

Benefits of Biochar and its Applications for Runoff Water Management

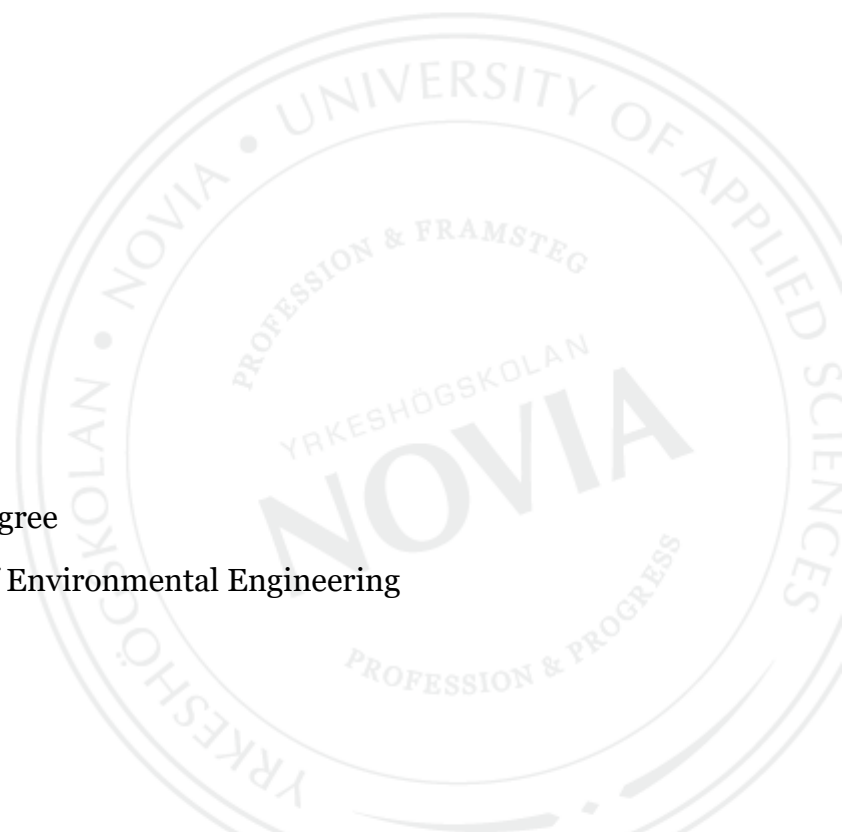
Literature Review and Laboratory Report

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Thesis for a Bachelor's- degree

The Degree Programme of Environmental Engineering

Vaasa 2018



BACHELOR'S THESIS

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Title: The Benefits of Biochar and its Applications in Runoff Water Management

Date February 2, 2018

Number of pages 43

Appendices 3

Abstract

The use of bio-filter applications has potential in reducing the nutrient load carried into receiving waters by agricultural runoff water, which is the biggest cause of surface water quality problems in Finland. The combined nutrient removal performance of biochar, sphagnum moss and woodchips were assessed in an 11-day column study using synthetic wastewater as the influent. The measured parameters included total phosphorous, phosphates, total nitrogen, total organic carbon, conductivity and the pH value. The performance of the filter columns was satisfactory, apart from poor removal efficiency of phosphates and total phosphorous.

This thesis consists of a literature review and a laboratory report. In the literature review, biochar is briefly discussed from several perspectives, with the emphasis being on its nutrient retention capacity. The discussion on the laboratory results is based on the literature review.

This thesis work was carried out with guidance from Willow Partners, a Finnish company with expertise on the use of willow biochar for soil amendment and water treatment purposes.

Language: English

Key words: Biochar, Eutrophication, Bio-filters, Runoff Water,

EXAMENSARBETE

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Utbildning och ort: Teknik, Vasa

Inriktning/alternativ/Fördjupning: Environmental Engineering

Handledare: Jonathan Fagerström, Charlotta Risku

Titel: The Benefits of Biochar and its Applications in Runoff Water Management.

Datum 2.2.2018 Sidantal 43

Bilagor 3

Abstrakt

I Finland uppmärksammas eutrofiering av ytvatten i ökande utsträckning. Eutrofieringen beror särskilt på kväve och fosfor som transporteras till vattnet framförallt på grund av jordbruk.

Forskning kring biokol har ökat de senaste tio åren, och det verkar som om biokol kan fungera effektivt i vattenrening och återvinning av näringsämnen.

Biokol undersöktes i laboratoriet tillsammans med mossa och träflis. I experimenten filtrerades konstgjort avloppsvatten och inskning av total fosfor, fosfater, totala kväve och totalt organisk kol mättes. Även förändringar i elektrisk ledningsförmåga och pH-värde registrerades. Med undantag av totala fosfor och fosfater, filtrerade materialet väl näringsämnena.

Slutarbetet gjordes i samarbete med Pajupojat Oy, som erbjöd filtermaterial och råd med teoridelen.

Språk: Engelska

Nyckelord: Biochar, Eutrofiering, Vattenrening

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Suuntautumisvaihtoehto/Syventävät opinnot: Environmental Engineering

Ohjaajat: Jonathan Fagerström, Charlotta Risku

Nimike: The Benefits of Biochar and its Applications in Runoff Water Management

Päivämäärä 2.2.2018 Sivumäärä 43

Liitteet 3

Tiivistelmä

Kaupunkien hulevesien, sekä maatalouden valumavesien aiheuttamat ongelmat Suomen pintavesissä saavat yhä enemmän huomiota. Saaristomeren, sekä pienten järvien suurin ongelma on rehevöityminen, jota aiheuttaa valumavesien mukanaan tuomat fosfori ja typpi.

Tutkimus biohiilen käytöstä maanparannusaineena ja aktiivihiihen korvikkeena vedenpuhdistuksessa on lisääntynyt kuluneen kymmenen vuoden aikana. Tätä lopputyötä varten tutkittiin biohiilen, rahkasammaleen sekä puuhakkeen ravinteidenpidätyskykyä 11 päivää kestäneessä laboriokokeessa. Näiden materiaalien kykyä pidättää fosfaatteja, kokonaisfosforia, kokonaistyppeä, sekä kokonaishiiltä mitattiin, sekä kirjattiin ylös myös muutokset pH-arvossa sekä sähkönjohtavuudessa. Fosforia ja fosfaatteja lukuun ottamatta materiaalien pidätyskyky oli tyydyttävä tai hyvä.

Pajupojat Oy avusti tämän lopputyön tekemisessä, tarjoamalla sekä suodinmateriaalit, että ohjausta teoriaosuuden kirjoittamisessa ja laboriokokeiden suunnittelussa.

Kieli: Englanti

Avainsanat: Biohiili, Ravinnekierrätys, Rehevöityminen,

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1. Introduction

According to a Eurobarometer survey carried out in 2012, a majority of citizens in the EU consider water related problems to be a serious concern, and nearly 75% consider that the EU should propose additional measures to mitigate water pollution from industry and agriculture [1]. The EU Water Framework Directive is the operational tool used in order to assess surface water quality in the EU member states. It defines the criteria for good ecological and biological condition in surface waters, and continues to have the goal to improve and maintain the quality of surface waters across Europe [2].

In the year 2013, the Finnish Environment Institute, SYKE, carried out an assessment on Finnish surface waters according to the EU Water Framework Directive, and found that while the majority of Finnish lakes and rivers were in good or excellent ecological condition, as much as 75 % of the coastal seawaters were discovered to be in poorer condition. The main detriment for coastal surface waters, as well as some smaller lakes in Finland is eutrophication. Over half of the excess nutrient load (e.g. phosphorous and nitrogen) causing this eutrophication comes from agriculture. [3]

In Finland, the legislation on construction and land use has provisions on runoff water management. The provisions are stated in the act 682/2014, in chapter 13 a. It is a requirement for construction projects to have a plan for the management of runoff waters, which include its infiltration, retention, conduction, sewerage and treatment. One of the goals of the legislation is to gradually end the conducting of runoff water into the wastewater sewers. [4]

In urban settings, soil sealing creates its own challenges when considering runoff water, especially during heavy rainfall. Urban runoff water and runoff water from industrial sites can carry many contaminants, including metals, pathogens, such as E. coli, and polycyclic aromatic hydrocarbons. Insufficient management of these runoff waters may negatively impact the quality of the receiving waters, and in some cases even create public health hazards. [5]

1.1 Pajupojat / Willow Partners

Pajupojat / Willow Partners is a Finnish company, started in 2014, whose business goal is to provide willow based biochar products for various purposes in agriculture and green infrastructure, including soil amendment and runoff water management. Pajupojat has also the expertise on the economic feasibility of different biochar projects. The company has its own biochar production as well as subcontracted production, and in Finland, Pajupojat is actively building up a network of providers of raw material. Varieties of willow (*Salix*) are used as the raw material, since according to research, willow biochar has the best porosity and specific surface area available. In addition, willow is the fastest growing species of trees in Finland, and therefore its cultivation for biomass is very efficient. In 2015 and 2016 Willow Partners participated in the RAKI project conducted by the Finnish Ministry of Environment. The goal of the project was to improve the quality of Finnish coastal seawaters by controlling the spreading of nutrients, especially nitrogen and phosphorous, into the sea. Willow Partners produce biochar by slow pyrolysis, in temperatures ranging between 350-700 °C. [6] [7]

Pajupojat Oy is affiliated with SalixEnergi Europa AB, a Swedish company which has focused on willow as a source of renewable energy. Salix Energi AB has licensed cuttings producers and retailers in 17 countries within Europe. [7]

1.2 Purpose

The goal of this thesis is to study and evaluate the use of biochar in combination with other biofilter materials for the removal of nutrients from polluted water. The potential benefits and weaknesses of adding biochar and / or sphagnum moss into existing applications, such as compost filter socks and denitrifying woodchip bioreactors, are estimated by collecting data from literature and carrying out practical laboratory experiments. Biochar filter socks could be used to manage the surface flow of polluted water in various rural and urban settings during heavy rainfall or increased water flows during the melting of snow and ice. Such settings include construction sites, landfills and compost facilities, industrial sites and agricultural land and forestry sites. Woodchip bioreactors can be used to treat the drainage water from agriculture, and their performance may be enhanced with the addition of biochar. Willow Partners provided the biofilter materials for the laboratory experiment, and guidance for the literature review.

1.3 Methods

The literature review provides the essential background information on the production and characteristics of biochar, as well as some of the results and findings from previous research in nutrient removal by biofilters. The laboratory tests were carried out in the spring of 2017, and they partly emulated the column studies presented in the literature review. Two different biofilter configurations were tested for their capacity to remove phosphorous, nitrogen and organic carbon from synthetic wastewater. The column types provided differing conditions in terms of pH and hydraulic retention time, and this was expected to have an effect on the nutrient removal efficiencies. Conclusions on the implications of the test results are based on the literature review. The parameters focused on during the laboratory work are total phosphorous, phosphates, total nitrogen, total organic carbon, conductivity and the pH value. The role of each of these parameters is briefly explained within the literature review.

1.4 Limits

Biofiltration of other typical urban and industrial runoff water pollutants, such as metals, organics and pathogens have been studied previously, but these were left out of the scope of this thesis. Due to limited availability of the Merck Spectroquant test kits, total nitrogen in the effluent samples was only measured on two occasions. The same limitation was true for nitrate. The synthetic wastewater did not contain nitrate, but one measurement was carried out in order to estimate the tendency of the filters to leach nitrate, or to promote nitrification.

Some of the column studies that are cited in the literature review lasted for several weeks. The column study carried out for this paper only lasted for 11 days, after initial trials and errors. In an attempt to compensate for the short duration, a synthetic wastewater with relatively high concentration of nutrients was used as the influent. The results in this thesis therefore are more likely to resemble the short term removal efficiency of these biofilter materials in worst case scenarios, than the long term nutrient removal efficiency from average runoff water.

The accuracy of the results for total organic carbon cannot be guaranteed, as the concentrations in the effluent samples were much too high for the calibration graph made for the equipment. Due to time constraints, it was not possible to repeat the total organic carbon analysis with diluted samples.

2. Theoretical background on biochar

Pyrogenic Carbonaceous Material (PCM) is an umbrella term used for all materials that contain organic carbon, and have been produced by thermochemical conversion. Such materials include, among others, charcoal, soot, activated carbon and biochar. Charcoal is produced by thermochemical conversion of biomass, and most commonly to be used for energy production purposes. If charcoal is processed further and activated by steam or addition of chemicals, the term activated carbon is used. Biochar is the product of thermochemical conversion of biomass, in an environment with limited oxygen. Biochar is used most commonly for environmental management, e.g. soil amendment purposes. Biochar can also be activated with various methods, but the use of the term “activated biochar” is discouraged. [8]

Biochar has been valued as a soil amendment for several centuries. There was scientific research on biochar as soil amendment already in the 19th century. However, very little research on biochar was carried out during the 20th century, possibly due to the increase in the popularity of inorganic fertilizers. During the past ten years biochar has begun to interest researchers again, and in fact the term biochar was introduced only as recently as 2006 to distinguish the product from charcoal. [8]

2.1 The Biochar value chain

There are broadly four main reasons why biochar production may be desirable: waste management, soil improvement, energy production, and the mitigation of environmental problems, namely the climate change and water pollution. It is important to highlight that biochar is not a single material, but different biochars can vary greatly in their important characteristics, depending on the raw material and the production method used. When biochar is produced for soil improvement or water pollutant removal, it needs to be carefully designed to fit the purpose. [8]

Biochar can be added to soils in order to improve crop yields, or alternatively, for the purpose of soil remediation. In soil, biochar can improve nutrient availability, the soil's physical properties and water relations, as well as microbial activity necessary for plants [8]. This can indirectly help improve the condition of waterways, as the retention of nutrients in the topsoil reduces the need for fertilizing the crops. [9]

On the other hand, in instances where no soil improvement is necessary or possible, the production of energy may be more desirable. Pyrolysis produces heat energy and various high-value energy carriers, which can include gases, oils and the biochar itself, which can be used as a charcoal fuel. Pyrolysis technology generally requires lower operating temperatures compared to incinerators, which together with the high carbon content in the residue makes the operation of pyrolysis easier than incineration or gasification. Due to upper size limitations, pyrolysis reactors may be best utilized for distributed energy systems, in comparison to incineration plants. Similar is true for waste management, in instances where organic waste needs to be transported long distances for disposal, as pyrolysis treatment reduces the weight and transportation costs of the waste. [8]

The biochar system is depicted in figure (1), which is based on the basic schematic by Lehmann [8].

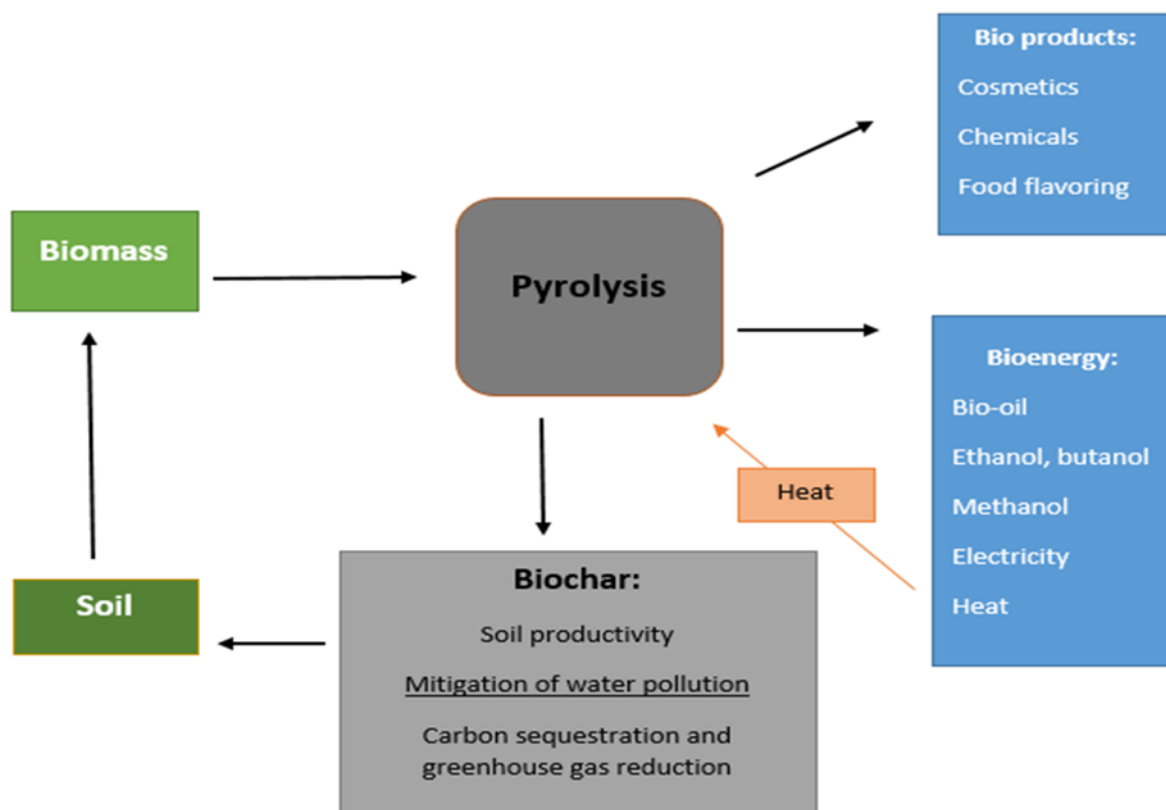


Figure 1. The biochar system

Pyrolysis means the thermal breaking down of substance, and is a very common natural phenomenon. The technology for producing biochar can be as basic as an earth kiln, which is simply a campfire which is covered by soil to keep away the oxygen. These, and other more basic slow pyrolysis methods are usually very polluting, as the black smoke, which contains the combustible biogas in vapour state, is released into the atmosphere. Modern slow pyrolysis methods control the emissions. More sophisticated technologies exist for fast pyrolysis, where up to 75% of the biomass is transformed into liquid bio-oil, by removing the pyrolysis vapours immediately from the reactor and condensing them. Fast pyrolysis, however, is usually not the best way to produce biochar, as the char yield is lower and most of it is combusted in order to maintain the process. [11]

The input biomass and the pyrolysis method determine the output of the system. When the desired output is a biochar product that can be used in water purification, possibly as an alternative to activated carbon, clean and naturally porous raw material, such as willow, is a good option [6]. The qualities of the biochar, such as cation exchange capacity, surface area and pH, can be optimized for nutrient removal by using the most appropriate pyrolysis method. Lehmann suggests that 450-550°C is probably the optimal production temperature. Due to its larger surface area, greater negative surface charge and charge density, biochar has a greater potential to adsorb cations per unit carbon compared to other soil organic matter, and these cations are well available for plant uptake, making biochar a good soil amendment material. Unlike other organic matter in soil, and despite its negative surface charge, biochar is also able to adsorb phosphate anions, but this mechanism is not fully understood. [9. p. 383]

Biochar can act as a carbon sink. It sequesters 3.5 times its own weight of CO₂, and once the carbon is sequestered in the biochar, it can remain stable in the soil for hundreds of thousands of years. [6][11]. More comprehensive systems analyses are needed in order to determine life-cycle greenhouse gas budget of biochar use, whether the system is actually carbon negative. The C balance is affected by the choice of raw material, as organic material which is decomposing is also emitting greenhouse gases, namely methane and nitrous oxide, while growing vegetation is continually capturing CO₂ via photosynthesis. Organic material treated with pyrolysis is lighter to transport, reducing the GHG-budget. On the other hand, primitive biochar production methods can be very polluting. In order to be competitive among other global climate change mitigation methods, significant commercialization of biochar products and pyrolysis technologies is necessary. For this reason the production of biochar for the sole purpose of carbon sequestration is unlikely to become widespread. However, combined with the several other benefits that can be gained, biochar processes have substantial potential. [8]

2.2 Biochar and nutrient removal

When biochar is produced for the specific purpose of being used as an adsorbent in water treatment, both the raw material and the type of pyrolysis process needs to be selected in a way that provides the desired surface characteristics in the product. Specific surface area, the type and density of surface charge, elemental composition (carbon, nitrogen, hydrogen, sulphur and oxygen), and functional groups on the surface are the characteristics that play a central role in the material's adsorption capacity. The variability in different types of biochar can be illustrated by studies made on the phosphorous adsorption capacity. For example, biochar produced from orange peel was found to have the P adsorption capacity of 1.2 mg P g⁻¹, while biochar made from anaerobically digested sugar beet tailings had a P adsorption capacity as high as 133.1 mg P g⁻¹. [12]

As an adsorbent, biochar has the benefit of being useful in soil amendment as well. When the biochar has become spent in its role as an adsorbent of nutrients, it can be applied to the soil where it can act as a fertilizer. The adsorption of ammonium ions, for example, has been reported to be reversible for biochar and thus bioavailable for plants. [13]

The pyrolysis type and process temperature is about as important as the raw material, when it comes to biochar properties. Biochar produced at higher temperatures contains less remaining volatiles, and more stable carbon and ash content. Higher temperatures also result in greater surface area, although at temperatures above 700-800°C the surface area begins to decrease again. The surface charge and pH of biochar also depend on the process temperature: the oxygenated compounds that occur on the surface of biochar have negative charges, and these compounds decrease at higher process temperatures. Wood biochars produced above 600°C have a reduced cation exchange capacity due to the lack of oxygenated compounds, and the surface charge is neutral or positive. [11]

Table (1) and Table (2) illustrate the variability in some biochar characteristics depending on the raw material and pyrolysis method. The numbers are based on average values found in literature by Ippolito et al. [14. pp.148-149]

Table 1. Characteristics of biochars of various raw materials [14]

Source	pH	Surface area (m ² /g)	CEC (mmol/kg)
Corn	9.27	107.2	607
Wheat/Barley	8.8	26.65	103
Rice straw	9.17	42.15	212
Hazelnut shells	7.86	467.5	83.8
Bagasse	7.59	113.6	115
Food waste	9.09	0.803	81
Other green waste (grass, leaves etc)	8.72	119.8	290
Softwoods	7.48	194.2	145
Hardwoods	7.94	171.3	138
Papermill waste	9.13	10.08	52
Poultry manure	9.8	50.35	538
Dairy manure	9.45	33.38	342
Sewage sludge	6.9	102.1	23.6

The choice of raw material has an effect on the pH of the biochar, although they tend to be alkaline or neutral. The surface area ranges from 0.8 m²/g to 467.5 m²/g, highlighting the significance of the raw material. The raw material also has an important effect on the biochar's cation exchange capacity (CEC). Willows are classified as hardwood [15]. However, the values above are averages for all hardwood biochars, and not the average of willows.

Table 2. Characteristics of biochars from different pyrolysis methods [14]

Pyrolysis temperature and type	pH	Surface Area (m ² /g)	CEC (mmol/kg)
Fast, 300-499°C	8.33	44.74	28.8
Fast, 500-699°C	7.7	40.99	No Data
Fast, 700-900°C	10.1	178.2	No Data
Slow, <300°C	5.01	1.686	327
Slow, 300-499°C	7.81	81.32	268
Slow, 500-699°C	9.09	180.5	218
Slow, 700-900°C	10.1	189.8	41.5

The data in Table (2) shows, nearly consistently, that the pH and surface area of the biochar increase with increasing pyrolysis temperature. Cation exchange capacity may be optimized by using slow pyrolysis and lower temperature. It is worth noting, that slow pyrolysis of organic matter also yields nearly even fractions of biochar, bio-oils and gases, while fast pyrolysis yields approximately 10% of biochar, 70% of bio-oil and 20% gases. [16]

2.3 Previous studies on biochar and nutrient removal

As mentioned in the beginning of this chapter, the research on biochar resurfaced only ten years ago, after being nearly non-existent for a century. Biochar studies have focused greatly on the soil improvement qualities, but research on water purification potential has also been carried out.

Adsorbents are used in the removal of soluble organic material in both water treatment and waste water treatment. The adsorbents need to have a very high specific surface area, and the surfaces should be relatively free from adsorbed material. The most commonly used adsorbent is activated charcoal. The surface of activated carbon is suitable for microbial activity, which also may improve adsorption. Bigger molecular weight of the solute and longer contact time increase adsorption. The pH value is also significant, as adsorption decreases with increasing pH value. [17. pp. 626-627]

Biochar has many of the same qualities as activated carbon, most importantly the porosity and large specific surface area. Activated carbon is known as an effective adsorbent of pollutants, and biochar can potentially be used in many of the same applications, as a cheaper option. Studies have shown that biochar is capable of reducing contaminants from water, including heavy metals such as zinc and lead, organics such as gasoline and pesticides, chemical and biological oxygen demand, nutrients and total suspended solids. [18]

The surface charge of biochar is usually negative. This consequently means that adsorption of phosphate anions by biochar is sometimes low. Lou, Rajapaksha, Ok and Chang suggest that despite its high surface area and oxygen functionality, biochar is rarely effective for the removal of phosphates or other anions. The surface charge of biochar is, however, pH dependent. When the net surface charge of any specific type of biochar is changed by lowering the pH, the pH value passes a so called point of zero charge. The pH value for reaching the point of zero charge is unique for each biochar type, and depends on the raw material, production temperature, and possible activation method used. The anion sorption capacity of biochar is at its greatest when the pH of the solution is below the pH_{PZC} value, and the capacity drops when the pH rises above it. The results of the experiments by Lou et al. reached only approximately 4% efficiency in phosphate removal by biochar, as the pH of the solution was above the pH_{PZC} of every biochar tested. [12]

Reddy, Xie and Dastgheibi state that biochar could potentially be used as an adsorbent for removing phosphates from water. In their column study they were able to reach 47% removal efficiency for phosphates, when using an influent with the relatively low phosphate concentration of 0.57 mg/l. When flushing the unwashed biochar with deionized water, it released 0.12 mg/l of phosphate. The final washing of the column with deionized water indicated that phosphates remain well adsorbed to biochar. [5 p.5]

Lukkarinen, Ranta-Korhonen, Seppäläinen and Soininen carried out a series of column tests with biofilters, and when filtering bog water through them, found that columns that had both biochar and woodchips in them merely leached phosphorous throughout their experiment.

Using biochar independently showed that it leached nitrogen as well as some zinc and copper into the influent. One of the biochar columns was leaching phosphorous, while the other one was removing it slightly. One explanation for this could be that the biofilm, which contributes to nutrient removal, was developing at different rates in the columns. Only moss filters were found to consistently reduce the chemical oxygen demand (COD) in water, while both woodchip and biochar filters were found to both decrease and increase the COD depending on the date of sampling. The influents had markedly lower concentrations of nutrients compared to the influent used in the laboratory experiment for this paper. [19 pp.43, 46-49]

According to the test results obtained by Sidibe, filtering grey water through biochar drastically increases both total nitrogen and nitrate concentrations in the effluent water. Only ammonium, NH_4 , concentrations were reduced by biochar filters, implying a nitrification process to have occurred. The ammonium concentrations varied greatly in both the influent and effluent. Activated charcoal had a superior performance in nitrogen removal compared to biochar. The removal of COD by biochar increased constantly during the 10-week period, beginning with a 70% efficiency and reaching a 98% efficiency at the end. The average efficiency for COD removal by biochar was 90%. The average COD in the feed water used in this study was 4630.5 mg/l. [20 pp.19-25]

The influent used by Berger had the mean concentrations of 95 mg/l for Tot-N. In this study, biochar filters were able to reduce nitrogen efficiently from greywater. Total nitrogen was removed with the efficiency of 90.94%. Ammonium was reduced with 2.7% efficiency, and nitrate with 19.8% efficiency. Salix biochar performed better than activated carbon in phosphorous removal (89% and 78%, respectively), and biochar's phosphate removal efficiency was 86%. According to these results, biochar's ability to remove total phosphorous and phosphates increases with time. The total phosphorous content in the influent was 3.6 mg/l. The COD removal in this study was as high as 99.1%, with the average COD of the influent being 1389 mg/l. [21 pp.22-37]

F.Gao et al. tested the ammonium (NH_4^+) sorption capacities of biochars produced from three different organic waste materials and using three pyrolysis temperatures. The highest biochar yield was gained at 300°C (41.5% for peanut shells), and the lowest yield at 600°C (22.6% for corncobs). The low temperature biochars were highly effective in ammonium adsorption, due to high adsorption capacities and fast adsorption kinetics. The effect of pH was tested by controlling the pH of the ammonium solution with NaOH and HCl solutions. The sorption of ammonium was high at all tested pH levels (1, 3, 5, 7, 9, 10 and 12), and peaked at pH=10, where the sorption capacity was 19.2 mg/g. Raising the temperature reduced ammonium adsorption, but even at 50°C the adsorption capacity was close to 10 mg/g. The relationship between adsorption capacity and temperature indicates that exothermal reactions control the adsorption. [13]

As Mohan et al. point out, that the lack of consistency in literature data makes direct comparisons of biochar types difficult. The different test results cited above are enough to illustrate this. There are numerous variables which differ in each experiment, and not all of them are always documented. The adsorption capacities for biochars have been reported at different temperatures, pH-values, biochar doses, adsorbate concentrations, biochar particle sizes and surface areas. The influents used can range from ground water and bog water to synthetic solutions and actual waste water. Column experiment results cannot be directly compared to batch experiment results. The raw material and pyrolysis conditions used may not always be sufficiently documented. Limiting test variables to one would help in comparisons. Mohan et al. also state that in order to assess reproducibility of tests results, it would be necessary to carry out more research with identical biochar preparation from the same raw material using the same adsorbents in adsorption studies. [16]

Biochar research has not been commonplace for long. Lehmann illustrates this by showing that the number of scientific publications on biochar in the context of soil management has grown rapidly during only the last 10 years, being nearly non-existent before that [8]. This may also explain the lack of consistency in the literature data.

3. Water treatment applications and the other bio-filter materials

The other two bio-filter materials studied in the experiment during this thesis are commonly used as growing medium for vegetation by gardeners. In comparison to biochar, obtaining sphagnum moss and woodchips requires less effort. The main requirement for their use in bio-filter applications is that they are clean from heavy metals and other pollutants.

3.1 Sphagnum Moss

Sphagnum moss has an ecologically important role, as it creates bogs. Because 90% of the plants cells are typically dead and empty, it has the ability to hold water up to 22 times its own weight. Peatlands that have formed during thousands of years store large amounts of carbon. They also create an ecosystem with particularly harsh conditions. Sphagnum moss attracts positively charged nutrients, such as potassium and calcium, and releases cations into the surroundings, making them acidic. This acidity means that peatlands have preservative properties. Moss has been used for centuries as a primitive method of wound packing due to its absorbency and anti-microbial properties. It also became very popular during the First World War as a wound packing material, when cotton became scarce. Its use reduced the number of deaths caused by infection and sepsis in wounded soldiers. [22]

The antibacterial properties of sphagnum moss have been shown in laboratory studies to inhibit biofilm formation. This tendency is so strong, that sphagnum moss has been used in the purification of water in swimming pools and cooling towers. [23] [24]

Lukkarinen, Ranta-Korhonen, Seppäläinen and Soininen carried out a series of column experiments to assess various biofilter materials, including moss for removing nutrients and metals. They found that moss removed as much as 90% from the total phosphorous, and 60% of the total nitrogen from the influent. Moss was also the only material that lowered the pH of the solution. The high efficiency was attributed to the longer hydraulic retention time. Only moss filters were found to consistently reduce the COD in water. [19]

3.2 Denitrification bioreactors

As an alternative, or an addition to conventional waste water treatment, constructed wetlands, are used in the removal of nutrients and other pollutants from water. In Europe, sub-surface flow reed beds are the most common type of constructed wetland, while large surface flow systems are more likely to be found in the US. Their construction and operation are relatively low cost, compared to conventional wastewater treatment. They may often operate without any mechanical or electrical equipment, and require little maintenance. Plant uptake is the central pollutant removal mechanism in constructed wetlands, although sedimentation, precipitation and several types of microbial removal also occur. [17 pp.574-580]

Woodchip bioreactors, or denitrifying bioreactors, are a type of sub-surface flow waste water treatment system that are aimed specifically to reduce the amount of nitrates in agricultural wastewater with relatively low sediment content. The drainage water flows slowly through a trench filled with woodchips, and the nitrates are removed through microbial activity. The process requires anaerobic conditions, as the microbes responsible for denitrification are also capable of using oxygen in their respiration. The woodchips provide the necessary carbon and substrate for the microbes. The flow of the water is controlled mechanically at the inlet and the outlet of the reactor. [25]

These reactors have been shown to be able to remove between 15-60% of the annual nitrate load in drainage flows, which is close to the efficiency of wetlands. The management of the reactor, the quality of the woodchip and the concentration of nitrates all affect the efficiency. The removal efficiency is better when the nitrate concentration in the drainage water is higher. [25]

These reactors are easy to install in existing agricultural drainage systems. They are placed at the edge of the field, and have minimal impact on the crop yield of the field. They carry a potential risk of producing nitrous oxide and methyl mercury. Nitrous oxide is a natural byproduct of denitrification, but usually only a very small fraction of the nitrogen is converted into it. Methyl mercury may form during slow flow periods, when the nitrates are depleted from the water in the reactor. One of the potential consequences of this is the microbial transformation of sulfate into hydrogen sulfide gas, producing a “rotten egg” smell. These same microbes also transform traces of mercury into more toxic methyl mercury, and therefore having the water in the reactor for too long should be avoided. [25]

The woodchips that are used in the denitrifying bioreactors tend to leach dissolved organic carbon (DOC). Experiments by Barrett, Halaburka and Luthy gave some indication that adding biochar to woodchip reactors can reduce the leaching of dissolved organic carbon, as well as improve the denitrification efficiency of the reactors. The results of their batch experiments saw the concentration of DOC being reduced nearly 50% within seven days, and they concluded that this was largely due to DOC sorption on the biochar surface. The improved denitrification efficiency achieved by coupling woodchips with biochar can be explained by the increased microbial activity. [26]

3.3 Compost filter socks

Compost filter socks are applicable for construction sites and other locations, where there is a sheet flow of polluted surface runoff water. A compost filter sock is a long mesh tube, filled with compost material from various sources. The used diameters range from 20 cm to 60 cm, depending on the requirements of the site. The mesh tubes are placed on a slope, perpendicular to the flow, and 30 meters of the tube is enough to manage the surface flow from an area of 1000m². The advantages of these compost mesh tubes include practicality, low cost and effectiveness in erosion control. They can be temporary, as in construction sites or during rain storms, or they can be seeded and left on site as a part of green infrastructure. Important considerations for ensuring optimal function are the material and pore size of the mesh, as well as the purity and particle size of the compost material used to fill the tube. Biodegradable mesh materials should be used when the tube is left permanently on site. Plant uptake improves the long term efficiency in permanent applications. [27]

The use of compost filter socks for the management of urban storm waters and the runoff waters of construction sites has been studied extensively by American universities and the Agricultural Research Service at the USDA (United States Department of Agriculture). USDA ARS has reported study results showing compost filter socks to be efficient in removing and reducing, among other things, coliform bacteria (74% removal efficiency), heavy metals, such as Cd, Cu, Ni, Pb and Zn (removal efficiencies ranging between 37% and 72%), diesel fuel (99% removal efficiency), motor oil (84% removal efficiency) and gasoline (43% removal efficiency). The removal efficiency of total phosphorous in studies has ranged between 59% and 65%. The removal of ammonium-nitrogen and nitrate has been less successful, with less than 20% efficiency. The Water Quality Program of the City of Chattanooga reported results from a field study, that compost filter socks removed parking lot storm water TSS (total suspended solids) by 99%, chemical oxygen demand by 92 % and oil by 74%. [27]

4. Theoretical background on the studied parameters

Phosphorous and nitrogen were the central focus of interest for this thesis, as they are the main contributors for surface water eutrophication (see chapter 1). Other data collected during the experiment included results on total organic carbon removal, pH and conductivity.

4.1 Conventional removal of phosphorous and nitrogen

In conventional waste water treatment, inorganic phosphorous is removed by chemical precipitation, using coagulants, such as lime, aluminium salts or iron salts. On average, sewage water contains 5-20 mg P L⁻¹ as total phosphorous, out of which 1-5 mg P L⁻¹ is organic and the rest inorganic. Inorganic phosphorous is present as orthophosphate (PO₄³⁻) and polyphosphates. Phosphate removal results in a sludge which requires appropriate disposal. [17 pp.623-624].

Several chemical, biological, ion exchange and membrane techniques are used for removing nitrogen from waste water. The common chemical method for nitrogen removal is reacting the ammonium ion (NH₄⁺) with hypochlorite to produce elemental nitrogen (N₂) into the atmosphere. Ammonium nitrogen can also be transformed into nitrogen gas, carbon dioxide and water, by a two-step biological process in which nitrification of ammonium is followed by a denitrification of nitrate. Nitrification is an aerobic microbial process carried out in an aeriated tank, while denitrification is an anaerobic process, which requires a carbon source for the microbes and a reducing agent, such as methanol (CH₃OH), and can either take place in a tank or in a carbon column provided with anoxic conditions. [28 p. 248]

4.2 Total organic carbon

Dissolved organic carbon is a general indicator of water pollution. It can often be in the form of toxic substances, and it results in oxygen demand in water. The two traditionally most common measures of oxygen demand are the biochemical oxygen demand (BOD) and the chemical oxygen demand (COD). The biochemical oxygen demand determines the biodegradable fraction in the wastewater and is usually measured by keeping the water sample in a controlled environment, at 20°C and in the dark, for five days, and observing the consumption of organic material by the aerobic bacteria. The chemical oxygen demand measures both the biodegradable and non-biodegradable organic content by oxidizing them in acidic conditions. A strong oxidizing agent, such as potassium dichromate ($K_2Cr_2O_7$), is needed for the COD-test. In comparison to BOD-tests, the COD-test is simpler, faster and more accurate, but also more expensive and produces toxic waste products. COD-tests can be replaced by testing the total organic carbon (TOC). TOC-tests are usually automated processes, where the organic carbon is measured in the form of CO_2 after catalytic oxidation. In natural waters, organic matter is oxidized by microbes, and if there is no sufficient aeration, such as turbulent flows, and high amount of organic matter, the water may become too depleted of dissolved oxygen to sustain higher aquatic life forms. [17 pp.109-110] [28 pp.282 189-191]

4.3 Conductivity and pH

The conductivity of water can be easily measured with the appropriate equipment. There are parameters available for determining the salinity of water based on the conductivity value. Conductivity is created by total dissolved solids (TDS), which includes dissolved salt, but also other compounds, such as dissolved organic matter. In clean saltwater TDS is equal to salinity, but in wastewaters, various organic substances such as urea (CH_4N_2O), increase conductivity. An estimate for the amount of TDS is calculated by multiplying the conductivity value with an empirical factor, which depends on the ionic constituents of the water in question. Agricultural leakages, which typically include chloride, nitrate and phosphate ions, will increase the conductivity of water. Due to its practicality, conductivity is often measured when evaluating the quality of surface waters, as changes in conductivity can be an indicator of pollution. [29]

Measuring the pH from water samples can serve many purposes. The pH of water affects the solubility, and therefore also coagulation and precipitation of substances, such as ammonia, phosphorous and trace metals. It has a great impact on microbial activity, and for example, denitrification reaction is optimized at pH-values between 6.5 and 7.5, and reduced outside these values. It is temperature dependent, as atmospheric CO_2 is very soluble, and forms weak carbonic acid in water, the pH values of samples change slowly when exposed to air and temperature change. [17 pp.51, 555, 610-612]

5. Laboratory experiment

The preparations for the laboratory experiment began in late April 2017. The first decision was to carry out a column study instead of a batch study. Second, the parameters for analysis were decided. The possibility to analyse heavy metals and pathogens in the samples was considered, but this was deemed to not fit the time schedule, as some standard solutions would have had to been ordered for the laboratory. The columns were produced from plastic bottles instead of glass or acrylic pipe, as these would have also had to been ordered. Before commencing the proper experiments on May 9th, some pilot filtration experiments were carried out in order to both practice the laboratory work, and to ensure that correct calibrations and dilution factors were being used. The duration of the proper laboratory experiment was 11 days, and to compensate for the short duration, an influent with relatively high nutrient content was used. Therefore the experiment resembled more a worst case scenario for biofilters, and not the average long term use for runoff water treatment.

5.1 Setup of filter columns

Three biofilter materials were used for the experiment; salix biochar, woodchips and sphagnum moss. In order to improve the reliability of the results, three parallel columns were produced for two different types of filter columns. The particle size distributions of the biochar and woodchips were uneven, and therefore these materials were sieved in a shaker. The purpose was to have the similar particle size distribution in each column. No sieving was deemed necessary for the sphagnum moss. The particle size distributions are shown in Table (3) and Table (4).

Table 3. Particle size distribution in the A-columns

Biochar size (mm)	Mass (g)	Woodchip size (mm)	Mass (g)
4-8	25	+16	30
2-4	25	8-16	30
1-2	30	1-8	30
0-1	10		
Total	90		90



Figure 2. The filter columns being constructed

The columns were produced from 2L plastic water bottles. The bottom of each bottle was removed, and the bottles were suspended upside down. A round patch of cloth was placed into the bottom of each column to prevent filter material from falling through the opening. A 90 gram layer of moss peat was placed at the bottom of the first three columns, labelled A₁, A₂ and A₃. This was followed by another patch of cloth, on top of which was placed a 180 gram layer of mixed woodchips and biochar. These had been mixed by shaking them in a large Erlenmeyer flask. A second 90 gram layer of moss peat was placed on top of the woodchips and biochar, separated by a cloth. The A-columns ended up with 90 grams of biochar, 90 grams of woodchips, and 180 grams of moss.

120 grams of each filter material was mixed together and this mix was placed into the B-filters. The particle size distribution was same as in the A-filters. There were also three patches of cloth placed in corresponding positions as in the A-filters. The filter column configurations are depicted in Figure (2) and Figure (3).

Table 4. Particle size distribution in B-columns

Biochar size (mm)	Mass (g)	Woodchip size (mm)	Mass (g)
4-8	33.5	+16	40
2-4	33.5	8-16	40
1-2	40	1-8	40
0-1	13		
Total	120		120

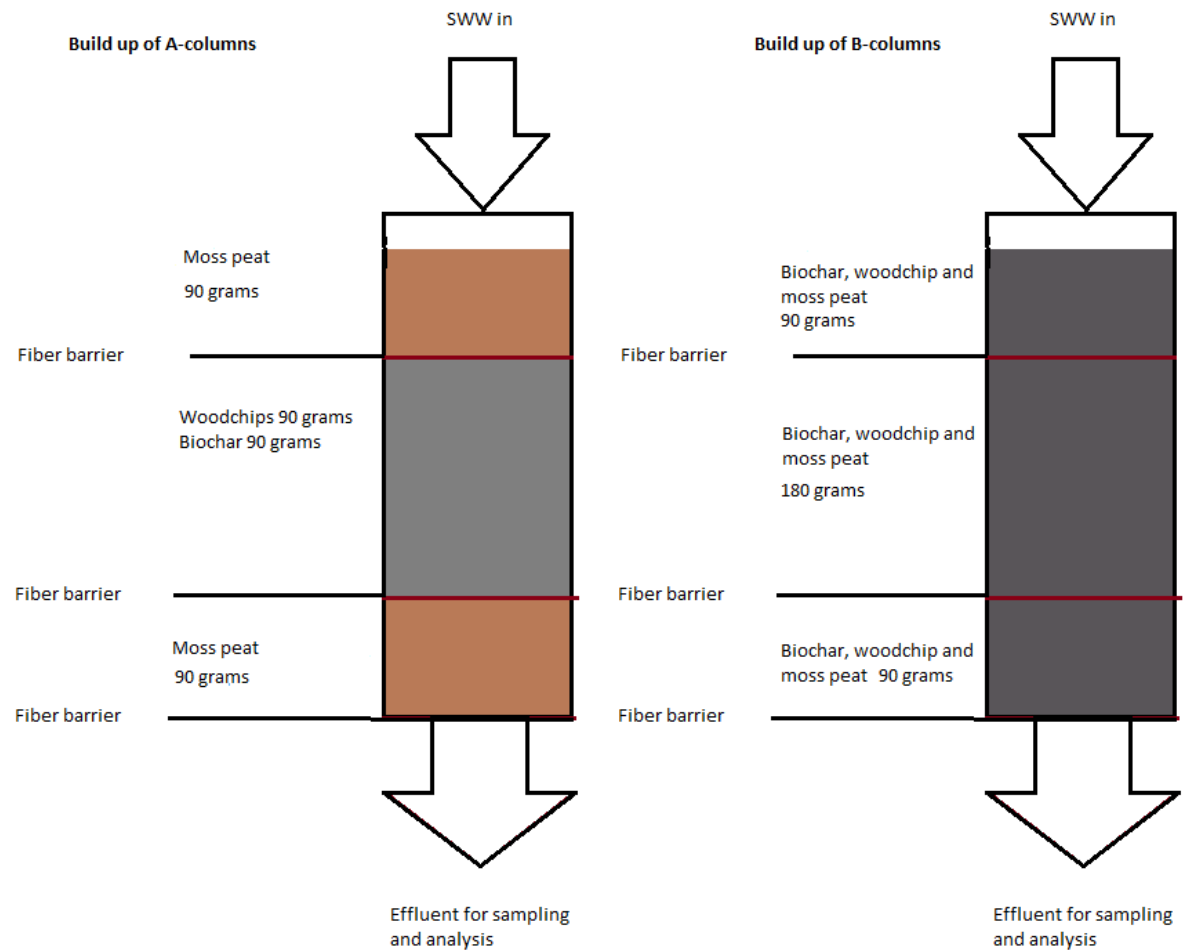


Figure 3. An illustration of the two filter column types

These columns were filled with distilled water for the duration of four days during Easter. After this, the water was let out. Analyses of these effluents were not carried out since the amount of suspended solids was high enough to block the syringe filters, despite the cloth that was placed at the columns' outlet. After flushing the columns with approximately 10 liters of distilled water the effluent turned clear enough for proper syringe filtration and laboratory analyses.

5.2 Synthetic wastewater

The synthetic wastewater (SWW) stock solution was produced by dissolving the following into 1000 ml of distilled water:

Table 5. Synthetic wastewater ingredients

Peptone	16 grams
Meat Extract	11 grams
Urea	3 grams
NaCl	0.7 grams
CaCl ₂ *2 H ₂ O	0.4 grams
MgSO ₄ *7 H ₂ O	0.2 grams
K ₂ HPO ₄ *3 H ₂ O	3.7 grams

This stock solution was divided into 11 small plastic bottles, each containing 90 ml. These bottles were stored in a freezer for the duration of the lab experiments. The SWW was produced on each experiment day by dissolving 90ml of the stock solution taken from the freezer into approximately 6 liters of distilled water.

Table (6) shows the averages of all parameters measured in the SWW during the experiment. All parameters were fairly consistent throughout the experiment. In terms of phosphorous, phosphates and total nitrogen, the SWW resembles typical sewage water.

Table 6. The average concentration of the parameters in the synthetic wastewater

SWW	Tot-P mg/L	PO ₄ -P mg/L	TOC mg/L	Tot-N mg/L	pH	EC mS
Average	9,3	7,2	213.6	71,3	7,3	180,0
Standard deviation	0,19	0,16		0,47	0,04	2,75
Number of measurements	6	6	1	2	9	8

5.3 Sampling and analyses

Every day, after producing the SWW, and feeding 750 ml of it to each of the columns, the final 250 ml of the effluent was collected for analyses. The suspended solids were removed by syringe filtration, using a fresh syringe and filter for each sample. Then the pH and conductivity were measured. After this the procedure for analyzing total phosphorous and phosphates was carried out, and this was the most time consuming part. On two days, the total nitrogen was measured while the total phosphorous samples were in the autoclave. Small samples were collected in the freezer every day, to be analyzed for total organic carbon on the final experiment day.

During the feeding of the columns, it was observed that the A-columns containing more moss had a much longer hydraulic retention time. Passing 750 ml of SWW through these filters took approximately three times longer than with the B-filters that contained less moss. Passing 750 ml of SWW through the B-columns took approximately five minutes, while more waiting was necessary with the A-columns.

Before the proper tests, some pilot measurements were carried out to determine proper dilution factors for phosphate and phosphorus analysis. When the proper data collection commenced on the 9th of May, approximately 2 L of SWW had already been poured through each column.

5.3.1 pH and conductivity

The pH and conductivity were measured from a portion of the sample immediately after syringe filtration, as the pH of the samples is affected by atmospheric CO₂ over time. The conductivity meter was calibrated with a KCl solution and the probe was rinsed with distilled water and dried with paper between each measurement.

The pH was measured in accordance to the standard SFS-3021. The temperature of the sample was not measured, but it was very likely to be close to room temperature, or the temperature recommended in the standard ($25\pm 2^\circ\text{C}$). From the pilot measurement it was known that the pH value of the samples would be either close to 7 or below that. Therefore only the buffer solutions for pH 4.01 (25°C) and pH 6.87 (25°C) were used. The lower pH buffer solution was produced by dissolving 10.12 g of potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) into distilled water in a 1000ml volumetric flask and filling up to mark. The neutral buffer was produced by dissolving 3.39 g of dried potassium dihydrogen phosphate (KH_2PO_4) and 4.43 g of dried di-sodium hydrogen phosphate dehydrate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$) into water in a 1000ml volumetric flask and filling up to mark. The buffer solutions were contained in small bottles and were used for calibrating the pH meter before the measurements each day. The pH probe was rinsed with distilled water and dried between measurements. It was not rinsed with the sample, against the recommendation in the standard. Also, the temperature of the solution was not monitored, even though the standard recommends it. With correct working methods and good equipment, ± 0.05 accuracy can be reached by using this method. [30]

5.3.2 Total phosphorous and phosphates

Phosphorous was determined by using the ammonium molybdate spectrometric method [31]. The principle of this method is to first react the orthophosphate (PO_4) with an acid solution containing molybdate and antimony ions, to form an antimony phosphomolybdate complex. This is followed by the reduction of the complex using ascorbic acid to form a strongly coloured molybdenum blue complex, whose absorbance is measured in order to determine the concentration of orthophosphate present. The same principle was used for determining total phosphorous, but before this, the polyphosphates were converted into orthophosphates by sulphuric acid hydrolysis and the organophosphates by mineralization via adding peroxodisulfite into the sample and placing the sample in the autoclave for 60 min at 120°C .

Three parallel measurements were performed on each sample on the first three days of phosphate determination. The SWW was also analysed in triplicate on the first three days. This was done in order to evaluate the quality of the practical work in the laboratory. As the results of each triplicate measurement were consistently very close, the laboratory work was deemed satisfactory, and on the following days only a single measurement was carried out for each sample. For total phosphorous, triplicates were analysed on the first two days.

A blank test was carried out on each analysis day, with the intention to ensure that the spectrophotometer gave zero result for absorbance for the blank sample, which contained all the same reagents as the other samples, but no effluent or SWW. The calibration graph for the spectrophotometer was made with the standard phosphate solutions according to the standard instructions. [31]

The final P concentration of the samples was calculated by the formula:

$$\rho P = \frac{(A - A_0) * V_{max}}{f * V_s}$$

Where,

A = the absorbance of the test portion

A₀ = the absorbance of the blank test

V_{max} = the volume of the 50ml volumetric flask

V = the volume of the effluent or SWW sample in the flask (ml)

f = the slope of the calibration graph, expressed in l/ml

To rule out the chance of contamination from the equipment used, one test was carried out by filtering distilled water with the syringe filters and analysing the sample for PO₄-P. The results showed that no PO₄-P contamination was caused by the equipment, and it was assumed that the equipment would not contaminate the samples with any of the other measured substances either.

5.3.3 Total nitrogen and nitrates

The nitrates were measured only once from two samples. This was carried out using a Merck Millipore test kit. Both samples tested below the 2.2 mg/l lower detection limit and no further nitrate analyses were deemed necessary.

Total nitrogen was tested with another test kit by Merck Millipore. The tests were made on the 17th and 19th of May. The SWW was tested in triplicate on both days to ensure the quality of practical laboratory work. The triplicates were accurate within 0.5mg error.

5.3.4 Total organic carbon

The TOC analysis was carried out on the final day of the experiments using the Shimadzu TOC-5000A apparatus. Samples that had been taken during the experiment days were stored in the freezer, and they were all analysed at one time, as the process was largely automated. The results showed concentrations much greater than the standard solutions used for the calibration of the equipment. The highest concentration in the standards was 25 mg/L, while the SWW was shown to have the concentration of 213.6 mg/L and the filtered effluents had concentrations up to 134.1 mg/L. These results cannot be viewed as accurate, and due to time constraints it was not possible to dilute and reanalyse the samples. However, these results were deemed reliable enough to perform internal comparisons within this paper between the performances of the column types.

6. Results

The results of the 11-day experiment are listed in this chapter. Most of the parameters were measured less than 11 times. It is therefore difficult to make reliable conclusions on the long term efficiency of these materials. However, the influent had much higher concentrations of nutrients that should be expected in average runoff water, and the results present the short term performance of the materials in worst case scenarios.

6.1 Data analysis

The data collected for the removal efficiencies of TOC, Tot-P and PO₄ was deemed sufficient for performing statistical comparisons. A series of t-tests were performed by using the Excel 2016 Data Analysis Tools in order to test two null hypotheses:

H₀(1) : There is no statistically significant difference between the filter columns with the *same* filter material composition, when comparing the removal efficiency of TOC, Tot-P and PO₄.

H₀(2) : There is no statistically significant difference between the filter columns with *different* filter material compositions, when comparing the removal efficiency of TOC, Tot-P and PO₄.

The performance of each filter column was independent of each other, and by calculating the standard deviations, unequal variance could be assumed. Thus, unpaired two sample t-tests with assumed unequal variance were used for the statistical analysis. 95% confidence level was used, and thus the critical P-value was 0.05, indicating that:

$P < 0.05 \rightarrow$ Hypothesis rejected

$P > 0.05 \rightarrow$ Hypothesis accepted

In order to test $H_0(1)$, six t-tests were performed for each parameter. First, columns A₁ and A₂ were compared, followed by columns A₁ and A₃, and finally columns A₂ and A₃. The B-columns were compared to each other in a corresponding manner.

After having tested $H_0(1)$, the second null hypothesis, $H_0(2)$, was tested for each parameter by comparing the results of the A-columns with the results of the B-columns.

Table (7) shows that $H_0(1)$ can be accepted throughout these results. There was no statistically significant difference among the filter columns of the same type, when considering the TOC, Tot-P and PO₄ removal efficiencies ($P > 0.05$).

Table 7. Results (p-values) of the t-tests (1)

P-values	Tot-P	PO	TOC
A1 / A2	0,204	0,491	0,896
A1 / A3	0,130	0,379	0,591
A2 / A3	0,802	0,874	0,634
B1 / B2	0,498	0,487	0,968
B1 / B3	0,865	0,905	0,977
B2 / B3	0,383	0,528	0,989

The other null hypothesis, $H_0(2)$, is rejected, according to P-values presented in table (8). The data of the removal efficiencies of TOC, Tot-P and PO₄ were different for A-columns and B-columns, and these differences were statistically significant ($P < 0.05$).

Table 8. Results (p-values) of t-the t-tests (2)

P-values	Tot-P	PO	TOC
A / B	0,0004	0,0176	0,0035

6.2 General overview of performance over time

The removal efficiencies change over time, and for this reason stating the average removal efficiency for each parameter over the 11-day period is not sufficient. There was no statistically significant difference among the filter columns of the same type. The results in Figure (4) are the averages of three samples analysed from three filter columns of the same type.

The A-columns show a more clear decrease in the general removal efficiencies. However, apart from phosphorous and phosphate removal, the A-columns performed better than the B-columns. This could best be explained by the longer hydraulic retention time, and possibly the lower pH-values created by the higher amount of moss.

There was a four day hiatus for filtration experiments, between the 12th of May and the 16th of May, during which the filter materials dried to some extent. This drying may have impacted the performance in some way. During the last two days, the A-filters were leaching phosphate into the effluent. The B-columns do not show an equally clear decrease in the removal efficiencies, apart from TOC, which on the other hand seemed to improve again on the last measurement. More detailed efficiency results are found in the Appendices.

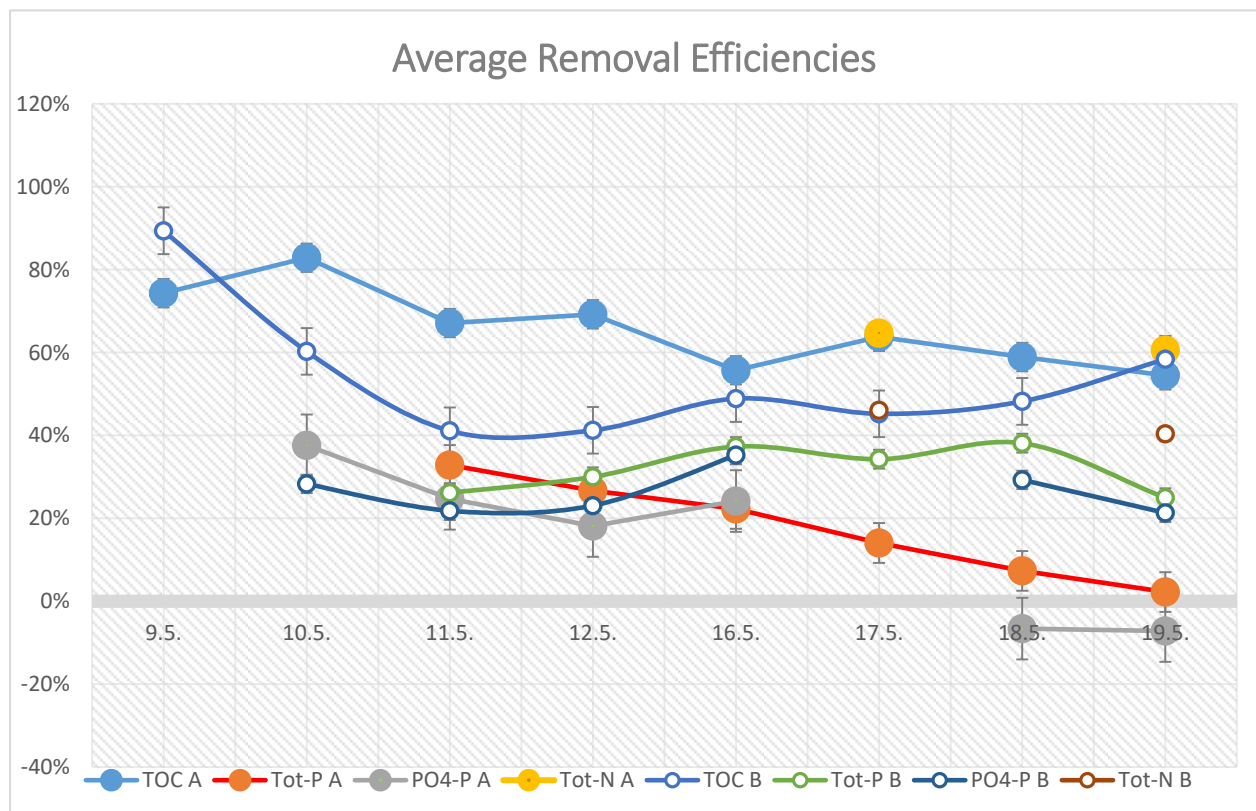


Figure 4. Average removal efficiencies during the experiment

6.3 Total phosphorous

The mean Tot-P removal efficiency was 18% for the A-columns and 32% for the B-columns. Initially, the A-columns performed slightly better at removing Tot-P from the SWW, but their performance deteriorated within a week, as can be seen in Figure (5). One of the A-filters reached zero removal efficiency by the end of the experiment. The B-columns' efficiency remained fairly consistent throughout the 11 days. The column A1 began declining in performance one day before columns A2 and A3. It was observed several times, that the retention time for A1 was slightly longer than for the other A-columns.

The standard deviation in the efficiency of the A-columns was 13% and 6% for the B-columns. The average Tot-P concentration of the SWW was 9.3 mg/L.

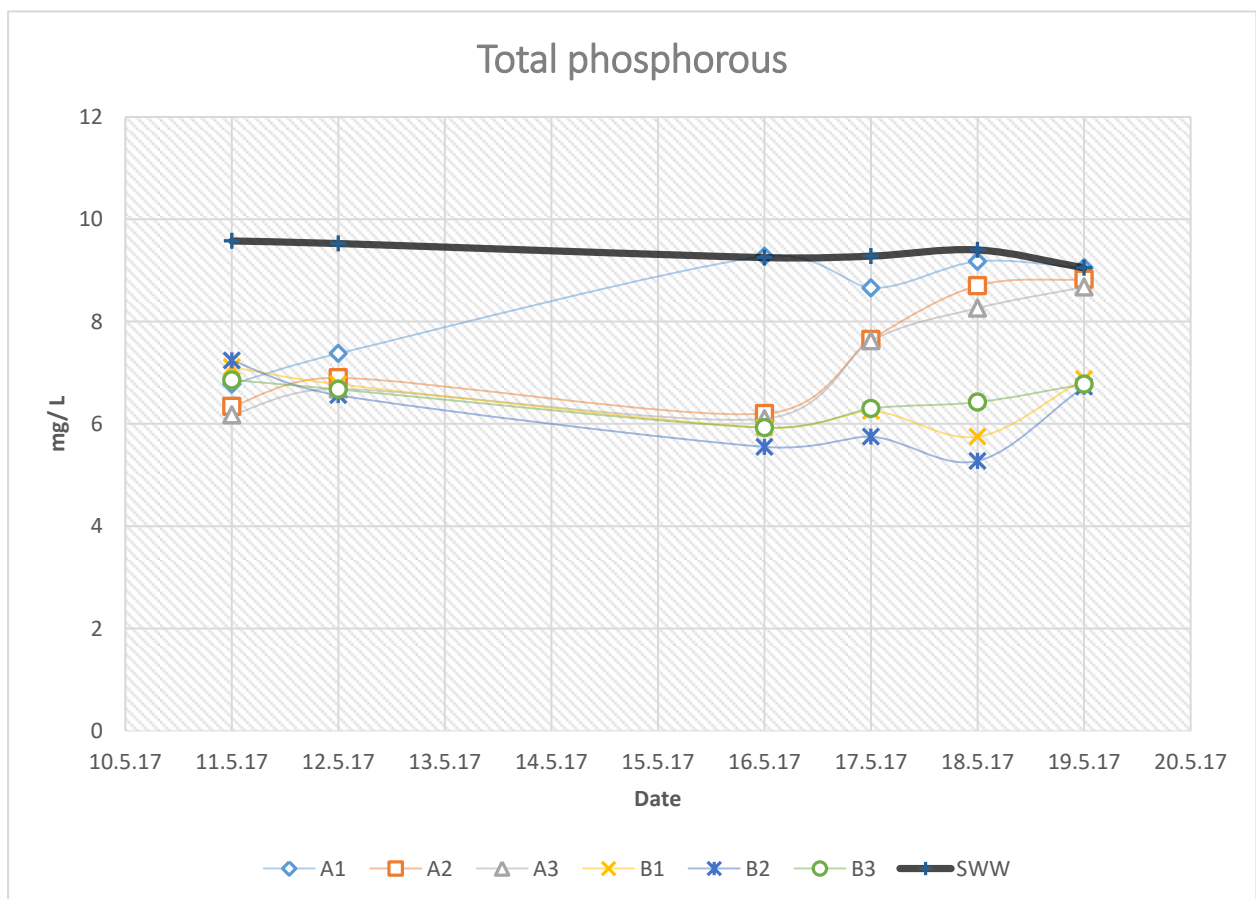


Figure 5 Measured Tot-P concentrations during the experiment

6.4 Phosphates

The mean $\text{PO}_4\text{-P}$ removal efficiency was 15% for the A-columns and 27% for the B-columns. Through time, the removal efficiency followed a similar pattern to the removal of Tot-P, in that the A-columns' removal ability decreased very clearly after a few days, while the B-columns were more consistent throughout the experiment. On the final two days of the experiment, all of the A-columns were releasing effluents with higher phosphate concentration than that of the SWW, as can be seen in Figure (6). Here, as with the total phosphorous, the column A1 had the poorest performance.

On the 17th of May, there was a likely measuring error in the laboratory. The $\text{PO}_4\text{-P}$ concentration of the SWW was slightly above 7 mg/L on all days, except on the 17th of May, when it was as high as 9.3 mg/L. Since there was no similar leap in the Tot-P concentration on that day, the phosphate sample was possibly contaminated, or there was a human error in the carrying out of the analysis. Therefore this data point was left out from the final results. The standard deviation was 18% for the A-columns, and 6% for the B-columns.

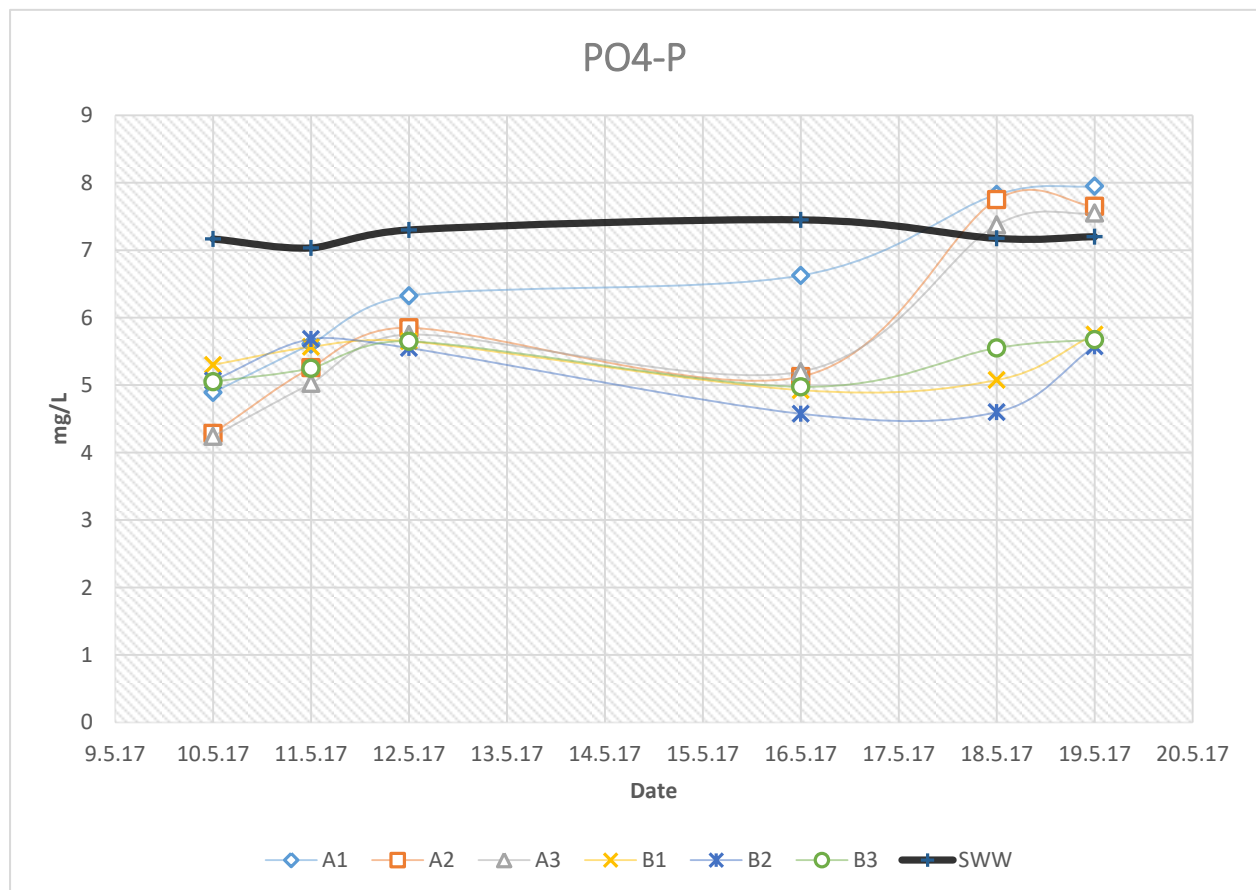


Figure 6. Measured $\text{PO}_4\text{-P}$ concentrations during the experiment

In order to assess the amount of phosphates leaching from the filter materials, the columns were flushed with distilled water before and after the SWW experiment, and the effluents collected for determining the concentration of $\text{PO}_4\text{-P}$. Table (9) shows that the A-columns were leaching more phosphates after the SWW experiments, and column A1, with the poorest performance and longest observed hydraulic retention time, was also leaching the most phosphate.

Table 9. Leached phosphates before and after experiments.

$\text{PO}_4\text{-P}$ (mg/L)	Before	After
A1	0,53	6,4
A2	0,25	5,79
A3	0,36	5,23
B1	0,35	1,91
B2	0,29	1,4
B3	0,39	1,81

6.5 Total Organic Carbon

Total organic carbon in the synthetic wastewater was only measured once. Also, the standards used for calibrating the measuring equipment had much lower TOC content than the tested effluent samples. The highest standard concentration was 25 mg/L, while the result for the SWW was 213.6 mg/L. Only the B-filters had concentrations below 25 mg/L on the first experiment day. Due to time constraints, it was not possible to carry out another set of analyses with diluted effluent samples. Consequently, the results here are not entirely reliable, and unfit to be compared to the results gained in other experiments. However, the data can be used for internal comparison in order to draw conclusions about the difference in the performance of the filter column types tested in this experiment. The mean TOC removal efficiencies were 65.8% for the A-filters and 54.1% for the B-filters. The patterns are similar for the filter columns of the same type, as can be seen in Figure (7). There was no statistically significant difference in the performance of the filter columns of the same type.

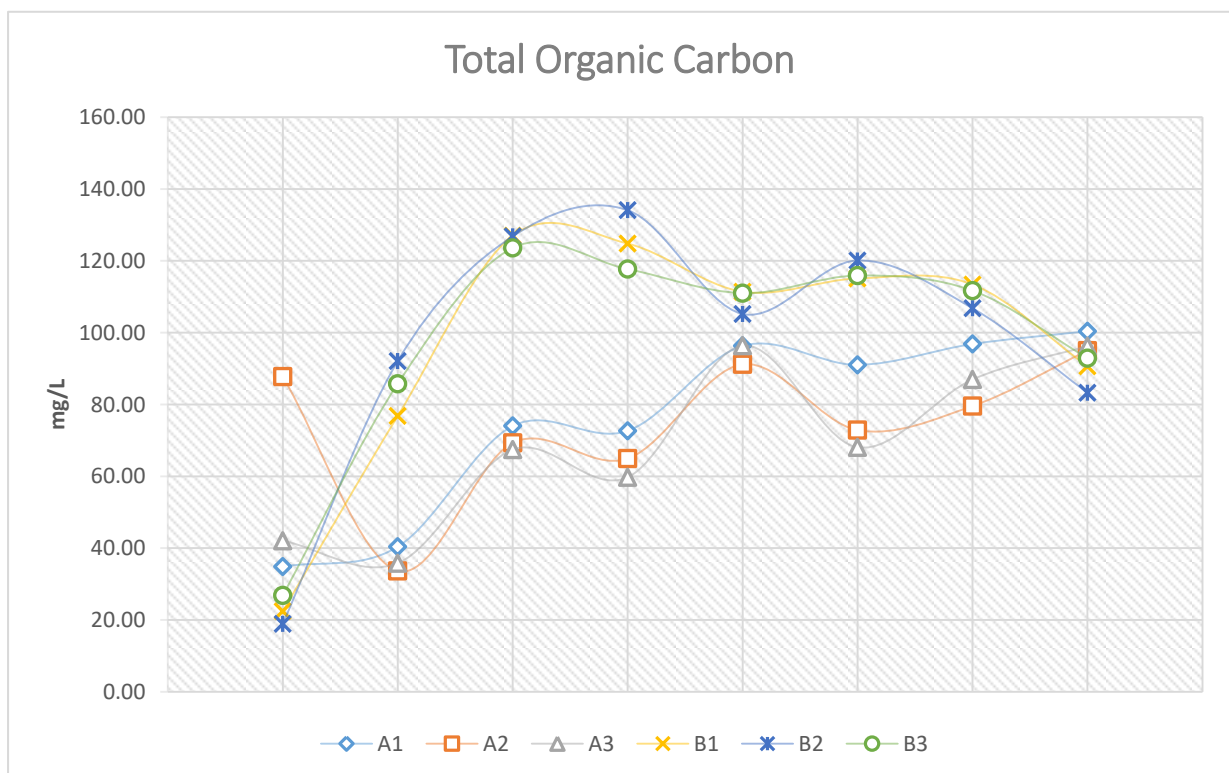


Figure 7. Measured total organic carbon concentrations of effluent samples. The SWW result is off the chart, at 213.6 mg/L.

Although these results are not fully accurate, they do seem to support the findings of Barrett et al., in that biochar is capable of adsorbing organic carbon from runoff water [26]. Here, the A-columns with less biochar and more sphagnum moss performed slightly better in the long run. This might be explained by the slower hydraulic retention time in the A-filters. The TOC-concentration in the SWW was very high, and because no sample was taken during the initial washings with distilled water, it is not possible to estimate how much organic carbon the filter materials might have leached.

After a steep decrease in the removal efficiency during the first three or four measurements, the B-columns' efficiency began to slowly improve, and on the final day, they were performing slightly better than the A-columns. The similar patterns suggest that the potential error in the measurements caused by the insufficient calibration range, or the lack of dilution of the samples, is a systematic one, and the graph illustrates the true tendencies of the columns, even though the exact values are probably inaccurate. On the final measurement, the columns were removing approximately 50% of the total organic carbon.

6.6 Total Nitrogen and nitrates

Total nitrogen was determined on two occasions near the end of the experiments; on the 17th and the 19th of May. The average efficiency for Tot-N removal was 63% for the A-columns, and 43% for the B-columns. The results were consistent and showed a minor decrease in the efficiency on the second measurement.

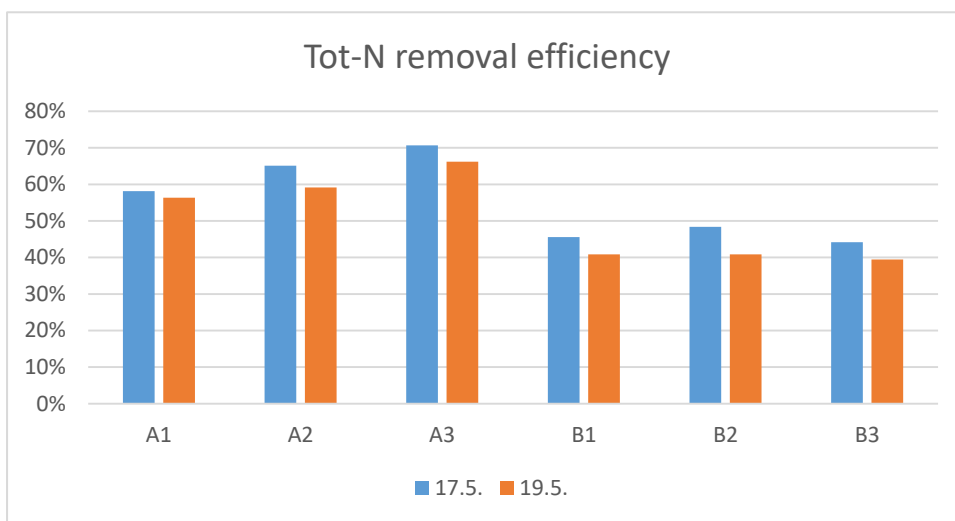


Figure 8. The total nitrogen removal efficiencies

The synthetic wastewater did not contain any nitrates. The NO₃ concentration was measured once from the effluents from columns A2 and B2, with results showing concentrations of 1.1 mg/L and 0.9 mg/L respectively. These results were both below 2.2 mg/L, which was the secure lower detection limit for the spectrometer used, and therefore their accuracy is not guaranteed. It is possible that the materials leached traces of NO₃-N, or that slight nitrification occurred during the filtration, but the results here suggest that the nitrate concentrations in the effluent remained very low.

6.7 Electric conductivity and pH

The pH of the SWW and the effluents were very stable throughout the experiment. As expected, the A-filters, which contained a larger proportion of sphagnum moss, had lower pH values than the effluents from the B-columns. All the effluents had lower pH-values than the SWW. A very slight increase in the pH values of the A-columns can be observed in figure (11).

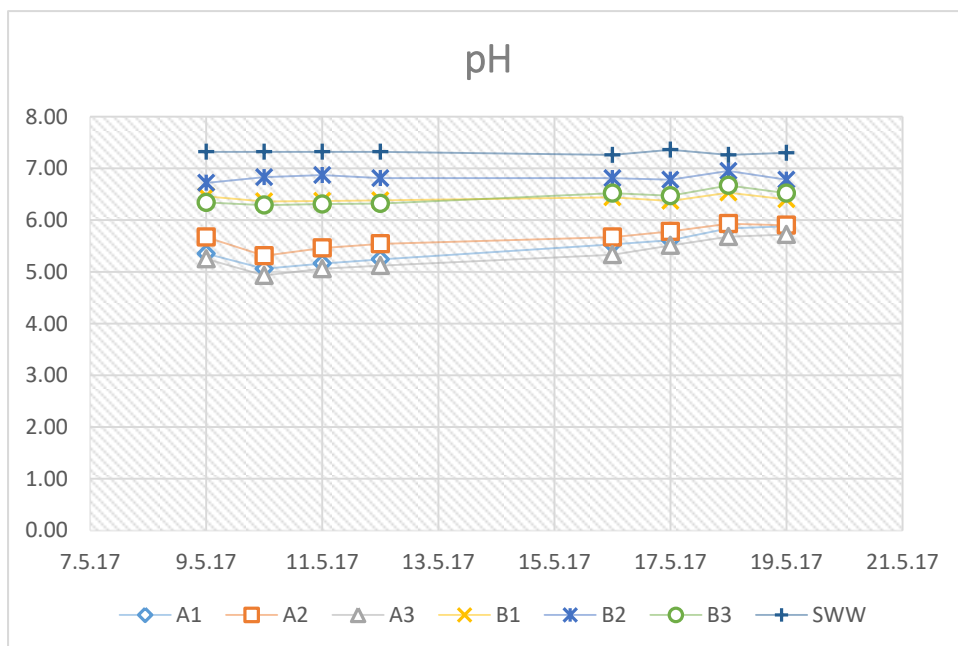


Figure 9 Measured pH values during the experiment

Figure (8) shows, that the A-columns decreased the conductivity of the SWW in the beginning of the experiment. The conductivities of all effluents increased steadily throughout the experiment.

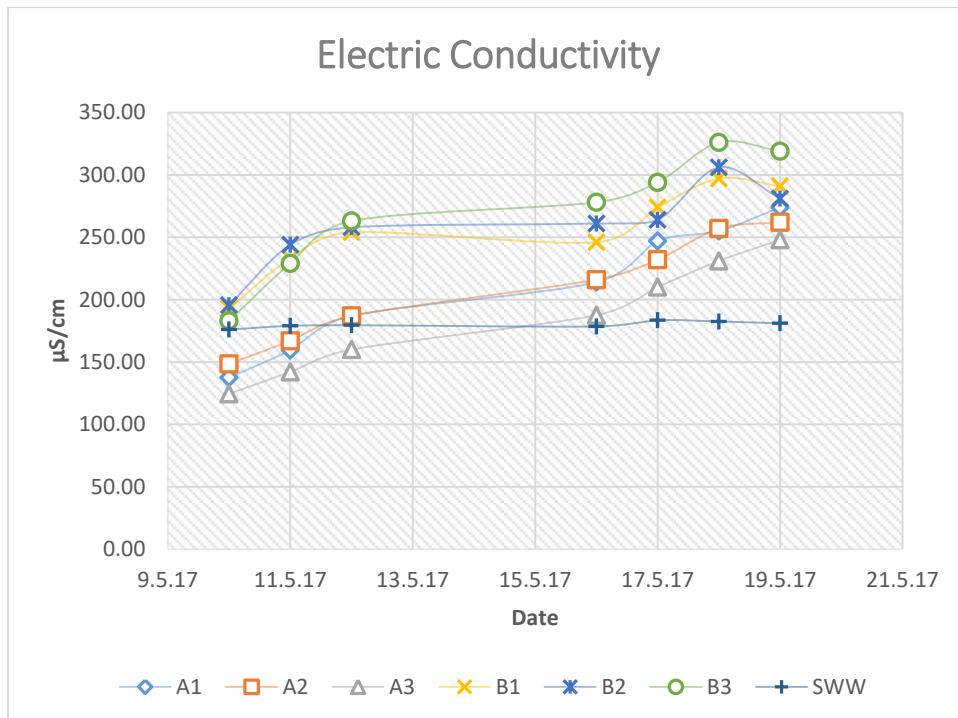


Figure 10. Measured conductivities during the experiment

After finishing the test series altogether, the filter columns were used for one additional filtration test where brine was used as the influent. The conductivities were much higher, and all filter columns reduced the conductivity approximately 20% - 30%.

Table 10. Conductivities when brine was used as influent (unit in mS/cm).

	A1	A2	A3	B1	B2	B3	SW
EC (mS/cm)	82,8	79,1	77,8	81,3	83,3	83,8	109,8

7. Findings

The biofilter materials were distributed evenly and at even fractions in the B-columns, and in the A-columns there was a greater fraction of sphagnum moss and smaller fractions of biochar and woodchips (see 5.1). Compared to the B-columns, the A-columns had a lower pH-value and a longer hydraulic retention time (i.e. the water made contact with the filter materials for a longer time). Both of these factors should improve adsorption, and it is true that the A-columns' removal performance was better for total nitrogen, total organic carbon and total dissolved solids (presented as conductivity). However, the A-columns' performance in phosphorous removal was poor. On the final days they were increasing the amount of phosphates in the wastewater, and after the experiments they were leaching considerable amounts of phosphate into the distilled water used for flushing the columns.

The results of Lukkarinen et al. showed that moss performed well in the removal of phosphorous [20]. However, the bog water used as influent in their experiments had a much lower concentration than the SWW in this paper. Lukkarinen et al. also point out that some of the nutrient removal by biochar is due to the biofilm that forms on its surface. This may be especially important in the case of the phosphate anion, as both biochar and sphagnum moss have negative surface charges. Moss may have negatively affected the formation of biofilm on the woodchip and biochar surfaces [24] [25]. This could partially explain the poor performance in phosphate removal from synthetic wastewater. Berger's results indicated that biochar's phosphorous removal efficiency improves through time [21]. This may be because the formation of biofilm takes time. This supports the theory that biofilm is important in biochar's phosphate removal mechanism, and sphagnum moss, with its antibacterial qualities, interferes with the formation of biofilm, and therefore phosphate removal by biochar. Vaasan Vesi, the local water department in Vaasa Finland, reports that in the year 2011 its wastewater treatment plant's average removal of phosphorous was 93%, an efficiency far superior to the one is reached with these biofilters. [32]

The effluents contained a high amount of suspended solids. This was especially noticed during the first days, when an attempt was made to filter the solids from the samples before analysis. The syringe filters were blocked, and vacuum filtration using membrane filters and a Buchner funnel was also unsuccessful. The amount of suspended solids decreased after a number of flushes. But this tendency may create problems with the practical applications, such as compost filter socks, as suspended solids might block the mesh, and are also considered a pollutant.

The pH-values did not fluctuate during the experiment. As expected, the effluents from the A-columns had lower pH-values, as these columns contained more sphagnum moss. Conductivity of all effluents increased steadily during the experiment, indicating an increase in the total dissolved solids. It is worth noting, that the effluents had higher concentrations of total dissolved solids than the influent.

Adding coagulants (e.g. lime or iron salts, see 2.1.1) could improve phosphorous removal by enabling precipitation. This may not be necessary for filtering waters with low nutrient concentration.

It is worth noting, that in this experiment the materials were given considerable stress. Each column had only 360 grams of filter material, and each received approximately six litres of synthetic wastewater, whose phosphorous and nitrogen concentrations were the equivalent of actual wastewater. Despite this, near the end of the experiment, the columns performed well at total nitrogen removal, one of the A-columns even at 70% efficiency. There was no nitrate in the influent, and a large amount of nitrogen removal may have occurred as adsorption of the ammonium cations onto the negatively charged biochar and sphagnum moss surfaces. No nitrification was detected.

To give some context to these results, the annual report of Vaasan Vesi relates that the average total nitrogen removal efficiency at their wastewater treatment plant was 39% in the year 2011 [32]. Also, the average efficiency of woodchip bioreactors has been reported to be 15%-60%. Put in this context, these filter columns all performed fairly well in the removal of nitrogen.

Total organic carbon seemed to be removed by the filter materials efficiently as well, although these results need to be approached with caution due to afore mentioned issues with the analysis that was carried out. These results seem to support the idea that dissolved organic carbon adsorbs well on biochar surfaces [26].

7.1 Possible improvements

Comparing the results of this paper to the previous research results cited in the theory section is complicated. The phosphorous concentration of the SWW used in this work was higher than the one used in the cited studies. Berger and Sidibe, for example, had fed much smaller volumes of greywater into the columns, albeit for a longer time period. The filter material configurations used in this work were unique, as is the case in several other column experiments done previously. This issue was briefly discussed in section 3.2.

For this work, the particle distributions, SWW concentrations and the pH of the effluent samples were well documented. However, the pH of each filter material was not determined independently, temperature was never measured and the comments on the differences in hydraulic retention time were based on casual observation, i.e. the contact time between the SWW and the filter materials was not measured in any way. There was also no data about the surface area of the biochar in this work. The amount of suspended solids in the samples before syringe filtration was not measured, although this would have been useful data. When considering the practical applications, such as compost filter socks, the chosen SWW was not ideal, as typical surface runoff water has much lower concentrations of nutrients.

A possible recommendation for future reference could be carrying out a column experiment as identical as possible to another one made before. Changing only one variable at a time can give more reliable data about the function of these biofilter materials, when comparing the results. A suggestion would also be to test filtration in two-stage configurations, as several stages are used in conventional wastewater treatment as well.

8. Conclusion

Biochar production has several benefits, including carbon sequestration, waste management purposes, energy production, soil improvement, and it can even be used as a cheaper alternative to activated carbon in removing pollutants from water. Many studies have shown that biochar can effectively remove pollutants from water, including nutrients, although the results have been somewhat inconclusive, especially about the removal of phosphate.

In order to reach the goals of the EU water framework Directive the use of bio-filter materials, such as biochar, moss and woodchips, in various filtration applications can potentially be helpful. The performance of denitrifying woodchip bioreactors can be improved by the addition of biochar that has been produced using the most appropriate raw materials and pyrolysis methods. Compost filter socks can be effectively utilized both in urban and in rural settings to manage water flows and the spreading of pollutants. Both biochar and sphagnum moss could be used as filter material in these filter socks, instead of, or as an addition to compost.

A column study was carried out in order to assess the performance of the three biofilter materials. All columns contained 360 grams of filter material, but the A-columns had a 50% moss, while the B-columns had 33% moss. This difference in the amount of moss played a key role in the performance difference between the column types, as moss improved water retention and lowered the pH value. The columns containing more moss performed better at removing TOC, Tot-N, and at reducing conductivity. However, the columns containing less moss had more stable removal efficiency of phosphorous. Due to biochar's negative surface charge, its ability to adsorb phosphates is small. However, microbial activity and biofilm formation may help removing phosphorous, and the difference in phosphorous removal performance could be partially explained by differences in microbial activity. Biochar promotes microbial activity due to its large surface area, while moss has strong antimicrobial properties, including its low pH value.

Although many of the substances were removed with efficiencies ranging between approximately 30-60% during the 11-day laboratory experiment, there was a slight downward trend in general efficiency over time. The efficiency in TOC-removal fluctuated the most, improving slightly on the final analysis day. It is safe to say that the columns containing more moss lost their ability to retain phosphates from the water within a few days, but conclusions about the long term performance in the removal of the other substances are difficult to make. Also, the test was carried out using a synthetic wastewater which did not resemble actual urban or agricultural runoff waters, but sewage water in terms of nutrient concentration.

As research on biochar in nutrient removal from water is relatively new, it is recommendable to increase the reproducibility of research results. There are numerous variables that need good documentation when carrying out biofilter research, including, for example, details on the filter material, the influent concentrations, biofilter particle size distribution, volumetric load, and duration of the experiment.

9. References

- [1] European Commission – Press Release, “Environment: Europeans call for stronger EU action on Water,” 2016. [Online]. Available: http://europa.eu/rapid/press-release_IP-12-289_en.htm?locale=EN. [Accessed 22 November 2017]
- [2] European Commission - Environment, “Introduction to the new EU Water Framework Directive,” 2016. [Online]. Available: http://ec.europa.eu/environment/water/water-framework/info/intro_en.htm. [Accessed 22 November 2017]
- [3] K. Haatainen and S. Mitikka, “The ecological status of Finland’s large lakes is good but the coastal waters are in a poor condition,” *Envelope – Newsletter of the Finnish Environment Institute SYKE*. 2013. [Online]. Available: http://mmm.multiedition.fi/syke/envelope/Envelope_2013_3/sivu_5.php. [Accessed 22 November 2017]
- [4] Land use and building act 2014/682, [Online]. Available: <http://www.finlex.fi/fi/laki/alkup/2014/20140682#Pidp450846464> [Accessed 23 November 2017]
- [5] K.R. Reddy, T. Xie and S. Dastgheibi, “Evaluation of Biochar as a Potential Filter Media for the Removal of Mixed Contaminants from Urban Storm Water Runoff”, *Journal of Environmental Engineering*, Vol. 140, no.12, pp. 2-10. 2014.
- [6] Pajupojat Oy, “Pajupojat Oy: Pajubiohiili,” 2017. [Online]. Available: <http://pajupojat.fi/paju/biohiili/>. [Accessed 22 November 2017]
- [7] Salix Energi Europa AB, “Front page: SalixEnergi,” 2017. [Online]. Available: <http://salixenergi.se/> [Accessed 23 November 2017]
- [8] J. Lehmann and S. Joseph, “Biochar for environmental management: an introduction,” *Biochar for environmental management: Science, technology and implementation*, pp. 2-11, 2015.
- [9] J. Lehmann, “Bioenergy in the black”, *Frontiers in Ecology and in the Environment*, vol. 5, issue 7, pp.381-387, 2007.

- [10] M.R. Fuchs, M. Garcia-Perez, P. Small and G. Flora, "Campfire lessons – breaking down the combustion production to understand biochar production", *The Biochar Journal*, 2014. [Online]. Available: <https://www.biochar-journal.org/en/ct/47>. [Accessed 18 December 2017].
- [11] M. Gray, "Biochar for stormwater treatment", *Worldwater Stormwater Management*, vol. 3, Issue 1, pp.16-17, 2015.
- [12] K.Lou, A.U. Rajapaksha, Y.S. Ok and S.X.Chang, 2016, "Pyrolysis temperature and steam activation effects on sorption of phosphate on pine sawdust biochars in aqueous solutions", *Chemical Speciation & Bioavailability*, Vol. 28 no.1-4, pp.42-50.
- [13] F. Gao, Y. Xue, P. Deng, X. Cheng & K. Yang, "Removal of aqueous ammonium by biochars derived from agricultural residues at different pyrolysis temperatures", *Chemical Speciation and bioavailability*, Vol. 27, Issue 2, pp.92-97. 2015.
- [14] J.A. Ippolito, K.A. Spokas, J.M. Novak, R.D. Lentz and K.B. Cantrell, "Biochar elemental composition and factors influencing nutrient retention", *Biochar for environmental management: Science, technology and implementation*, pp.148.149, 2015.
- [15] Meier, E, "The Wood Database" 2008-2016. [Online]. Available: <http://www.wood-database.com/white-willow/>. [Accessed 30 January 2018].
- [16] D. Mohan, A. Sarswat, Y.S. Ok and C.U. Pittman Jr., "Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review" *Bioresource Technology*, Vol. 160, pp. 191-202, 2014.
- [17] N.F. Gray, *Water Technology, an Introduction to Environmental Scientists and Engineers*, 3rd ed., London: Elsevier, 2010.
- [18] Pacific Northwest Pollution Prevention Resource Center (PPRC), "Emerging Best Management Practices in Stormwater: Biochar as Filtration Media," 2014.[Online] Available: http://pprc.org/wp-content/uploads/2014/08/Emerging-Stormwater-BMPs_Biochar-as-Filtration-Media_2014.pdf [Accessed 20 December 2017].
- [19] L. Lukkarinen, T. Ranta-Korhonen, S. Seppäläinen and H. Soininen, "Valumavesien käsittelyyn soveltuvat biosuodatinmateriaalit ja niiden laboratoriotestaukset", *Biosuodattimet metsätalouden vesiensuojelussa*, Mikkeli UAS, pp. 37-53, 2016.
- [20] M. Sidibe, (2014). *Comparative study of bark, bio-char, activated charcoal filters for upgrading greywater*, Thesis for a Master's degree in EnvEURO. Swedish University of Agricultural Sciences, Department of Energy and Technology, Uppsala.

- [21] C. Berger, (2012). *Biochar and activated carbon filters for greywater treatment – comparison of aorganic matter and nutrient removal*, Thesis for a Master’s degree in EnvEURO. Swedish University of Agricultural Sciences, Department of Energy and Technology, Uppsala.
- [22] L. Boissoneault, “How humble moss healed the wounds of thousands in World War I”, 2017. [Online]. Available: <https://www.smithsonianmag.com/science-nature/how-humble-moss-helped-heal-wounds-thousands-WWI-180963081/>. [Accessed 30 January 2018]
- [23] D.R. Knighton and V. Fiegel, “Making the most out of moss”, 2012. [Online]. Available: https://www.wqpmag.com/sites/wqpmag.com/files/12_tu_cws_0912WQP.pdf . [Accessed 13 January 2018]
- [24] B. Dickhudt, “The battle against biofilm”, 2012. [Online]. Available: https://www.wqpmag.com/sites/wqpmag.com/files/18_app_cws_1212WQP.pdf . [Accessed 13 January 2018]
- [25] L. Christianson and M. Helmers, “Woodchip bioreactors for nitrate in agricultural waters”, 2011. [Online] Available: <file:///H:/Research%20methods/iowabioreactor.pdf> [Accessed 15. January 2018]
- [26] C. Barrett, B. Halaburka and R. Luthy, “Optimizing Denitrification in Stormwater using Woodchip Bioreactor”, *Re-inventing the Nation’s Urban Water Infrastructure*, 2014. [Online] Available: http://renuwit.org/wordpress/wp-content/uploads/pdf/Barrett_Abstract.pdf [Accessed 15. December 2017]
- [27] American Association of State Highway and Transportation Officials, US Army Corps of Engineers, United States Department of Agriculture and U.S. Environmental Protection Agency. “Federal specifications for compost filter socks for sediment and erosion control”, 2008. [Online] Available: https://www.nurserygrowers.org/pdf/FilterSocks_Jan2014.pdf [Accessed 15. January 2018]
- [28] S.E. Manahan, “Water chemistry, Green science and technology of nature’s most renewable resource”, 2011. Taylor and Francis Group, LLC, CRC Press, Florida USA p.248.
- [29] Fondriest Environmental Inc., “Fundamentals of Environmental Measurements, Conductivity, Salinity and Total Dissolved Solids”, 2014. [Online] Available: <http://www.fondriest.com/environmental-measurements/parameters/water-quality/conductivity-salinity-tds/#cond9> , [Accessed 16 January 2018]
- [30] Finnish Standards Association, “Veden pH-arvon määrittys. SFS 30121”, 1979.

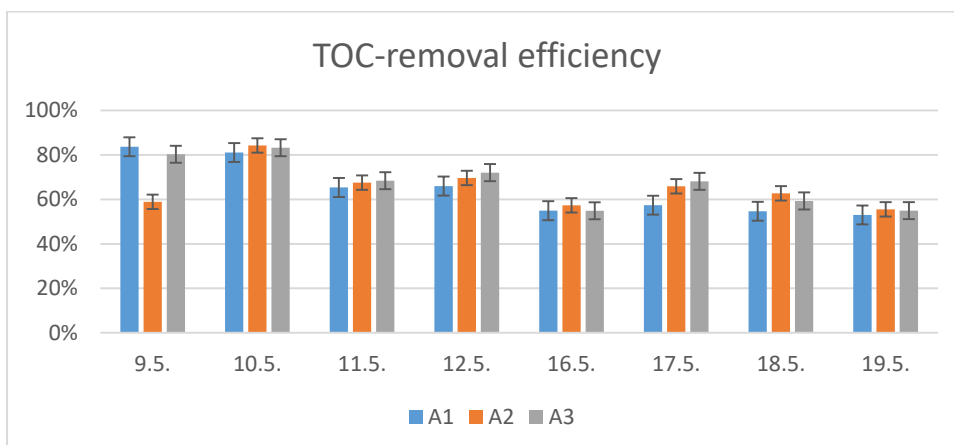
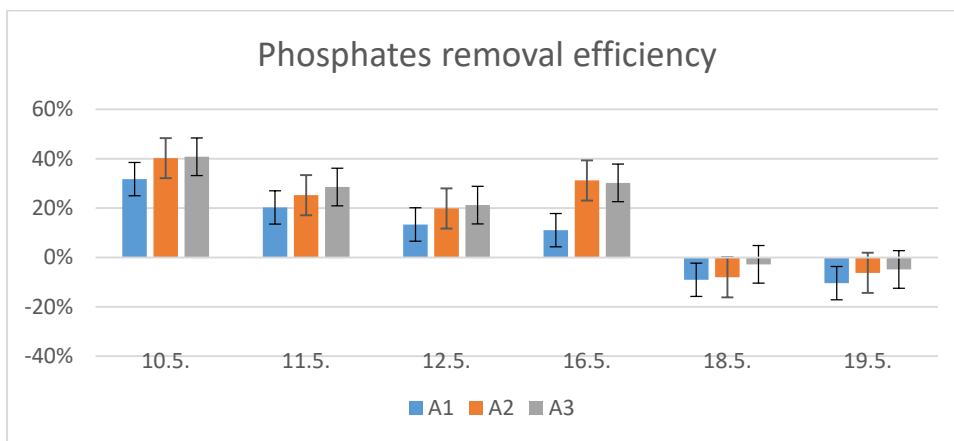
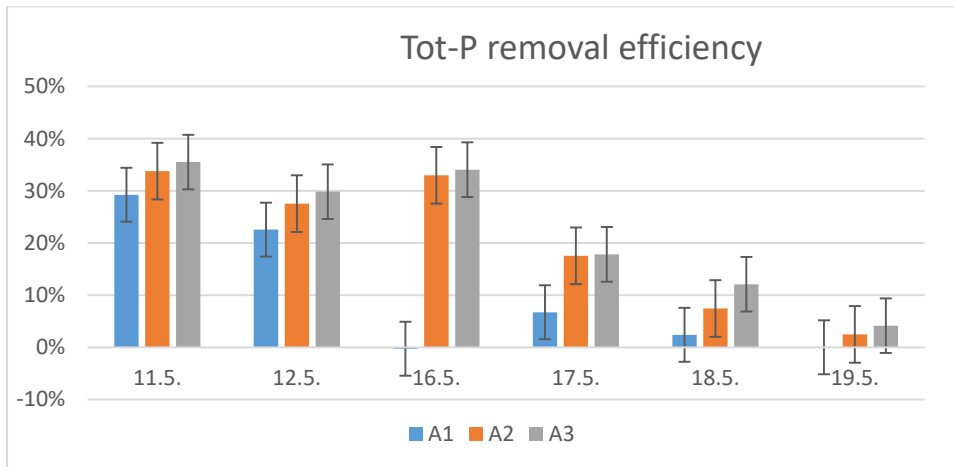
[31] Finnish Standards Association, "Water quality. Determination of phosphorous. Ammonium molybdate spectrometric method. SFS-EN ISO 6878", 2004.

[32] Vaasan Vesi, "Vaasan Veden Vuosikertomus 2011", 2011. [Online] Available: <http://docplayer.fi/43153768-Vaasan-veden-vuosikertomus-2011.html> , [Accessed 30 January 2018]

Appendix 1: The equipment and methods used during the laboratory experiment

Parameter	Apparatus	Standard method
Tot-P PO4-P	Shimadzu UV-1650PC spectrophotometer	SFS-EN ISO 6878 Autoclave used in Tot-P analysis
Tot-N NO3-N	Nova 60 spectrometer Merck Millipore's Spectroquant cuvette test kit Range: Tot-N, 10 – 150 mg/l NO3 2,2 - 79,7 mg/l	Test kit instructions
TOC	Shimadzu TOC-5000A	Apparatus instructions
pH	Mettler Toledo S20 SevenEasy pH	SFS 3021
Conductivity	Mettler Toledo S30 SevenEasy Conductivity	No standard. Calibration with a <u>KCl</u> solution

Appendix 2: Removal efficiencies of the A-columns



Appendix 3: Removal efficiencies of the B-columns

