine treatment wetland complex. *Ecological Engineering* 80, 181–190.
- Ligi, T., Truu, M., Truu, J., Nölvak, H., Kaasik, A., Mitsch, W.J. and Mander, Ü. (2014b) Effects of soil chemical characteristics and water regime on denitrification genes (*nirS*, *nirK*, and *nosZ*) abundances in a created riverine wetland complex. *Ecological Engineering* 72, 47–55.
- Liira, M., Kõiv, M., Mander, Ü., Mötlep, R., Vohla, C. and Kirsimäe, K. (2009) Active Filtration of Phosphorus on Ca-Rich Hydrated Oil Shale Ash: Does Longer Retention Time Improve the Process? *Environmental Science & Technology* 43(10), 3809–3814.
- Liu, C.X., Xu, K.Q., Inamori, R., Ebie, Y., Liao, J. and Inamori, Y. (2009) Pilot-scale studies of domestic wastewater treatment by typical constructed wetlands and their greenhouse gas emissions. *Frontiers of Environmental Science & Engineering in China* 3(4), 477–482.
- Liu, H.B., Zhao, F., Mao, B.Y. and Wen, X.H. (2012) Enhanced nitrogen removal in a wastewater treatment process characterized by carbon source manipulation with biological adsorption and sludge hydrolysis. *Bioresource Technology* 114, 62–68.
- Lofthfield, N., Flessa, H., Augustin, J. and Beese, F. (1997) Automated gas chromatographic system for rapid analysis of the atmospheric trace gases methane, carbon dioxide, and nitrous oxide. *Journal of Environmental Quality* 26(2), 560–564.
- Lovley, D.R. and Klug, M.J. (1983) Sulfate Reducers Can out-Compete Methanogens at Fresh-Water Sulfate Concentrations. *Applied and Environmental Microbiology* 45(1), 187–192.
- Mander, Ü., Dotro, G., Ebie, Y., Towprayoon, S., Chiemchaisri, C., Nogueira, S.F., Jamsranjav, B., Kasak, K., Truu, J., Tournebize, J. and Mitsch, W.J. (2014) Greenhouse gas emission in constructed wetlands for wastewater treatment: A review. *Ecological Engineering* 66, 19–35.
- Mander, Ü., Järveoja, J., Maddison, M., Soosaar, K., Aavola, R., Ostonen, I. and Salm, J.O. (2012) Reed canary grass cultivation mitigates greenhouse gas emissions from abandoned peat extraction areas. *Global Change Biology Bioenergy* 4(4), 462–474.
- Mander, Ü., Kuusemets, V., Lõhmus, K., Mäuring, T., Teiter, S. and Augustin, J. (2003) Nitrous oxide, dinitrogen and methane emission in a subsurface flow constructed wetland. *Water Science and Technology* 48(5), 135–142.
- Mander, Ü., Lõhmus, K., Teiter, S., Mäuring, T., Nurk, K. and Augustin, J. (2008) Gaseous fluxes in the nitrogen and carbon budgets of subsurface flow constructed wetlands. *Science of the Total Environment* 404(2–3), 343–353.
- Mander, Ü., Lõhmus, K., Teiter, S., Nurk, K., Mäuring, T. and Augustin, A. (2005) Gaseous fluxes from subsurface flow constructed wetlands for wastewater treatment. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering* 40(6–7), 1215–1226.

- Mander, Ü., Maddison, M., Soosaar, K. and Karabelnik, K. (2011) The Impact of Pulsing Hydrology and Fluctuating Water Table on Greenhouse Gas Emissions from Constructed Wetlands. *Wetlands* 31(6), 1023–1032.
- Melian, J.A.H., Rodriguez, A.J.M., Arana, J., Diaz, O.G. and Henriquez, J.J.G. (2010) Hybrid constructed wetlands for wastewater treatment and reuse in the Canary Islands. *Ecological Engineering* 36(7), 891–899.
- Middlebrooks, E.J., Pano, A. (1983) Nitrogen removal in aerated lagoons. *Water Res.* 17 (10), 1369–1378.
- Miner, J.R. (1974) Odors from confined livestock production: a state of the art. EPA-660/2-74-023. U.S. EPA, Washington D.C., pp. 125.
- Molle, P., Lienard, A., Boutin, C., Merlin, G. and Iwema, A. (2005) How to treat raw sewage with constructed wetlands: an overview of the French systems. *Water Science and Technology* 51(9), 11–21.
- Morari, F. and Giardini, L. (2009) Municipal wastewater treatment with vertical flow constructed wetlands for irrigation reuse. *Ecological Engineering* 35(5), 643–653.
- Mõtlep, R. (2010) Composition and diagenesis of oil shale industrial solid wastes. *Dissertationes Technologiae Circumiectionum Universitatis Tartuens.* 48 p.
- Mõtlep, R., Kirsimäe, K., Talviste, P., Puura, E., Jürgenson, J. (2007) Mineral composition of Estonian oil shale semi-coke sediments. *Oil Shale* 24(3), 405–422.
- Mõtlep, R., Sild, T., Puura, E. and Kirsimäe, K. (2010) Composition, diagenetic transformation and alkalinity potential of oil shale ash sediments. *Journal of Hazardous Materials* 184(1–3), 567–573.
- Nilsson, C., Renman, G., Westholm, L.J., Renman, A. and Drizo, A. (2013) Effect of organic load on phosphorus and bacteria removal from wastewater using alkaline filter materials. *Water Research* 47(16), 6289–6297.
- Noorvee, A., Põldvere, E. and Mander, Ü. (2007) The effect of pre-aeration on the purification processes in the long-term performance of a horizontal subsurface flow constructed wetland. *Science of the Total Environment* 380(1–3), 229–236.
- Oonk, H. (2010) Literature review: methane from landfills. *Sustainable Landfill Foundation* 75p.
- Öövel, M., Tarajev, R., Kull, A. and Mander, Ü. (2005) Tertiary treatment of municipal wastewater in a floodplain peatland. *Water Resources Management* III 80, 433–444.
- Pangala, S.R., Reay, D.S. and Heal, K.V. (2010) Mitigation of methane emissions from constructed farm wetlands. *Chemosphere* 78(5), 493–499.
- Patterson, A.A., Davey, K., Farnan, N. (2001) Peat bed filters for on-site treatment of septic tank effluent. In: Patterson, R.A. and Jones, M.J. (Eds), *Advancing On-site Wastewater Systems*, Armidale, Landfax Labs, Armidale., 315–322.
- Pester, M., Knorr, K.H., Friedrich, M.W., Wagner, M. and Loy, A. (2012) Sulfate-reducing microorganisms in wetlands – fameless actors in carbon cycling and climate change. *Frontiers in Microbiology* 3.
- Pícek, T., Cizkova, H. and Dusek, J. (2007) Greenhouse gas emissions from a constructed wetland – Plants as important sources of carbon. *Ecological Engineering* 31(2), 98–106.
- Põldvere, E., Karabelnik, K., Noorvee, A., Maddison, M., Nurk, K., Zaytsev, I. and Mander, Ü. (2009) Improving wastewater effluent filtration by changing flow regimes-Investigations in two cold climate pilot scale systems. *Ecological Engineering* 35(2), 193–203.
- Põldvere, E., Noorvee, A., Karabelnik, K., Maddison, M., Nurk, K., Zaytsev, I. and Mander, Ü. (2010) A case study of the performance of pilot scale light weight

- aggregates (LWA) based hybrid soil filters in Estonia. *Desalination* 250(1), 361–367.
- Prieme, A. and Christensen, S. (2001) Natural perturbations, drying-wetting and freezing-thawing cycles, and the emission of nitrous oxide, carbon dioxide and methane from farmed organic soils. *Soil Biology & Biochemistry* 33(15), 2083–2091.
- Reddy, K.R., DeLaunne, R.D. (2008) *Biogeochemistry of Wetlands: Science and Applications*. 800p.
- Reddy, K.R., Patric Jr., W.H. (1984). Nitrogen transformation and loss in flooded soils and sediments. *CRC Crit. Rev. Environ. Control* 13, 273–309.
- Reis, M.A.M., Almeida, J.S., Lemos, P.C. and Carrondo, M.J.T. (1992) Effect of Hydrogen-Sulfide on Growth of Sulfate Reducing Bacteria. *Biotechnology and Bioengineering* 40(5), 593–600.
- Rendek, E., Ducom, G. and Germain, P. (2006) Carbon dioxide sequestration in municipal solid waste incinerator (MSWI) bottom ash. *Journal of Hazardous Materials* 128(1), 73–79.
- Reshef, D.N., Reshef, Y.A., Finucane, H.K., Grossman, S.R., McVean, G., Turnbaugh, P.J., Lander, E.S., Mitzenmacher, M. and Sabeti, P.C. (2011) Detecting Novel Associations in Large Data Sets. *Science* 334(6062), 1518–1524.
- Revitt, D.M., Eriksson, E. and Donner, E. (2011) The implications of household grey-water treatment and reuse for municipal wastewater flows and micropollutant loads. *Water Research* 45(4), 1549–1560.
- Robertson, G.P. and Tiedje, J.M. (1987) Nitrous-Oxide Sources in Aerobic Soils – Nitrification, Denitrification and Other Biological Processes. *Soil Biology & Biochemistry* 19(2), 187–193.
- Rosso, D. and Stenstrom, M.K. (2008) The carbon-sequestration potential of municipal wastewater treatment. *Chemosphere* 70(8), 1468–1475.
- RT I, 1 13.06.2013, 13 (2013) Requirements for wastewater discharge into water bodies and target values (Reovee puhastamise ning heit- ja sademevee suublasse juhtimise kohta esitatavad nõuded, heit- ja sademevee reostusnäitajate piirmäärad ning nende nõuete täitmise kontrollimise meetmed). Accepted by the Government of the Republic of Estonia on 29.11.2012, Regulation No 99.
- Shaw, L.J., Nicol, G.W., Smith, Z., Fear, J., Prosser, J.I. and Baggs, E.M. (2006) *Nitrosospira* spp. can produce nitrous oxide via a nitrifier denitrification pathway. *Environmental Microbiology* 8(2), 214–222.
- Simek, M. and Cooper, J.E. (2002) The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *European Journal of Soil Science* 53(3), 345–354.
- Sklarz, M.Y., Gross, A., Yakirevich, A. and Soares, M.I.M. (2009) A recirculating vertical flow constructed wetland for the treatment of domestic wastewater. *Desalination* 246 (1–3), 617–624.
- Song, K., Lee, S.H., Mitsch, W.J. and Kang, H. (2010) Different responses of denitrification rates and denitrifying bacterial communities to hydrologic pulsing in created wetlands. *Soil Biology & Biochemistry* 42(10), 1721–1727.
- Søvik, A.K., Augustin, J., Heikkinen, K., Huttunen, J.T., Necki, J.M., Karjalainen, S.M., Klove, B., Liikanen, A., Mander, Ü., Puustinen, M., Teiter, S. and Wachniew, P. (2006) Emission of the greenhouse gases nitrous oxide and methane from constructed wetlands in Europe. *Journal of Environmental Quality* 35(6), 2360–2373.
- Stieglmeier, M., Mooshammer, M., Kitzler, B., Wanek, W., Zechmeister-Boltenstern, S., Richter, A. and Schleper, C. (2014) Aerobic nitrous oxide production through

- N-nitrosating hybrid formation in ammonia-oxidizing archaea. *Isme Journal* 8(5), 1135–1146.
- Teepe, R., Brumme, R. and Beese, F. (2001) Nitrous oxide emissions from soil during freezing and thawing periods. *Soil Biology & Biochemistry* 33(9), 1269–1275.
- Teiter, S. and Mander, Ü. (2005) Emission of N_2O , N_2 , CH_4 , and CO_2 from constructed wetlands for wastewater treatment and from riparian buffer zones. *Ecological Engineering* 25(5), 528–541.
- Thomas, K.L., Lloyd, D. and Boddy, L. (1994) Effects of Oxygen, Ph and Nitrate Concentration on Denitrification by *Pseudomonas* Species. *Fems Microbiology Letters* 118(1–2), 181–186.
- Thomson, A.J., Giannopoulos, G., Pretty, J., Baggs, E.M. and Richardson, D.J. (2012) Biological sources and sinks of nitrous oxide and strategies to mitigate emissions. *Philosophical Transactions of the Royal Society B-Biological Sciences* 367(1593), 1157–1168.
- Uibu, M., Kuusik, R. and Veskimäe, H. (2008) Seasonal binding of atmospheric CO_2 by oil shale ash. *Oil Shale* 25(2), 254–266.
- Uibu, M., Uus, M. and Kuusik, R. (2009) CO_2 mineral sequestration in oil-shale wastes from Estonian power production. *Journal of Environmental Management* 90(2), 1253–1260.
- Uibu, M., Velts, O. and Kuusik, R. (2010) Developments in CO_2 mineral carbonation of oil shale ash. *Journal of Hazardous Materials* 174(1–3), 209–214.
- van den Bosch, P.L.F., van Beusekom, O.C., Buisman, C.J.N. and Janssen, A.J.H. (2007) Sulfide oxidation at halo-alkaline conditions in a fed-batch bioreactor. *Biotechnology and Bioengineering* 97(5), 1053–1063.
- van der Gon, H.A.D., van Bodegom, P.M., Wassmann, R., Lantin, R.S., Metra-Corton, T.M. (2001) Sulphate-containing amendments to reduce methane emissions from rice fields: mechanisms, effectiveness and costs. *Mitigation and Adaption Strategies for Global Change* 6, 71–89.
- Vohla, C., Kõiv, M., Bavor, H.J., Chazarenc, F. and Mander, Ü. (2011) Filter materials for phosphorus removal from wastewater in treatment wetlands-A review. *Ecological Engineering* 37(1), 70–89.
- Vohla, C., Põldvere, E., Noorvee, A., Kuusemets, V. and Mander, Ü. (2005) Alternative filter media for phosphorous removal in a horizontal subsurface flow constructed wetland. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering* 40(6–7), 1251–1264.
- Vymazal, J. (2005) Horizontal sub-surface flow and hybrid constructed wetlands systems for wastewater treatment. *Ecological Engineering* 25(5), 478–490.
- Vymazal, J. (2007) Removal of nutrients in various types of constructed wetlands. *Science of the Total Environment* 380(1–3), 48–65.
- Vymazal, J. (2011a) Constructed Wetlands for Wastewater Treatment: Five Decades of Experience. *Environmental Science & Technology* 45(1), 61–69.
- Vymazal, J. (2011b) Long-term performance of constructed wetlands with horizontal sub-surface flow: Ten case studies from the Czech Republic. *Ecological Engineering* 37(1), 54–63.
- Vymazal, J. (2014) Long-Term Treatment Efficiency of a Horizontal Subsurface Flow Constructed Wetland at Jimlikov, Czech Republic. *Environmental Engineering and Management Journal* 13(1), 73–80.

- Vymazal, J. and Kröpfelova, L. (2009a) Removal of organics in constructed wetlands with horizontal sub-surface flow: A review of the field experience. *Science of the Total Environment* 407(13), 3911–3922.
- Vymazal, J. and Kröpfelova, L. (2008) *Wastewater Treatment in Constructed Wetlands with Horizontal Sub-Surface Flow*. Springer, Dordrecht, The Netherlands. Pp. 566.
- Vymazal, J. and Kröpfelova, L. (2009b) Removal of Nitrogen in Constructed Wetlands with Horizontal Sub-Surface Flow: A Review. *Wetlands* 29(4), 1114–1124.
- Vymazal, J. and Kröpfelova, L. (2011) A three-stage experimental constructed wetland for treatment of domestic sewage: First 2 years of operation. *Ecological Engineering* 37(1), 90–98.
- Wen, Y., Xu, C., Liu, G., Chen, Y. and Zhou, Q. (2012) Enhanced nitrogen removal reliability and efficiency in integrated constructed wetland microcosms using zeolite. *Frontiers of Environmental Science & Engineering* 6(1), 140–147.
- Widdel, F. (1988) Microbiology and ecology of sulfate and sulfur reducing bacteria. In: Zehnder A J B (ed) *Biology of Anaerobic Microorganisms*. John Wiley & Sons, New York. . pp 469–586.
- Zhilina, T.N. and Zavarzin, G.A. (1994) Alkaliphilic Anaerobic Community at Ph-10. *Current Microbiology* 29(2), 109–112.
- Zhu, G.B., Wang, S.Y., Feng, X.J., Fan, G.N., Jetten, M.S.M. and Yin, C.Q. (2011) Anammox Bacterial Abundance, Biodiversity and Activity in a Constructed Wetland. *Environmental Science & Technology* 45(23), 9951–9958.
- Zurita, F., Anda, De J., Belmont, M.A. (2009) Treatment of domestic wastewater and production of commercial flowers in vertical and horizontal subsurface-flow constructed wetlands. *Ecological Engineering* 35, 861–869.

SUMMARY IN ESTONIAN

Kasvuhoonegaaside lendumine ja reoveepuhastuse efektiivsus erinevate filtermaterjalidega pinnasfiltrites

Tehismärgalade sh pinnasfiltersüsteemide kasutamine reoveepuhastuses on viimase paarikümne aasta jooksul jõudsasti arenenud. Uute tehnoloogiate väljatöötamine on võimaldanud rajada hästi toimivaid süsteeme ning märkimisväärselt on paranenud ka reovee puhastusefektiivsus, muutes need süsteemid oluliseks ökotehnoloogiliseks alternatiiviks konventsionaalsetele reoveepuhastitele. Kuna tehismärgalad on disainitud nii, et neis oleks võimalik rakendada looduslikke puhastusprotsesse, tuleb nende rajamisel arvestada paljude teguritega. Kaheks kõige olulisemaks parameetrikts tehismärgalade rajamisel on vee viibeaja ning filtermaterjali valik. Need määravad suures osas ära nii vee puhastamise efektiivsuse märgalas kui ka kasvuhoonegaaside emissiooni märgala filtermaterjali pinnalt.

Tehismärgala orgaanika eemaldamise ning lämmastikuärastuse efektiivsuse määrab peamiselt hapniku kättesaadavus puhastussüsteemis. Näiteks lämmastikuärastuseks on vaja aeroobseid tingimusi, mis võimaldab orgaanilisel ainel ja ammoniumlämmastikul nitrifikatsiooniprotsessis oksüdeeruda nitraadiks. An-aeroobses keskkonnas muudetakse need denitrifikatsiooni teel gaasilisteks lämmastikuühenditeks, mis süsteemist atmosfääri lenduvad. Fosforiärastuseks on reeglina vaja aga pikemat viibeaga ning ärastuse efektiivsus sõltub peamiselt filtermaterjali valikust, sest selle poolt fosfori adsorptsioon või sadestamine on peamised protsessid fosfori eemaldamisel reoveest. Seejuures on mikroobne ning taimedepoolne eemaldamine marginaalse tähtsusega. Pinnasfiltrites kasutatavad filtermaterjalid peavad olema ühelt poolt heade hüdrauliliste omadustega ent teisest küljest ka suure eripinnaga, et võimaldada kõrgemat puhastusefektiivsust.

Käesoleva doktoritöö peamiseks eesmärgiks oli uurida erinevate filtermaterjalide mõju hallvee ja asulareovee puhastamiseks pinnasfiltersüsteemides ning nende mõju kasvuhoonegaaside emissioonile.

Doktoritöö materjal koguti kolme välikatse käigus, milles keskenduti Filtralite® ja Filtralite-P® kergkruusa erinevate fraktsioonide ning turba ja hüdratiseerunud tuhaplatoo sette uurimisele hallvee ja asulareovee puhastusefektiivsusele ning kasvuhoonegaaside emissioonile tehismärgalast. Lisaks on väitekirjas analüüsitud ja võrreldud ka teadusartiklites esitatud reoveepuhastuses enimrakendatud tehismärgalatüüpide uurimuste tulemusi, kus peamisteks filtermaterjalideks olid liiv, kruus ning kergkruus. Hallvett puhastav katse-süsteem koosnes neljast paralleelselt toimivast hübriidsest (vertikaal- ja horisontaalvoolulised filtrid) pinnasfiltersüsteemist ning filtermaterjalidena kasutati erineva terasuurusega Filtralite® ning Filtralite-P® kergkruusa ning hüdratiseerunud põlevkivituhaplatoo setet. Katse viidi läbi kahel erineval hüdraulilisel koormusel ning ligikaudu kahe-aastase perioodi jooksul. Uurimistöö teises eksperimendis selgitati horisontaalvoolulise pinnasfiltri mõju asulareovee

puhastamisele ning kasvuhoonegaaside emissioonile, kasutades filtermaterjalidena hästi lagunenud turvast ning hüdratiseerunud põlevkivituhaplatoo setet. Eksperimendis olid kasutuses viis paralleelset horisontaalvoolulist pinnasfiltrit, mis täideti turba, tuhasette või nende kahe kombinatsiooniga vahekorras 5/1, 3/1 ja 1/1. Uurimistöö kolmandas faasis analüüsiti täismõõdulise horisontaalvoolulise pinnasfiltri mõju kasvuhoonegaaside emissioonile, kasutades filtermaterjalina põlevkivituhaplatoo setet ning rakendades kahte erinevat hüdraulilist režiimi.

Hallvee puhastamiseks rajatud hübriidsed pinnasfiltrid toimisid efektiivselt ka kõrge reostuskoormuse korral. Filtralite® kergkruusal põhinevad süsteemid eemaldasid kuni 55% süsteemi sisenevast üldlämmastikust, kuid ka tuhaplatoo settega täidetud süsteem suutis vähendada lämmastiku kontsentratsiooni 46%. Hüdratiseerunud tuha fosfori sidumise efektiivsus oli aga 89%, mis ületas enam kui kaks korda Filtralite®-iga täidetud süsteemide efektiivsust (40–44%). Orgaanika vähendamise seisukohalt näitasid parimaid tulemusi vertikaalvoolulised filtrid, saavutades vähendamise efektiivsuse 75–85%. Turba ning tuhaplatoo settega katse puhul jäi lämmastikuärastus mõnevõrra madalamaks, olles vaid 36%. Seevastu fosforiärastus neis filtrites, kus oli kõige enam tuhaplatoo setet, ulatus 99%-ni. Filtrid, kus domineerivaks filtermaterjaliks oli turvas, kaotasid oma fosfori ärastuse efektiivsuse juba esimese nelja kuu jooksul. Väga kõrge fosfori eemaldamise efektiivsus on peamiselt tingitud reaktiivsete Ca-mineraalide (tähtsaimad neist portlandiit ja ettringiit) esinemisest hüdratiseerunud tuhaplatoo settes, mille abil fosfor sadestatakse reoveest Ca-fosfaadina. Uurimistulemuste põhjal võib järeldada, et hüdratiseerunud tuhaplatoo sete on efektiivne ning odav alternatiiv fosfori eemaldamiseks nii hallveest kui ka reoveest, võrreldes näiteks keemilise sadestamisega raudsulfaadi abil.

Peamiseks probleemiks tuhafiltrite puhul on aga väga kõrge pH, mis puhasti väljavoolus võib ulatuda kuni 12-ni. Käesoleva uurimuse tulemused näitavad, et probleemi on võimalik lahendada näiteks turba kaasabil, kuid need kaks materjali ei tohiks asetseda ühes süsteemis, sest seeläbi langeb süsteemi puhastusefektiivsus ning pH puhverdamise võime. Kõrge pH on peamiseks teguriks ka toksiliste ühendite (ammoniaak ja bisulfiidioonid) tekkeks tuhaplatoo settega täidetud filtrites juhul, kui on piisavalt lämmastikku ja orgaanilist ainet ning keskkond on anaeroobne.

Kasvuhoonegaaside mõõtmised viidi läbi asulareovett puhastavates katse-süsteemides, selgitamaks põlevkivituhaplatoo sette mõju CO₂, CH₄ ja N₂O emissioonile horisontaalvoolulistest tehismärgaladest. Mõlemas uurimuses tuli selgelt välja, et need filtrid, kus tuhaplatoo sete on peamine filtermaterjal, on emissioonid oluliselt madalamad võrreldes näiteks turba-, liiva- või kruusafiltritega. Väga madalad CO₂ emissioonid tuhafiltrites on tingitud peamiselt samadest Ca-mineraalidest, mis mängivad olulist rolli fosforiärastuses. Need mineraalid reageerivad süsinikdioksiidiga ning moodustavad seeläbi kaltsiumkarbonaadi. Siinkohal on aga oluline vältida CO₂ difusiooni filtermaterjali, sest liialt aktiivne kaltsiumkarbonaadi sadestamine vähendab süsteemis fosfori sadestamise efektiivsust. Lisaks CO₂-le olid ka CH₄ emissioonid märkimis-

väärselt madalamad võrreldes turbafiltriga või tavapäraste filtermaterjalidega, mis on tingitud peamiselt ülimalt aluselisest keskkonnast ning kõrgest sulfaatiooni sisaldusest. Küll aga oli märgata väga kõrgeid CH₄ emissioone kolmanda uurimise lõpuperioodil, kui filtersüsteem hakkas tugeva hüdraulilise koormuse tõttu ummistuma. Sarnane dünaamika oli jälgitav ka dilämmastikdioksiidi puhul, mille kõrgeimaid emissioonid ilmnescid just perioodil, kui süsteem oli kergelt ummistunud. Üldjuhul aga oli N₂O emissioon võrreldav tavapäraste filtersüsteemidega ning oluliselt madalamaid emissioone katsesüsteemides ei esinenud. N₂O emissioonid olid märkimisväärselt kõrged ka kevadel, kui toimus filtri sulamine ning seeläbi jääkihi alla lõksu jäänud gaasi lendumine.

Uurimistulemuste põhjal saab järeldada, et hüdratiseerunud tuhaplatoo sete on sobilik filtermaterjal fosfori ärastamiseks erinevatest reovetest, eeskätt horisontaalvoolulistes pinnasfiltrites. Katsed näitasid, et ka kuni kaheaastase eksperimendiperioodi jooksul ei ole märgata tuhasette fosforiärastuse efektiivsuse langust. Lämmastikuärastus on aga suurem just aeroobsetes vertikaalvoolulistes filtrites, kuhu sobivad kõige paremini suure eripinnaga filtermaterjalid nagu näiteks purustatud kergkruus. Lisaks saab järeldada, et hüdratiseerunud tuhaplatoo settega täidetud horisontaalvoolulised filtrid on eeskätt sobilikud sekundaarseks või tertsiaalseks puhastuseks, peamiselt just fosfori eemaldamiseks. Tuhaplatoo setet järelpuhastina kasutades väheneb süsteemi siseneva orgaanika ning lämmastiku hulk ning see võib omakorda vähendada olulisel määral kahjulike kaasühendite nagu näiteks ammoniaak, vesiniksulfiid- ja bisulfiidioon teket.

ACKNOWLEDGEMENTS

I am especially grateful to my supervisors, Prof. Ülo Mander and Dr. Marika Truu, for their guidance and support during my studies. Many thanks to my colleagues, Dr. Kaido Soosaar, Dr. Jaan Pärn and Dr. Martin Maddison, for being great companions on various expeditions and fieldworks. I am also thankful to my colleagues, Prof. Jaak Truu, Prof. Kalle Kirsimäe, Dr. Margit Kõiv-Vainik, Dr. Riho Mõtlep, Dr. Kristjan Karabelnik, Dr. Alar Teemusk, Kristjan Oopkaup and Mikk Espenberg for their great assistance and advice. Colleagues from the Estonian Fund for Nature and Department of Geography are also acknowledged. Finally, I would like to thank my family for their immense support and encouragement.

This study has been financially supported by the Ministry of Education and Research of the Republic of Estonia (grants IUT2-16 and SF0180127s08), the European Regional Development Fund (Centre of Excellence in Environmental Adaption ENVIRON, and the Centre of Excellence EcolChange), the Estonian Environmental Observatory Biosphere-Atmosphere Science and Development Programme: BioAtmos (KESTA, SLOOM12022T), the EU through the European Regional Development Fund (KESTA, SLOOM12093T) and by the 7th EU Framework project No 232274 “SANBOX – Development of an innovative sanitation and wastewater treatment system for remotely located tourist facilities”.

APPENDIX

Supplementary Table 1. Characteristics of the vertical and horizontal subsurface flow filters studied in current thesis. The median water treatment efficiency and greenhouse gas emissions values at various hydraulic loading regimes (HLR) are shown. N is the number of gas and water samples analysed, Δ pH is the difference between inflow and outflow pH, Ref. indicates current study publications where the data are available, n.a. – not available.

Filter material	Wastewater type	Filter type	HLR (L d ⁻¹)	n (gas ^g /water ^w)	Purification efficiency (%)			ΔpH	Greenhouse gas emissions			Ref.
					TOC ¹ /COD ²	TN	TP		CO ₂ -C (mg m ⁻² h ⁻¹)	CH ₄ -C (μg m ⁻² h ⁻¹)	N ₂ O-N (μg m ⁻² h ⁻¹)	
Filtralite [®] (2–4 mm)	Greywater	VF	32.5	14 ^w	81.5 ²	48.2	34.9	+1.1	n.a	n.a	n.a	I
Filtralite [®] (4–10 mm)		VF	32.5	14 ^w	80.8 ²	51.9	37.6	+1.1	n.a	n.a	n.a	
Filtralite [®] (4–10 mm, crushed)		VF	32.5	14 ^w	88.2 ²	51.6	37.8	+1.2	n.a	n.a	n.a	
			80	13 ^w	82.8 ²	65.4	12.5	+0.8	n.a	n.a	n.a	
Filtralite-P [®]		HF	32.5	14 ^w	0–6.5 ²	0.8–6.7	5.1–9.7	+1.4–1.6	n.a	n.a	n.a	
									n.a	n.a	n.a	
			80	13 ^w	20.3 ²	-7.1	7.1	+0.8	n.a	n.a	n.a	
HOSA (5–20 mm)		VF	32.5	14 ^w	78.7 ²	53.2	80.7	+1.1	n.a	n.a	n.a	
			80	13 ^w	74.3 ²	54.5	39.3	+0.9	n.a	n.a	n.a	
		HF	32.5	14 ^w	4.9 ²	-8.5	38.8	+2.2	n.a	n.a	n.a	
			80	13 ^w	15.3 ²	-11.1	54.8	+1.6	n.a	n.a	n.a	
									n.a	n.a	n.a	

Filter material	Wastewater type	Filter type	HLR (L d ⁻¹)	n (gas ^g /water ^w)	Purification efficiency (%)			ΔpH	Greenhouse gas emissions			Ref.
					TOC ¹ /COD ²	TN	TP		CO ₂ -C (mg m ⁻² h ⁻¹)	CH ₄ -C (μg m ⁻² h ⁻¹)	N ₂ O-N (μg m ⁻² h ⁻¹)	
Peat	Municipal wastewater	HF	60	14 ^g 4 ^w	-66.3 ¹	25.2	47.0	-0.15	168.7	28.2	42.1	III
Peat/HOSA 5/1		HF	60	14 ^g 4 ^w	-33.0 ¹	19.2	58.7	+1.1	1.3	237.3	24.6	
Peat/HOSA 3/1		HF	60	14 ^g 4 ^w	-71.1 ¹	20.7	86.9	+3.6	-7.6	374.0	50.5	
Peat/HOSA 1/1		HF	60	14 ^g 4 ^w	-35.3 ¹	36.7	98.1	+5	-7.8	66.9	40.9	
HOSA (0–20 mm)		HF	60	14 ^g 4 ^w	57.4 ¹	24.2	99.0	+5	-6.1	13.1	18.9	
HOSA (5–20 mm)		HF	540	224 ^g 184 ^w	52 ¹	44	n.a.	+5	-3.3	93.3	5.7	IV
		HF	540–900	216 ^g 184 ^w	46 ¹	43	n.a.	+5	2.6	95.6	8.6	
Sand, gravel, LECA	Various	HF	500	11 ^g 10 ^w	72.5 ²	44	69.5	n.a.	137.0	6400.0	130.0	II

CURRICULUM VITAE

Name: Kuno Kasak
Date of birth: 28.12.1987
Nationality: Estonian
Marital status: Married, 1 child
Address: Tiigi 57-16, 5041, Tartu, Estonia
Phone: +372 53 44 85 83
E-mail: kuno.kasak@ut.ee

Education

2010–2012 University of Tartu, Institute of Ecology and Earth Sciences,
Department of Geography, MSc in Environmental Engineering
2007–2010 University of Tartu, Institute of Ecology and Earth Sciences,
Department of Geography, BSc in Environmental Engineering
1995–2007 Tõrva Gymnasium

Career

05.2011 – Estonian Fund for Nature; Project manager and expert
01.2014 – University of Tartu, Institute of Ecology and Earth Sciences,
Department of Geography; Specialist in environmental technology
08.2012–04.2013 Alkranel Ltd; environmental specialist
08.2012–12.2013 University of Tartu, Institute of Ecology and Earth
Sciences, Department of Geography; Project manager

Additional studies

08.2015 International Summer School on Global Greenhouse Gases.
University of Edinburgh, Edinburgh, UK.
08.2014 Visiting research scholar at the University of California,
Berkeley and DOE Joint Genome Institute. Berkeley, CA,
USA
04.2014 LI-COR Eddy Covariance Training. LI-COR GmbH, Vienna,
Austria.
12.2013 Treatment Wetlands. Florida Gulf Coast University, Naples,
FL, USA
09.2013 Training course for water sampling. Tallinn, Estonia.
08.2013 Advanced operation and theory of quantum cascade laser
spectrometers. Aerodyne Research Inc, Billerica, MA, USA
05.2013 Flux Measurement Techniques for non CO2 GHG: methods,
sensors, database and modelling. Poznan University of Life
Sciences, Mierzecin, Poland.

Conference presentations

- 17–23.04.2016 European Geosciences Union General Assembly. Oral presentation “Nitrogen gas emissions and their genetic potential in tropical peatlands of French Guiana”, Vienna, Austria.
- 13–18.09.2015 WETPOL 2015 – 6th International Symposium on Wetland Pollutant Dynamics and Control: oral presentation “Nitrogen gas and methane emissions from tropical peatlands in French Guiana and Uganda”, York, UK
- 31.05–4.06.2015 Society of Wetland Scientists Annual Meeting “Changing climate. Changing wetlands”: oral presentation “Nitrogen gas emissions from tropical peatlands in French Guiana and its genetical potential” Providence, RI, USA
- 5–6.03.2015 European Sustainable Phosphorus Conference: oral presentation “Preventing phosphorus losses from agriculture using novel model based approaches” Berlin, Germany
- 14–18.09.2014 Wetlands Biodiversity and Services: Tools for Socio-Ecological Development: oral presentation “Greenhouse gas emissions from tropical peatlands in French Guiana”, Huesca, Spain
- 25–27.06.2012 International Symposium on Ecotechnologies for Wastewater Treatment, Technical, Environmental and Economic Challenges: oral presentation “The Impact of Pulsing Hydrology on Greenhouse Gas Emissions From Constructed Wetlands for Wastewater Treatment”, Santiago de Compostela, Spain
- 23–25.05.2011 Sixth International Conference on Sustainable Water Resources Management: oral presentation “Phosphorus removal from greywater in an experimental hybrid compact filter system”, Riverside, CA, USA

Publications

Kasak, K., Mõtlep, R., Truu, M., Truu, J., Kõiv-Vainik, M., Espenberg, M., Paiste, P., Kirsimäe, K., Mander, Ü. 201X. Hydrated oil shale ash mitigates greenhouse gas emissions from horizontal subsurface flow filters for wastewater treatment. (submitted)

Kasak, K., Piirimäe, K., Vahtrus, S. 2016. Veekaitsemeetmed põllumajanduses: käsiraamat tootjale (Water protection measures in agriculture: handbook for farmer). Estonian Fund for Nature, 148p.

Pärn, J.; Mander, Ü., Aasa, A., Egorov, S., Filippov, I., Gabiri, G., Gheorghe, I., Järveoja, J., **Kasak, K.,** Laggoun-Défarge, F., Maddison, M., Mitsch, W.J., Öskarsson, H., Pellerin, S., Salm, J.-O., Sohar, K., Soosaar, K., Teemusk, A., Tenywa, M.M., Villa, J.A., Vohla, C. 2015. **Global boundary lines of N₂O and CH₄ emissions in peatlands.** The role of natural and constructed wetlands in nutrient cycling and retention on the landscape, 16, 87-102, Springer, 10.1007/978-3-319-08177-9_7

Kasak, K., Mander, Ü., Truu, J., Truu, M., Järveoja, J., Maddison, M., Teemusk, A. 2015. **Alternative filter material removes phosphorus and mitigates greenhouse gas emissions in horizontal subsurface flow filter for wastewater treatment.** Ecological Engineering, 77, 242–249, 10.1016/j.ecoleng.2015.01.038

Kasak, K.; Truu, M.; Truu, J.; Mander, Ü. 2014. **Fosfori eemaldamine reoveest põlevkivituhasette abil horisontaalvoolulises pinnasfiltersüsteemis: mõju kasvuhoonegaaside emissioonile.** *Publicationes Instituti Geographici Universitatis Tartuensis*, 111, 330–341, Tartu

Kasak, K.; Järveoja, J.; Maddison, M.; Truu, M.; Mander, Ü. 2014. **Süsiniku- ja lämmastikugaaside vood Prantsuse Guajaana troopilistel turbaaladel.** *Publicationes Instituti Geographici Universitatis Tartuensis*, 111, 296–306, Tartu

Kasak, K.; Lotman, S.; Talpsep, I.; Piirimäe, K. 2014. **Fosfori ärakanne põllumajandusmaastikult – mõju Eesti veekogudele ja võimalikud meetmed selle vähendamiseks.** Fosfor – aegade algusest tänapäevani. *Schola Geologica X*, 78–82, Tartu

Mander, Ü.; Dotro, G.; Ebbe, Y.; Towprayoon, S.; Chiemchaisri, C.; Nogueira, S.F.; Jamsaranjav, B.; **Kasak, K.;** Truu, J.; Tournebize, J.; Mitsch, W.J. 2014. **Greenhouse gas emission in constructed wetlands for wastewater treatment: a review.** Ecological Engineering, 66, 19–35, <http://dx.doi.org/10.1016/j.ecoleng.2013.12.006>

Mander, Ü.; Tournebize, J.; **Kasak, K.;** Mitsch, W.J. 2014. **Climate regulation by free water surface constructed wetlands for wastewater treatment and created riverine wetlands.** Ecological Engineering, 72, 103–115 <http://dx.doi.org/10.1016/j.ecoleng.2013.05.004>

Uusitalo, R.; Närvänen, A.; Rasa, K.; Salo, T.; Koskiaho, J.; Puustinen, M.; Brax, A.; Erkkilä, E.; Vilhunen, S.; Joki-Heiskala, P.; Kaseva, A.; Huhta, E.; Leskinen, P.; Liira, M.; Saaremäe, E.; Poolakese, M.; Tamm, T.; **Kasak, K.;** Talpsep, I.; Tamm, I. 2013. **Active Wetlands – the use of chemical**

amendments to intercept phosphate runoffs in agricultural catchments.
Jokioinen, Finland: Maa- ja elintarviketalouden tutkimuskeskus MTT

Karabelnik, K.; Kõiv, M.; **Kasak, K.**; Jenssen, P.D.; Mander, Ü. 2012. **High-strength greywater treatment in compact hybrid filter systems with alternative substrates.** Ecological Engineering, 49, 84–92.

Talpsep, I., **Kasak, K.**, Piirimäe, K., Tamm, I. 2012 Tehismärgalad: põllumees puhastab vett. (Constructed Wetlands: Farmer Treats Water) Estonian Fund for Nature, 75 p.

Kasak, K., Karabelnik, K., Kõiv, M., Jenssen, P.D., Mander, Ü. 2011. **Phosphorus removal from greywater in an experimental hybrid compact filter system.** Water Resources Management VI, WIT Transactions on Ecology and the Environment (649–657). WIT Press

ELULOOKIRJELDUS

Nimi: Kuno Kasak
Sünniaeg: 28.12.1987
Kodakondsus: eestlane
Perekonnaseis: abielus, 1 laps
Aadress: Tiigi 57-16, 5041, Tartu, Eesti
Telefon: +372 53 44 85 83
E-post: kuno.kasak@ut.ee

Haridus

2010–2012 Tartu Ülikool, Ökoloogia ja Maateaduste Instituut, Geograafia osakond, MSc keskkonnatehnoloogias
2007–2010 Tartu Ülikool, Ökoloogia ja Maateaduste Instituut, Geograafia osakond, BSc keskkonnatehnoloogias
1995–2007 Tõrva Gümnaasium

Teenistuskäik

05.2011– Eestimaa Looduse Fond, Projektijuht ja ekspert
01.2014– Tartu Ülikool, Ökoloogia ja Maateaduste Instituut, Geograafia osakond, keskkonnatehnoloogia spetsialist
08.2012–04.2013 Alkranel OÜ; keskkonnaspetsialist
08.2012–12.2013 Tartu Ülikool, Ökoloogia ja Maateaduste Instituut, Geograafia osakond, projektijuht

Täiendõpe

08.2015 Suvekool: “International Summer School on Global Greenhouse Gases. University of Edinburgh”, Edinburgh, Suurbritannia.
08.2014 Välisvisiit uurimistöö läbiviimiseks Berkely ülikoolis. Berkeley, California, Ameerika Ühendriigid
04.2014 LI-COR Eddy Covariance Training. LI-COR GmbH, Viin, Austria.
12.2013 Treatment Wetlands. Florida Gulf Coast University, Naples, Florida, Ameerika Ühendriigid
09.2013 Veeproovivõtjate koolituskursus, Tallinn, Eesti.
08.2013 Advanced operation and theory of quantum cascade laser spectrometers. Aerodyne Research Inc, Billerica, MA, USA
05.2013 Suvekool “Flux Measurement Techniques for non CO2 GHG: methods, sensors, database and modelling. Poznan University of Life Sciences”, Mierzecin, Poola.

Konverentsiettekanded

- 17–23.04.2016 European Geosciences Union General Assembly: suuline ettekanne “Nitrogen gas emissions and their genetic potential in tropical peatlands of French Guiana”, Viin, Austria.
- 13–18.09.2015 WETPOL 2015 – 6th International Symposium on Wetland Pollutant Dynamics and Control: suuline ettekanne “Nitrogen gas and methane emissions from tropical peatlands in French Guiana and Uganda”, York, Suurbritannia
- 31.05–4.06.2015 Society of Wetland Scientists Annual Meeting “Changing climate. Changing wetlands”: suuline ettekanne “Nitrogen gas emissions from tropical peatlands in French Guiana and its genetical potential” Providence, RI, Ameerika Ühendriigid
- 5–6.03.2015 European Sustainable Phosphorus Conference: suuline ettekanne “Preventing phosphorus losses from agriculture using novel model based approaches” Berliin, Saksamaa
- 14–18.09.2014 Wetlands Biodiversity and Services: Tools for Socio-Ecological Development: suuline ettekanne “Greenhouse gas emissions from tropical peatlands in French Guiana”, Huesca, Hispaania
- 25–27.06.2012 International Symposium on Ecotechnologies for Wastewater Treatment, Technical, Environmental and Economic Challenges: suuline ettekanne “The Impact of Pulsing Hydrology on Greenhouse Gas Emissions From Constructed Wetlands for Wastewater Treatment”, Santiago de Compostela, Hispaania
- 23–25.05.2011 Sixth International Conference on Sustainable Water Resources Management: suuline ettekanne „Phosphorus removal from greywater in an experimental hybrid compact filter system“, Riverside, CA, Ameerika Ühendriigid

Publikatsioonid

Kasak, K., Mõtlep, R., Truu, M., Truu, J., Kõiv-Vainik, M., Espenberg, M., Paiste, P., Kirsimäe, K., Mander, Ü. 201X. Hydrated oil shale ash mitigates greenhouse gas emissions from horizontal subsurface flow filters for wastewater treatment. (esitatud)

Kasak, K., Piirimäe, K., Vahtrus, S. 2016. Veekaitsemeetmed põllumajanduses: käsiraamat tootjale. Eestimaa Looduse Fond, 148 lk.

Pärn, J.; Mander, Ü., Aasa, A., Egorov, S., Filippov, I., Gabiri, G., Gheorghe, I., Järveoja, J., **Kasak, K.**, Laggoun-Défarge, F., Maddison, M., Mitsch, W.J., Óskarsson, H., Pellerin, S., Salm, J.-O., Sohar, K., Soosaar, K., Teemusk, A., Tenywa, M.M., Villa, J.A., Vohla, C. 2015. **Global boundary lines of N₂O and CH₄ emissions in peatlands.** The role of natural and constructed wetlands in nutrient cycling and retention on the landscape, 16, 87-102, Springer, 10.1007/978-3-319-08177-9_7

Kasak, K., Mander, Ü., Truu, J., Truu, M., Järveoja, J., Maddison, M., Teemusk, A. 2015. **Alternative filter material removes phosphorus and mitigates greenhouse gas emissions in horizontal subsurface flow filter for wastewater treatment.** Ecological Engineering, 77, 242–249, 10.1016/j.ecoleng.2015.01.038

Kasak, K., Truu, M.; Truu, J.; Mander, Ü. 2014. **Fosfori eemaldamine reoveest põlevkivituhasette abil horisontaalvoolulises pinnasfiltersüsteemis: mõju kasvuhoonegaaside emissioonile.** *Publicationes Instituti Geographici Universitatis Tartuensis*, 111, 330–341, Tartu

Kasak, K., Järveoja, J.; Maddison, M.; Truu, M.; Mander, Ü. 2014. **Süsiniku- ja lämmastikugaaside vood Prantsuse Guajaana troopilistel turbaaladel.** *Publicationes Instituti Geographici Universitatis Tartuensis*, 111, 296–306, Tartu

Kasak, K., Lotman, S.; Talpsep, I.; Piirimäe, K. 2014. **Fosfori ärakanne põllumajandusmaastikult – mõju Eesti veekogudele ja võimalikud meetmed selle vähendamiseks.** Fosfor – aegade algusest tänapäevani. *Schola Geologica X*, 78–82, Tartu

Mander, Ü.; Dotro, G.; Ebbe, Y.; Towprayoon, S.; Chiemchaisri, C.; Nogueira, S.F.; Jamsaranjav, B.; **Kasak, K.**, Truu, J.; Tournebize, J.; Mitsch, W.J. 2014. **Greenhouse gas emission in constructed wetlands for wastewater treatment: a review.** Ecological Engineering, 66, 19–35, <http://dx.doi.org/10.1016/j.ecoleng.2013.12.006>

Mander, Ü.; Tournebize, J.; **Kasak, K.**; Mitsch, W.J. 2014. **Climate regulation by free water surface constructed wetlands for wastewater treatment and created riverine wetlands.** Ecological Engineering, 72, 103–115 <http://dx.doi.org/10.1016/j.ecoleng.2013.05.004>

Uusitalo, R.; Närvänen, A.; Rasa, K.; Salo, T.; Koskiahio, J.; Puustinen, M.; Brax, A.; Erkkilä, E.; Vilhunen, S.; Joki-Heiskala, P.; Kaseva, A.; Huhta, E.; Leskinen, P.; Liira, M.; Saaremäe, E.; Poolakese, M.; Tamm, T.; **Kasak, K.**; Talpsep, I.; Tamm, I. 2013. **Active Wetlands – the use of chemical amendments to intercept phosphate runoffs in agricultural catchments.** Jokioinen, Finland: Maa- ja elintarviketalouden tutkimuskeskus MTT

Karabelnik, K.; Kõiv, M.; **Kasak, K.**; Jenssen, P.D.; Mander, Ü. 2012. **High-strength greywater treatment in compact hybrid filter systems with alternative substrates.** Ecological Engineering, 49, 84–92.

Talpsep, I., **Kasak, K.**, Piirimäe, K., Tamm, I. 2012 Tehismärgalad: põllumees puhastab vett. Eestimaa Looduse Fond, 75 lk.

Kasak, K., Karabelnik, K., Kõiv, M., Jenssen, P.D., Mander, Ü. 2011. **Phosphorus removal from greywater in an experimental hybrid compact filter system.** Water Resources Management VI, WIT Transactions on Ecology and the Environment (649–657). WIT Press

DISSERTATIONES TECHNOLOGIAE CIRCUMIECTORUM UNIVERSITATIS TARTUENSIS

1. **Sille Teiter.** Emission rates of N₂O, N₂, CH₄ and CO₂ in riparian grey alder forests and subsurface flow constructed wetlands. Tartu, 2005, 134 p.
2. **Kaspar Nurk.** Relationships between microbial characteristics and environmental conditions in a horizontal subsurface flow constructed wetland for wastewater treatment. Tartu, 2005, 123 p.
3. **Märt Öövel.** Performance of wastewater treatment wetlands in Estonia. Tartu, 2006, 148 p.
Sergei Yurchenko. Determination of some carcinogenic contaminants in food. Tartu, 2006, 143 p. Published in *Dissertation Chimicae Universitatis Tartuensis*, 51.
4. **Alar Noorvee.** The applicability of hybrid subsurface flow constructed wetland systems with re-circulation for wastewater treatment in cold climates. Tartu, 2007, 117 p.
Ülle Jõgar. Conservation and restoration of semi-natural floodplain meadows and their rare plant species. Tartu, 2008, 99 p. Published in *Dissertation Biologicae Universitatis Tartuensis*, 139.
5. **Christina Vohla.** Phosphorus removal by various filter materials in subsurface flow constructed wetlands. Tartu, 2008, 103 p.
6. **Martin Maddison.** Dynamics of phytomass production and nutrient standing stock of cattail and its use for environment-friendly construction. Tartu, 2008, 87 p.
7. **Marika Truu.** Impact of land use on microbial communities in Estonian soils. Tartu, 2008, 126 p.
8. **Elar Põldvere.** Removal of organic material, nitrogen and phosphorus from wastewater in hybrid subsurface flow constructed wetlands. Tartu, 2009, 107 p.
9. **Margit Kõiv.** Treatment of landfill leachate and municipal wastewater in subsurface flow filters using mineralized peat and hydrated oil shale ash. Tartu, 2010, 147 p.
10. **Jaanis Juhanson.** Impact of phytoremediation and bioaugmentation on the microbial community in oil shale chemical industry solid waste. Tartu, 2010, 95 p.
Aare Selberg. Evaluation of environmental quality in Northern Estonia by the analysis of leachate. Tartu, 2010, 117 p. Published in *Dissertation Chimicae Universitatis Tartuensis*, 99.
11. **Riho Mõtlep.** Composition and diagenesis of oil shale industrial solid wastes. Tartu, 2010, 127 p.
12. **Igor Zaytsev.** Bioaugmentation in LWA-filled horizontal subsurface flow filters for wastewater treatment: Impact of flow regime, temperature and donor system Tartu, 2010, 97 p.

13. **Siiri Velling.** Microbial BOD biosensor for wastewater analysis. Tartu, 2011, 79 p.
14. **Riina Lepik.** Biodegradability of phenolic compounds as single and mixed substrates by activated sludge. Tartu, 2011, 153 p.
15. **Liis Marmor.** Ecology and bioindicative value of epiphytic lichens in relation to air pollution and forest continuity. Tartu, 2011, 98 p.
16. **Martin Liira.** Active filtration of phosphorus in Ca-rich hydrated oil shale ash: precipitation mechanisms and recovery. Tartu, 2012, 84 p.
17. **Kristjan Karabelnik.** Advanced design and management of hybrid constructed wetlands: environmental and water purification effects. Tartu, 2012, 128 p.
18. **Hiie Nõlvak.** Influence of qPCR workflow on target gene enumeration from environmental samples in the case of bioremediation potential estimation. Tartu, 2012, 136 p.
19. **Merlin Raud.** Study of semi-specific BOD biosensors for biosensor-array. Tartu, 2013, 103 p.
20. **Ivar Zekker.** Enrichment of anaerobic ammonium oxidizing bacteria for nitrogen removal from digester effluent and anammox process acceleration by intermediate compounds. Tartu, 2013, 142 p.
21. **Annika Uibopuu.** Communities of arbuscular mycorrhizal fungi in spruce forest ecosystem and their effect on performance of forest understorey plant species. Tartu, 2013, 104 p.
22. **Jekaterina Jefimova.** Leaching of polycyclic aromatic hydrocarbons (PAHs) and heavy metals from the oil shale processing wastes and from waste-based products. Tartu, 2015, 184 p.
23. **Teele Ligi.** Bacterial community structure and its genetic potential for nitrogen removal in the soils and sediments of a created riverine wetland complex. Tartu, 2015, 127 p.