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UPTEC W 17 004
Examensarbete 30 hp
Mars 2017

Evaluation of bark material and granulated active carbon for treatment of perfluoroalkyl substances (PFASs) in wastewater

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ABSTRACT

Evaluation of bark material and granulated active carbon in treating perfluoroalkyl substances (PFASs) using wastewater

Per- and polyfluoroalkyl substances (PFASs) are a group of artificial chemicals which have been used in a wide area of applications such as surface protection agents in cloths and different industrial applications. It has been found that PFASs are potentially toxic and are frequently found in the environment due to their persistent and mobile properties. Effluents from wastewater treatment plants (WWTPs) have been identified as an important point source of PFASs. Bark, by-product from the paper and wood industry, is a low-cost adsorbent and has the potential to be used as a filter material for PFASs in WWTPs. In this study, the removal of PFASs in wastewater has been investigated using granulated active carbon (GAC) (n = 2) and bark (n = 2) in a pilot scale experiment at Kungsängsverket, Uppsala over a period of five weeks. The specific objects included: i) investigate the influence of flow-rate (10, 30 40 and 60 Ld^{-1}) on the removal efficiency of PFASs in the GAC and bark filters, ii) investigate the influence of particle size of bark on the removal efficiency of PFASs and iii) establish what circumstances that potentially promotes removal of PFASs in GAC and bark filters.

The results showed that GAC was the most effective method compared to bark, with a reduction of 73-93%, with increasing efficiency under low flow (10-30 L d^{-1}) conditions. The removal efficiency of bark was 45% with a particle size of 2-5 mm and under low flow conditions (10-30 L d^{-1}), while under high flow conditions (60 L d^{-1}) with the same particle size the removal of PFASs was not efficient, instead the total PFAS concentration increased with 40%. In contrast, bark with a particle size of 5-7 mm proved to be not efficient in removing PFASs (removal efficiency = 0%). In general, the removal efficiency increased with smaller particle size of the adsorbent and lower flow rate. The results indicate that bark may be a low-cost alternative in reducing PFASs from wastewater, under certain conditions.

Keywords: PFAS, WWTP, bark, GAC, flow, particle size, adsorption, COD, TOT-N, TSS, SPE, GFF, precursors.

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ISSN 1401-5765

REFERAT

Utvärdering av bark material och granulerat aktivt kol vid behandling av perfluoralkyla ämnen (PFAS) i avloppsvatten

Per- och polyfluroalkyla ämnen (PFAS) är en familj av artificiella fluorerade organiska föreningar som har använts sedan 1950-talet i en rad olika applikationer, såsom impregnering i kläder. Studier har visat att PFAS är potentiellt toxiska och att de förekommer globalt på grund av deras persistenta och mobila egenskaper. Spillvatten från avloppsreningsverk etablerats som en betydande källa för PFAS. Bark, vilket är en biprodukt från pappers- och träindustrin, är ett poröst material vilket möjligen kan användas som adsorbent av PFAS. Denna studie har jämfört effektiviteten hos granulerat aktivt kol (GAC) och bark för att minska PFAS i avloppsvatten. Experimentet var utformat som ett småskaligt kolonn-experiment vid Kungsängsängsverket, Uppsala, och pågick under en fem veckors period. Frågeställningen var att i) studera vilka effekter flödes-hastigheten (10, 30, 40 och 60 L d^{-1}) har på reduktionen av PFAS hos GAC och barkfiltren, ii) studera vilka effekter partikelstorleken hos bark har på reduktion av PFAS och iii) redogöra vilka förhållanden som potentiellt gynnar reduktionen av PFAS i GAC och bark filtren.

Resultaten visade att GAC var det mest effektiva av de två materialen, med en total reduktion på 73-93% av PFAS, med ökande effektivitet under låga flödesförhållanden (10-30 L d^{-1}). Bark minskade den totala mängden av PFAS med 45% då partikelstorleken var 2-5 mm och under låga flödesförhållanden (10-30 L d^{-1}) medan bark med samma partikelstorlek under ökade flödesförhållanden (60 L d^{-1}) visade en ökning på 40% av PFAS i det utgående vattnet. Bark med en partikelstorlek på 5-7 mm visade ingen reduktion av PFAS. Generellt visade resultaten att reduktionen av PFAS ökar under låga flödesförhållanden och minskad partikelstorlek. Resultaten visade att bark kan vara ett alternativt material för att minska PFAS i avloppsvatten förutsatt att gynnsamma förhållanden upprätthålls.

Nyckelord: PFAS, avlopsreningsverk, bark, GAC, reduktion, flöde, partikelstorlek, adsorption, TOT-N, COD, TSS, SPE, GFF, precursors.

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ISSN 1401-5765

PREFACE

This master´s thesis report has been made as the conclusive part of the M.Sc. in Environmental and Water Engineering at Uppsala University and the Swedish University of Agricultural Sciences (SLU), corresponding to 30 ECTS. The project was established at Kungsängsverket, Uppsala, providing the influent waste water and the necessary facilities for the experiment. The chemical analyses were made at the laboratory at the Department of Energy and Technology as well as the persistent and organic pollutants (POPs) laboratory at the Department of Aquatic Sciences and Assessment (SLU). The supervisor of this project has been Sahar Dalahmeh, researcher at the Department of Energy and Technology, SLU. Lutz Ahrens, docent at the Department of Aquatic Sciences and Assessments, SLU, acted as subject reviewer for this thesis and Fritjof Fagerlund acted as final examiner.

Firstly I would like to thank Sahar Dalahmeh, for all the support and engagement she provided during this long journey. I would also like to thank Lutz Ahrens for giving great support, always taking time to answering any of my questions and providing with valuable input on the report.

A special thanks go out to Johanna Krona, whom I worked long hours with in the lab and carrying out the practical part of the project. Without Johanna's help, I am sure that this project would not have been possible.

Finally, I would like to thank my friends and family for their wonderful support during this long journey, especially to Linnéa, who has always been there, encouraging and believing in me.

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Uppsala 2017

POPULÄRVETENSKAPLIG SAMMANFATTNING

Under den senare delen av 1900-talet har det uppstått ett ökat intresse för miljöfrågor, inte minst på grund av de pågående klimatförändringar som världen står inför utan också för de ämnen vi får i oss via den mat vi äter och det vatten vi dricker. Sedan 1950-talet har en grupp ämnen kallade; Per- och polyfluoroalkyla ämnen (PFAS), använts i mängder av områden såsom textilier och industrier eftersom att de har unika egenskaper som kan stöta ifrån både smuts och vatten. Länge skedde det lite forskning om dessa ämnen men i och med en studie som gjordes i början av 2000-talet visade att dessa ämnen finns i såväl människor som djur över hela världen har intresset och oron stigit kring dessa ämnen explosionsartat. Det visade sig att dessa ämnen finns i miljön eftersom att de lätt transporteras eftersom de är lättlösliga och ackumuleras eftersom att de är mycket svårnedbrytbara.

Efter detta världsomvälvande resultat har många forskare fokuserat på hur dessa ämnen faktiskt kommer ut i miljön. Många källor har hittats, däribland avloppsreningsverk som har framförts som en av de största källorna till PFAS i miljön. Då PFAS är mycket små och svårnedbrytbara renas inte dessa ämnen med hjälp av de tekniker som vanligen används vid avloppsreningsverk, vilket har resulterat i att nya avancerade tekniker har utvecklats. Tyvärr är de tekniker som anses vara effektiva för att reducera PFAS dyra, vilket gör att även billiga och enkla tekniker behövs. Filterbäddar av bark har potential att vara en alternativ behandlingsmetod då bark har en porös struktur som kan adsorbera små föroreningar som PFAS. Syftet med denna studie har varit att jämföra granulerat aktivt kol (GAC) med bark för att undersöka hur effektiva dessa två material är för att reducera PFAS från avloppsvatten hämtat från Kungsängsverket, Uppsala. Studien avsedda också att studera effekterna av flöde och partikelstorlek för att se vilka effekter de har reduktionen av PFAS.

Denna studie visade att GAC var det mest effektiva filtret i att reducera PFAS från avloppsvatten och visade en total reduktion på upp till 73-93%, där reduktionen ökade med minskat flöde. Bark visade olika effektivitet på reduktionen beroende på förutsättningar som flöde och partikelstorlek. Det visade sig att bark hade en reduktion på 40-45% med partikelstorlek på 2-5 mm under låga flöden (10-30 L d^{-1}). Bark med en partikelstorlek på 2-5 mm under höga flöden visade en ökning på 40%, vilket anats bero på biologisknedbrytning av ämnen som kemiskt liknar PFAS molekyler. Bark med en partikelstorlek på 5-7 mm visade sig inte ha någon effekt på halten PFAS i avloppsvatten. Under experimentet skedde också igensättning av filterbäddarna, speciellt bark (2-5 mm), detta eftersom att avloppsvatten innehåller mycket partiklar som fastnar i filtret och hindrar genomflödet av vatten. Bark kan alltså under vissa förhållanden vara effektiv i att rena avloppsvatten från PFAS men tyvärr är filtren känsliga för att bli igensatta om vattnet innehåller mycket partiklar.

Evaluation of bark material and granulated active carbon for treatment of perfluoroalkyl substances (PFASs) in wastewater

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1 INTRODUCTION

1.1 BACKGROUND

Per- and polyfluoroalkyl substances (PFASs) are a collection of highly fluorinated organic compounds, and have been widely used since the 1950s in a variety of different areas due to their unusual chemical properties (Ahrens, 2011). These fluorinated compounds are both lipophobic and hydrophopic, and thus effective as surface protecting agents in cloths and furniture, and as components in fire retardants, among other areas (Schultz *et al.*, 2003). Inconveniently, studies show that PFASs may pose a risk to the environment, and the extensive use of these compounds in the past decade may therefore be problematic. PFASs are thermally, chemically and biologically persistent, and as a consequence difficult to degrade (Järnberg *et al.*, 2007). Giesy & Kannan (2001) showed that PFASs were found in animals globally, and other studies further suggest that PFASs are not only occurring in the environment and in animals, but in humans as well (Yamashita *et al.*, 2005; Kannan *et al.*, 2004; Ostertag *et al.*, 2009). Due to PFASs mobile and accumulative nature, concerns have been raised about their potential toxicological effects (Kallenborn *et al.*, 2004; Bonefeld-Jorgensen *et al.*, 2011).

PFASs are universally found in the environment and the main sources of PFASs are suggested to be discharge from wastewater treatment plants (WWTPs), leachate from landfills, consumer products, surface runoff from roads and airports, industrial applications and waste among other sources (Busch *et al.*, 2010; Ahrens *et al.*, 2011; Kim & Kannan, 2007). Other substantial point sources might be fire-training sites (Moody *et al.*, 2002). Of all the potential sources of PFASs, several reports indicate that WWTPs are the main source (Ahrens *et al*., 2009). This is assumingly because of the insufficient treatment of highly fluorinated compounds in present WWTPs, and therefore new treatment techniques of wastewater are needed (Schultz *et al.*, 2006).

Since conventional wastewater treatment processes have proven to have little or no effect in reducing PFASs in wastewater residue there is a need to develop more efficient techniques for PFAS treatment in wastewater (Sinclair & Kannan, 2006; Zhang *et al.*, 2013). A variety of methods have been used and proved successful in reducing PFASs, for instance the use of activated carbon and different high capacity filtration techniques, such as nano filtration (NF) and reverse osmosis (RO) (Ochoa-Herrera & Sierra-Alvarez, 2008; Appleman *et al.*, 2013). These techniques are unfortunately expensive, which has created a demand for other low-cost alternatives that can produce similar results as the activated carbon, the NF and the RO technique. Since further studies are needed to find other low-cost

alternatives this thesis report offers a comparative study of granulated activated carbon (GAC) and bark, which is a low-cost material that potentially can be used as an adsorbent of PFASs.

1.2 AIM AND OBJECTIVES

The main purpose of this thesis was to investigate the removal of PFASs from treated wastewater using bark and activated carbon as adsorbents in a comparative column experiment. The objectives were:

i) To investigate the influence of flow-rate (10, 30 40 and 60 L d^{-1}) on the removal efficiency of PFASs in the GAC and bark filters.

ii) To investigate the influence of particle size of bark on the removal efficiency of PFASs

iii) Based on the removal efficiency of PFASs achieved in this experiment; establish what circumstances that potentially promotes removal of PFASs in GAC and bark filters.

In order to provide a deeper understanding of the filters' function, a study of the chemical oxygen demand (COD), total nitrogen (TOT-N) and total suspended solids (TSS) were incorporated in the study. Apart from the experimental study, a literature study was made that focuses on the chemical properties and usage of the PFASs. Potential problems and dangers with PFASs and which techniques that are being used to clean wastewater of PFASs are also included in the literature study.

2 THEORY

2.1 PER- AND POLYFLUOROALKLY SUBSTANCES (PFASs)

2.1.1 CHARACTERISTICS OF PFASs

PFASs are a family of manufactured highly fluorinated compounds. The generic formula of PFASs is C_nF_{2n+1}–R, where "n" refers to the numbers of carbon atoms of the molecule while R refers to the specific functional group of the molecule. Perfluoroalkyl substances are referred to as a carbon chains where all H-atoms have been replaced by an F-atom, namely fully fluorinated. Polyfluoroalkyl substances refer to carbon molecules that are only partly fluorinated (Järnberg *et al.,* 2007; Buck *et al.*, 2011). PFASs are used because of their ability to be both hydrophobic and lipophobic, meaning they are both water and fat repellent (Järnberg *et al.,* 2007; Borg & Håkansson, 2012). PFASs are also characterized by being persistent; this is a result of the strong covalent bonds between the atoms as well as the shielding effect provided by the fluorine atoms. Since there are many PFASs with different carbon-chain lengths and functional groups, several subgroups have been derived to simplify the categorization of the substances (Buck *et al.*, 2011). In this report several compounds within the subgroups perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and perfluorooctane sulfonamide (FOSAs) are studied.

The categorization of PFASs is correlated to the functional group of the specific subgroup, but also the length of the carbon string (Buck *et al.,* 2011). It is assumed that the functional group and carbon length are characteristics that influence the specific chemical properties (i.e the hydrophobic/lipophobic and persistent properties) of each compound (Borg & Håkansson, 2012; Rahman *et al.,* 2014). Perfluoroalkyl carboxylic acids (PFCAs) are a subgroup of PFASs with the general formula C_nF_{2n+1}–COOH, were COOH is a carboxylic functional group (Buck *et al.*, 2011; Wang *et al.*, 2013). Amongst PFCAs perfluorooctanoic acid (PFOA) is the most studied compound. PFSAs are also amongst the most studied subgroups, mainly since PFSAs are frequently found in high concentrations in the environment (Buck *et al.*, 2011). PFSAs are characterized by having sulfonic acid as its functional group (SO_3H). Amongst the other groups being studied are perfluorooctanesulfonamides (FOSAs), perfluoroalkyl sulfonameidoacetic acids (FOSAAs) and fluorotelomer sulfonates (FTSAs). FOSAs, FOSAAs and FTSAs are not as common as PFCAs and PFASs but do also occur in WWTPs (Ahrens *et al.*, 2011; Buck *et al.*, 2011; Zhang *et al.*, 2013).

2.1.2 PRODUCTION AND LEGESLATION OF PFASs

In 2009 PFOS was added to the Stockholm Convention list of prohibited persistent organic pollutants (POP's), due to its persistent nature (Ahrens, 2011). Since PFOS has been added to the list of POP's the use of other PFASs with shorter carbon-chains have replaced the use of PFOS, contributing to an increase of a variety of PFASs to the environment (Ahrens, 2011; Rahman *et al.*, 2014). Several jurisdictional incentives have been made nationally, for instance in some countries in Europe and North America, to reduce and monitor the use of PFASs. The environmental protection agency in the U.S. (USEPA) has made several actions to monitor the import and manufacturing of PFOS and related compounds (USEPA, 2016a). In Sweden there are no national regulations of PFASs with the exception of guidelines regarding the recommended concentrations of PFASs in drinking water (Livsmedelsverket, 2016). There are in total eleven PFASs that have been added to the list of compounds that should be monitored when determining the concentration of PFASs in water. The national food agency of Sweden recommends that drinking water should contain less than 90 ng L^{-1} of these eleven PFAS compounds (Livsmedelsverket, 2016).

2.1.3 EXPOSURE AND TOXICOLOGICAL EFFECTS OF PFASs

Due to PFASs persistent and mobile properties it is of great interest to establish the toxicological effects of these compounds (Kannan *et al.*, 2004; Houde *et al.*, 2006; Olsen *et al.*, 2007). The main source of exposure towards humans is intake via food and water as well as inhalation of dust particles (Buck *et al.*, 2011). Also due to PFASs stable properties it has been found that these compounds are bioaccumulative and biomagnifying in the environment, and therefore causing an increase of concentration higher up in the food chain (Giesy & Kannan, 2001; Schultz *et al.*, 2006). According to several studies, elevated concentrations of PFASs have some toxicological effects in humans and animals (Hekster *et al.*, 2003). Studies have indicated that some PFASs are disruptive towards the endocrine system of humans and animals (DeWitt, 2015). Since the endocrine system is a vital part in regulating the hormone levels in animals and humans, endocrine disruptors may affect the reproduction abilities (Zimmermann, 2016). In fact, studies have found a correlation between sexual reproduction abilities as well as semen quality and high levels of PFASs (Joensen *et al.*, 2009; Bonefeld-Jorgensen *et al.*, 2011; Long *et al.*, 2013). Other effects are the potential carcinogenic properties of PFASs. Researchers have found that occurrence of high concentration of PFASs in humans can be correlated to some types of breast cancers, but further studies are required (Bonefeld-Jorgensen *et al.*, 2011; Barry *et al.*, 2013). Further studies are also required for verifying the correlation between hyperactivity disorders such as attention deficit disorder (ADD) and attention deficit hyperactivity disorder (ADHD) and high concentrations of PFASs in children (Hoffman *et al.*, 2010; Stein & Savitz, 2011).

2.1.4 OCCURRENCE OF PFASs IN WASTEWATER

To address the issue of removing PFASs from the environment several potential point sources have been recognized, amongst those are wastewater treatment plants (WWTPs). Möller *et al.* (2010) studied the occurrence of PFASs along the river Rhen, Germany, to determine the flux of different PFASs to the North Sea and to identify if there were any potential point sources along the river. Möller *et al.* (2010) showed that River Rhine itself contributed with roughly 60 tonnes of PFASs yr^{-1} to the North Sea, originating mainly from landfills and WWTPs along the river. Analogous results were also attained by Ahrens *et al.* (2009) in a similar study. The occurrence of PFASs in WWTPs is presumed to be a result of a different factors, such as leakage of PFASs form products such as clothing, industrial application and a variety of different consumer products (Möller *et al.*, 2010; Ahrens *et al.*, 2011). In addition to leakage of PFASs from different products, another major pathway of PFASs to WWTPs is the degradation of so called precursors.

Precursors are organic compounds with similar chemical structure to those of PFASs. Since precursors are structurally similar to PFASs and are more easily degraded, precursors have the potential to transform into PFASs (Buck *et al.*, 2011). Precursors have been found in several wastewater treatment plants and due to the favorable conditions inside conventional WWTPs, which stimulates biological degradation, precursors have the potential to degrade, causing an increase of PFASs through the treatment chain at WWTPs (Sinclair & Kannan, 2006; Zhang *et al.*, 2013). Zhang *et al.* (2013) studied the fate of PFASs inside two WWTPs in China. Zhang *et al.*, (2013) found that there was an increase of PFASs inside one of the plants, which was likely a result of the degradation of precursors. A comparable study made by Sinclair & Kannan (2006) showed analogous results to those of Zhang *et al*. (2013) showing either no decrease or, in fact, an increase of PFASs in the WWTP's residue. The increase of PFASs was also assumed to be because of degradation of precursors.

2.2 TREATMENT OF PFASs IN WASTEWATER SYSTEMS

Many conventional treatment techniques such as medium pressure membrane filters (around 100-400 kPa), biological treatment techniques and several types of chemical treatment steps have been found to be inefficient in removing PFASs from wastewater (Sinclair & Kannan, 2006; Zhang *et al.*, 2013). As a result, many studies have been conducted to establish potential wastewater techniques that are effective in removing PFASs. Amongst techniques that have been proved most successful in removing PFASs are high pressure membrane filters such as reverse osmosis filter (RO) and nano filtration units (NF) and activated carbon filters (Zhang *et al.*, 2012; Rahman *et al.*, 2014).

2.2.1 NANOFILTRATION

Nano filtration (NF) is an expensive technique that uses membranes with small pores and high pressure to separate contaminants from water. Nano filters membranes are usually made of polymers or ceramic with a pore size of 1 to 10 nm. The basic principle of these filters is to hinder compounds larger than the pores to pass the filter membranes. The NF's are fed with water where a portion (permeate) is passed through the filters pores under high pressure (4-20 bar), and compounds larger than the size of the pores are removed (Zhang *et al.*, 2012). Nano filters are effective in removing small compounds with the size of less than 1000 Daltons (g mol^{-1}) such as pesticides, pharmaceuticals and PFASs (Zhang *et al.*, 2012). Both large-scale and laboratory scale experiments have shown that nano filters are effective in reducing PFASs (Appleman *et al.*, 2013; Rahman *et al.*, 2014). A study made by Appleman *et al.* (2013) showed ,through a small scale laboratory experiment with artificial gray water, that nano filters were able to reduce PFASs to above 93%. The main issue with nano filters is the filters' tendency to clog, therefore interrupting the treatment process (Zhang *et al.*, 2012; Appleman *et al.*, 2013).

2.2.2 REVERSE OSMOSIS

Similar to NF reverse osmosis filters (RO) are expensive and advanced high pressure membrane techniques. RO uses a semipermeable membrane with a pore size of 0.1 to 5.000 nm under high pressure to hinder the natural process of osmosis. Osmosis is the tendency to even the concentration from an area with low concentration (high potential energy) to an area of high concentration (low potential energy) driven by osmotic pressure. When applying an external pressure on a solution with low potential energy, in this case incoming water with high concentration of i.e. PFAS, one can reverse the flow through the semipermeable membrane. This means that the incoming water with high concentration and low potential energy can be driven to an area of low concentration. The reversed osmosis thereby forces the incoming water through the membrane and in the process the membrane removes any unwanted compounds (Zhang *et al.*, 2012). RO filters are efficient in removing small compounds and ions. One of the uses of RO is to remove salinity from water (Zhang *et al.*, 2012). Similar to NF filters, RO filters are efficient in reducing PFASs (Thompson *et al.*, 2011). Studies have found that there are major reduction of PFAS in the WWTPs using RO's in comparison to WWTPs using conventional treatment techniques (Thompson *et al.*, 2011). In a comparative study using different treatment methods at seven different water treatment plants located in the U.S. showed that the plant that use RO filters were the most efficient in removing PFASs (Quiñones & Snyder, 2009). In the plant using RO filters all the PFASs were reduced to below the detection limit, the WWTP were even effective in removing short carbon chained PFASs (Quiñones & Snyder, 2009).

2.2.3 ACTIVATED CARBON

Activated carbon is a highly porous material made by coal, wood and lignite. Activated carbon can be divided into either granular (GAC), with particle size between 1.2 to 2 m and a specific area of 500-1500 m^2 g^{-1}, and powdered activated carbon (PAC) (Çeçen & Aktaş, 2011). Since activated carbon is a highly porous it has been used to adsorb a wide range of pollutants. GAC also has the potential to carry biofilm, which has the potential to degrade pollutants (Velten *et al.*, 2011). GAC is mainly used to remove organic pollutants from drinking water, such as PFAS and pharmaceuticals, but also odor and taste related pollutants (USEPA, 2016b). Different circumstances may affect the adsorption of organic pollutants such as dissolved organic matter (DOM). Due to DOMs hydrophobic properties, it has the potential to hinder the adsorption of other hydrophobic pollutants, such as PFASs. Temperature, pH as well as the molecule size of the pollutants may also affect the adsorption capacity (Çeçen & Aktaş, 2011). Due to activated carbons physical properties GAC and PAC filters have been found to be effective in reducing PFASs from water, however some differences have been found between GAC and PAC regarding the materials removal efficiency of PFASs (Appleman *et al.*, 2013; Rahman *et al.*, 2014). In a laboratory scale experiment made by Hansen *et al.* (2010) a study of adsorption of PFASs to both PAC and GAC were made, and according to the results PAC were two times more effective than GAC in reducing PFASs in wastewater. Hansen *et al.* (2010) did also find that the longer carbon chained PFASs were more effectively reduced, which have been verified in other related studies (Appleman *et al.*, 2013). Other large-scale studies have also shown that GAC is less effective in reducing shorter chained PFAS compounds from water, also branched isomers have been proven to be harder to reduce using activated carbon (Eschauzier *et al.*, 2012). Also GAC has proven to be sensitive to clogging, a common problem in filter-bed techniques (Svenskt Vatten AB, 2013; Lidegren, 2015).

2.2.4 BARK FILTER

Bark is a lignin based organic material, usually found as a byproduct from the wood and paper industry. The presumption behind using bark for treating PFASs is that bark has similar properties as GAC, since bark's porous structure may promote adsorption of small hydrophobic organic pollutants. Few studies have been made to investigate the potential of bark in water treatment and no studies have been made on barks potential to reduce PFASs. A study made by Dalahmeh *et al.* (2012) compared bark, charcoal, sand and foam, in treating grey water. According to her study, pine bark was one of the most effective materials in reducing nutrients such as COD and TOT-P as well as pathogens. Another study made by Dalahmeh *et al.* (2014) found that bark used in grey water treatment has a diverse and rich bacterial culture, which potentially can degrade pollutants. Bark has also been proven to be effective in adsorbing heavy metals such as nickel (Ni II) (Salem & Awwad, 2014). Bark waste has also been used as filters to treat odor in connection to composting facilities (Berg, 2001).

3 MATERIAL AND METHODS

3.1 TARGET ANALYTES

In this study compounds within the groups; PFCAs, PFSAs, FOSAs, FOSAs and FTSAs were studied. The target compounds, as well as chemical structures of each compound are presented in Table 1.

Table 1. Target compounds of each subgroup with name, acronym and chemical structure as well as molecular weight of each compound.

Acronym[a]	**Name**[a]	**Structure**[a]	**Molecula weight (g mol^{-1})**[b]
PFCAs			
PFBA	Perfluorobutanoic acid	$C_3F_7CO_2H$	213.4
PFPA	Perfluoropentanoic acid	$C_4F_9CO_2H$	263.05
PFHxA	Perfluorohexanoic acid	$C_5F_{11}CO_2H$	313.06
PFHpA	Perfluoroheptanoic acid	$C_6F_{13}CO_2H$	363.07
PFOA	Perfluorooctanoic acid	$C_7F_{15}CO_2H$	413.08
PFNA	Perfluorononanoic acid	$C_8F_{17}CO_2H$	463.09
PFDA	Perfluorodecanoic acid	$C_9F_{19}CO_2H$	513.1
PFUnDA	Perfluoroundecanoic acid	$C_{10}F_{21}CO_2^-H$	563.11
PFDoDA	Perfluorododecanoic acid	$C_{11}F_{23}CO_2H$	613.12
PFTriDA	Perflurotrideconatic acid	$C_{12}F_{25}CO_2H$	712.13
PFTeDA	Perfluorotetradecanoic acid	$C_{13}F_{27}CO_2H$	
PFSAs			
PFBS	Perfluorobutane sulfonic acid	$C_4F_9SO_3H$	300.12
PFHxS	Perfluorohexane sulfonic acid	$C_6F_{13}SO_3H$	400.14
PFOS	Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	500.16
PFDS	Perflourodecane sulfonic acid	$C_{10}F_{21}SO_3H$	600.18
FOSAs			
FOSA	Perflouroctane sulfonmide	$C_8F_{17}SO_2NH_2$	499.18
FOSAAs			
EtFOSAA	N-ethylperfluooctane-sulfonamidoacetic acid	$C_8F_{17}SO_2N(C_2H_5)CH_2$-$CH_2OH$	585.2

FTSAs			
6:2 FTSA	6:2 fluorotelomer sulfonic acid	$C_8H_4F_{13}SO_3H$	428.13

[a](Rahman *et al.*, 2014), [b](Aylward & Findlay, 2007)

3.2 COLUMN EXPERIMENT

3.2.1 KUNGSÄNGSVERKET

Kungsängsverket, Uppsala, is designed to treat 4800 m^3 h^{-1} wastewater, mainly originating from the city of Uppsala. At Kungsängsverket, mechanical, biological and chemical treatment methods are used to remove pollutants from the wastewater (Uppsala Vatten, 2014). The wastewater influent at the WWTP is passing first a mechanical filtration step (1) and thereafter it is separated in three different treatment stages named Block A, Block B and Block C. In these blocks pre-sedimentation (2) and biological treatment (3) is conducted (Figure 1). After the biological treatment water from each block is merged together to go through the final lamella sedimentation step (4) before being discharged to Fyrisån, the local recipient (Uppsala Vatten, 2014).

At Kungsängsverket, PFASs have been found in high concentrations throughout the treatment-chain, indicating that PFASs are not effectively reduced (Glimstedt, 2016). When implementing a PFAS treatment step using filter bed techniques it is important that solids are removed since it may clog the filterbeds (Svenskt Vatten AB, 2013). Unfortunately the experimental set-up in this study could not be installed after the final treatment step (4), were the majority of the solids would have been removed, since the location did not provide the required facilities, such as work-space and electricity (Figure 1). The column experiment conducted in this study was therefore implemented after the biological treatment at block B, since the site supported the required facilities (Figure 1).

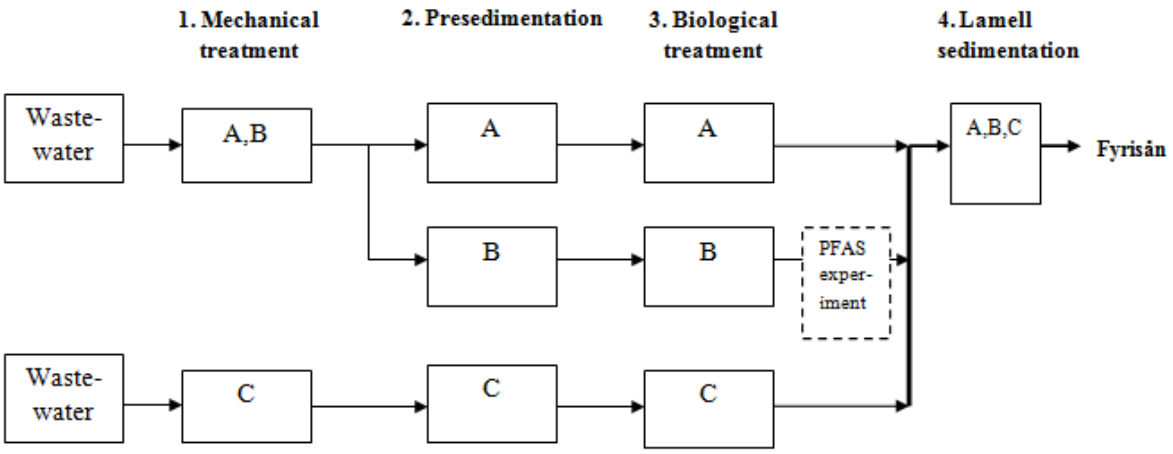


Figure 1. Wastewater treatment steps (1-4) of each block, A, B and C at Kungsängsvärket, Uppsala and the location of the column experiment.

1. Mechanical treatment: Removal of sediment and large particles is done through two filtration steps at Kungsängsverket (Figure 1). First the water passes through large screens (0.5-3 mm), to remove particles such as paper and tissues. The second step is an aerated sand trap which uses air to give a rotational motion of the water which keeps the organic material and sludge afloat while the sand on the other hand sediment (Svenskt Vatten AB, 2013; Uppsala Vatten, 2014).

2. Pre-sedimentation: Pre-sedimentation step is used to remove any particles that may have a negative effect on the biological treatment (Figure 1). In order to achieve a higher removal rate, iron(III) chloride ($FeCl_3$) is added, a common flocculation agent at WWTPs (Svenskt Vatten AB, 2013; Uppsala Vatten, 2014).

3. Biological treatment: Removal of organic matter, biological oxygen demand (BOD), nitrogen and part of the phosphorous is achieved at Kungsängsverket using an active sludge process (Figure 1) (Svenskt Vatten AB, 2013; Uppsala Vatten, 2014)

4***. Lamella sedimentation***: The final step of the treatment utilizes chemical treatment and plate sedimentation to remove flocks and phosphorus that have not been removed during the previous steps (Figure 1) (Svenskt Vatten AB, 2013; Uppsala Vatten, 2014). As flocculation agent iron (III) chloride is used (Uppsala Vatten, 2014).

3.2.2 EXPERIMENTAL SET-UP

The entire column experiment was stretched over five weeks were 2 GAC and 2 bark filters were fed with effluent wastewater from the biological treatment step at block B (Figure 1). The four filters were fed according to the steps (1-3) below, describing the daily flow and sampling procedure of the filters Figure 2. The steps below were repeated daily during the entire experimental period.

1. *Collecting filter influent*

   The inflow of the filters was collected in four 80 L barrels (one for each filter) in the morning (around 9 am) from the end of the basin at block B with equal volume water distributed in each barrel using a submersible pump (one barrel for each filter). From the influent a 1 L subsample was collected (Figure 2).

2. *Feeding filters during the course of the day (24 h)*

   The inflow wastewater to the filters was distributed during the course of the day (24 h) from the 80 L barrels into the filters using peristaltic pumps (Figure 2). The peristaltic pumps were feeding the filters continuously with 50 mL min^{-1} and to achieve the desired flow described in

   Table 2 and Table 3, timers were connected to the peristaltic pumps. The filter effluent was separated via a three-way valve (Figure 3), where approximately 50 % off the total volume was collected in collector tanks from each column per day, the rest of the water was discharged.

3. *Collecting daily sample*

   After step 2 had been completed the collector tanks were emptied and a 1 L daily sample of each filter effluent was collected in polypropylene bottles (PP-bottles) (Figure 2). When the third step was finalized, the procedure was repeated.

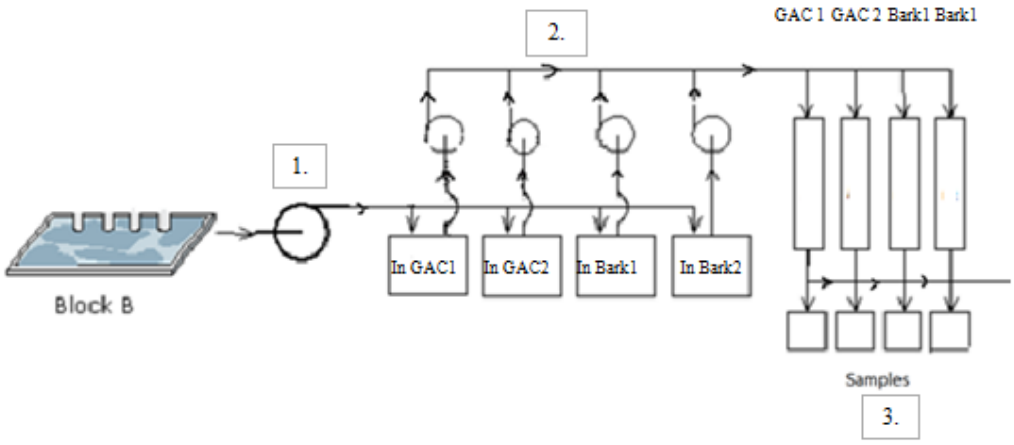


Figure 2. Experimental-setup of how water was pumped from the basin at block B each day during the entire experimental period. First (1) a submerged pump filled four 80 L barrels (In GAC1, In GAC2, In Bark1 and In Bark2). Secondly (2) the filters (GAC1, GAC2, Bark1 and Bark2) were fed with equal volume wastewater with four peristaltic pumps. Of the filter effluent two 1 L samples were collected (3) before the procedure was repeated.

The four columns (5 cm diameter x 100 cm height) were filled with filter materials, two of the columns were filled with pine bark, referred to as Bark1 and Bark2, and two columns were filled with GAC, referred to as GAC1 and GAC2. The columns were composed of a 50 cm filter bed and, to hinder the filters from being flushed out, a 3-cm upper and lower drainage layer of gravel (0.5-2 cm) were installed (Figure 3). Exact weight and height properties of the filter layer are presented in Table. A and Table. B in the Appendix. The columns were operated under saturated flow and the outlets were placed a few cm above the upper surface of the top gravel layer (Figure 3). To provide space for accumulation of water head in case of loss of hydraulic conductivity in the filter beds due to clogging, 30-50 cm free column space was left on the top of the upper drainage layer. Columns, collection barrels and other details were made of PP-plastic, while valves were made of brass and tubes were made of silicon.

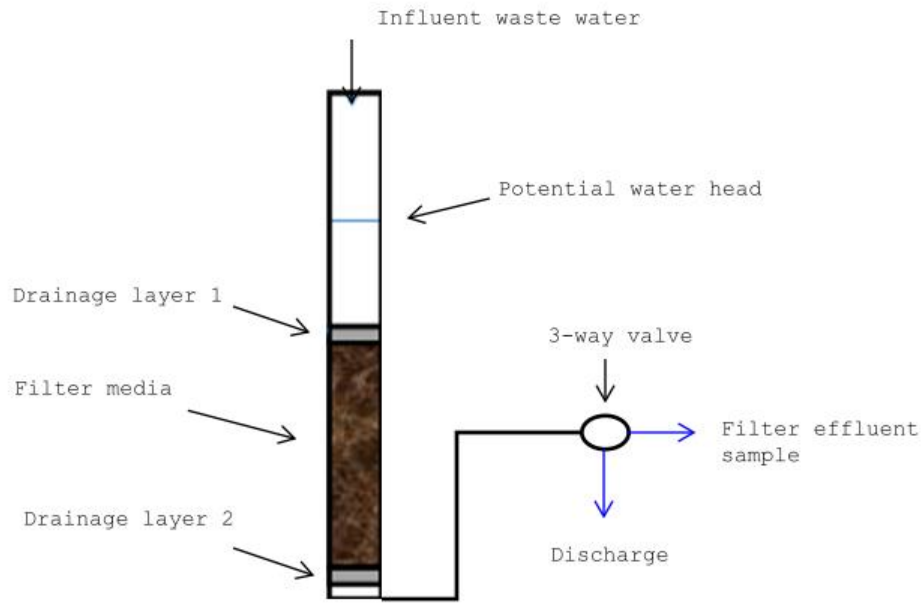


Figure 3. Schematic diagram of the filter layers, water distribution and water collection from the filters.

3.2.3 EXPERIMENT PERIODS AND CLOGING

The wastewater collected at block B contained a high amount of suspended particles, which caused the filters to clog on two occasions during the entire experiment (period A2 and period B1). Since filter beds were clogged, they had to be removed and replaced with clean filter material to improve the stability of the experiment. Since the filter beds were replaced, the entire experiment had to be divided into five different periods, to conduct a more structural evaluation of the filters removal of PFASs over the entire experiment. Each of the periods represented one week of the entire experimental period, named: A1, A2, B1, C1 and C2 (

Table 2, Table 3). The label, A, B and C, of each experiment period refers to the filter beds used for the GAC and the bark filters during the experiment. Consequently, the transition between the periods (A2-B1 and B1-C1) represents a clogging occasion. The numbers (1 or 2) of each label refers to how long time the filters A, B and C had been in use, which was either 1 week (0-7 days) or 2 weeks (8-14 days) (

Table 2, Table 3). In addition to replacing the clogged filters with clean material, other adjustments had to be implemented.

To hinder further clogging several changes had to be implemented. Firstly the flow rate was changed between the periods (A1-C2) to establish a more stable water build up, which consequently resulted in different retention times for the waste water inside the filters (Table 2, Table 3). Secondly the particle

size of the bark filters was adjusted (Table 3). The particle size was different between the first two periods, A and B (particle size 2-5 mm), and the final period C (particle size 5-7 mm) since the filters containing bark (2-5 mm) were the most sensitive to clogging (

Table 2). The GAC filters were of the same particle sizes between the periods since larger GAC material was not available in this study (Table 3).

Table 2. Filter-settings for the two GAC filters such as flow-rate, time after start and particle size for correlating period, weeks and dates.

		A1	**A2**	**B1**	**C1**	**C2**
Dates	-	2/3-7/3/2016	11/3-18/3/2016	31/3-6/4/2016	13/4-19/4/2016	20/4-27/4/2016
Type	-	GAC	GAC	GAC	GAC	GAC
Filter-bed volume	L	0.9	0.9	0.9	0.9	0.9
Flow rate	L d^{-1}	60	10	30	30	40
Retention time	min d^{-1}	21	128	42	42	32
Time after start	d	0-7	8-14	0-7	0-7	8-14
Particle size	mm	2	2	2	2	2

Table 3. Filter-settings for the two Bark filters such as flow-rate, runtime and particle size for correlating period, weeks and dates.

		A1	**A2**	**B1**	**C1**	**C2**
Dates	-	2/3-7/3/2016	11/3-18/3/2016	31/3-6/4/2016	13/4-19/4/2016	20/4-27/4/2016
Type	-	Bark	Bark	Bark	Bark	Bark
Filter-bed volume	L	0.9	0.9	0.9	0.9	0.9
Flow rate	L d^{-1}	60	10	30	30	40
Retention time	min d^{-1}	21	128	42	42	32
Time after start	d	0-7	8-14	0-7	0-7	8-14
Particle size	mm	2-5	2-5	2-5	5-7	5-7

3.2.4 SAMPLING

From the filter influent and effluent, 2 samples of 1 L each (one in reserve) were collected and kept in the fridge at 2^{o}C until analysis. During the weekends of the experiment period (Friday to Sunday), the influent and effluent water from each filter were accumulated in PP-barrels and then merged together before 2 L composite samples were collected on Monday morning. The daily samples were then mixed together to create a composite weekly sample for each sampling point. The composite weekly samples were of 1 L. For each of the weekly composite samples from the filters roughly 200 mL was added from each sampling day, so that 1 L composite sample could be detained. Full disclosure of each composite sample of can be attained in the appendix, section 8.2.

3.3 PHYSICAL PROPERTIES OF THE FILTERS

3.3.1 ELECTRON MICROSCOPY

Environmental Scanning Electron Microscopy (ESEM) (Hitachi TM-1000) was conducted to produce a high resolution depiction of the surface of the GAC and bark filter particles. ESEM uses an electron beam that is focused to the surface of the sample were it is kept in a gaseous environment, creating a high resolution depiction of a specific sample area (Clarke & Eberhardt, 2002; Donald, 2003). In this experiment one sample of 1 g of the bark and GAC material were collected respectively to perform ESEM scan upon. For the analysis an area that resembled the overall appearance of the sample were selected. Three analyses were conducted on each of the particle samples at resolutions: x-300, 1500 and 5000 (μm), to provide an overview of a large sampling area as well as an amplified view of the pore complexion.

3.3.2 SIEVING ANALYSIS

The basic principal of sieving analysis is to use a mechanical device (Figure 4) that shakes the sieves to differentiate the particles based on the sizes of the particles (Leschonski, 1979). Bark was sieved using three sieves with the size of 4, 2 and 1 mm in diameter and were shaken for 15 min using three different samples. Similarly, for GAC, sieves with a diameter of 2 and 1 mm were used and were also shaken for 15 min at two different occasions. The particle size was for GAC 2 mm during all periods and the size of bark during period A1, A2 and B1 were 2-5 mm while the bark during period C1 and C2 were 5-7 mm.

Figure 4. Electrical sieving machine used for shaking sieves to distribute particles with different sizes

3.4 CHARACTERIZATION OF THE WASTEWATER

Analysis of COD, TSS and TOT-N was done according to the plan presented in Table 4. The analysis was made once a week, with the exception of the first week. The analyses were performed on fresh filter influent and effluent on one of the week days since it is not possible to conduct COD, TSS and TOT-N analysis on pooled samples (Ibanez, 2007). The dates of analysis were chosen on random. The extractions of PFASs were made on all the composite weekly samples, which is marked with a (x) in Table 4. Extraction of PFASs from the filter media were only made on the final week of the experiment, which also is marked with a (x).

Table 4. Experimental plan with the analysis day and correlating date for the conventional analysis of COD, TSS and TOT-N as well as the weekly samples in which extraction of PFASs from water and solids were conducted. The dates in which extraction were made is marked with a (x).

	A1	**A2**	**B1**	**C1**	**C2**
COD, TSS, TOT-N	-	D15(17-mar)	D17(31-mar)	D29(20-apr)	D35 (26-apr)
Extraction (water)	x	x	x	x	x
Extraction (solids)	-	-	-	-	x

3.4.1 COD-ANALYSIS

COD-analysis was conducted on the filter influent and effluent with a Spectroquant® COD Cell Test (Hg-free) kit. COD refers to the chemical oxygen demand, and was analyzed to estimate the amount of organic material in the wastewater. The test procedure was done by adding 2.0 mL water sample to chemically prepared cells, containing $K_2Cr_2O_7$ in a sulfuric acid solution. The cells were then heated

to 148 °C for two hours in a thermostat. The reaction in the cells resulted in a color shift that was analyzed in a spectrophotometer to determine the amount of COD in the sample. If the analysis was performed the day after sampling day the sample were acidified to hinder potential reduction of COD (Ibanez, 2007).

3.4.2 TSS-ANALYSIS

In this experiment TSS was analyzed in the filter influent and effluent of the GAC and bark filters in order to analyze the removal of solids in the filters. In order to analyze the TSS the water samples were filtrated through 2 µm glass fiber filters (GF-filters) using a vacuum unit. After the filtration, the GF-filters were dried at 105 °C for 1 h and left to dry and cool to room temperature in a desiccator. The GF-filters were weighed before and after TSS filtration. The concentration of TSS in the sample was obtained from the difference in weight divided by the sample volume used for the test.

3.4.3 TOT-N ANALYSIS

In this experiment all forms of nitrogen in the samples were transformed to nitrate. The transformation of the nitrogen compounds to nitrate were conducted with a Spectroquant® Crack Set 20, where two reagents and 10 mL of the water sample were mixed and then heated in a thermostat to 120 °C for one hour causing all the nitrogen to oxidize into nitrate. After the samples cooled to room temperature, the nitrate level was analyzed using a Spectroquant® nitrate test. The analysis was conducted by adding two reagents to 0.50 mL of the pretreated sample which caused a reaction resulting in a color change, which was then analyzed using a spectrophotometer.

3.5 ANALYSIS OF PFASs

Since PFASs occur ubiquitously in the environment, they also occur in the lab and on the laboratory equipment, leading to concerns about potentially contaminate the samples when performing analyses. To avoid any contamination the equipment that was used in analyses and extractions were thoroughly cleaned with methanol, or ethanol, before being dish washed. Also, all the glassware were burnt overnight at 400 °C. All the equipment was then covered in aluminum foil to decrease any further contamination. If the equipment were to be used for extraction, the equipment was cleaned three times with methanol before usage. The smaller parts (valves, plugs and syringes) were cleaned two times with methanol and left in a methanol bath placed in a sonication bath for 15 min before usage.

3.5.1 ANALYSIS OF PFASs IN THE LIQUID PHASE

To analyze PFASs in the water samples, solid phase extraction (SPE) was conducted, following the procedure described by Ahrens *et al.* (2009). Before initiating the extraction, each weekly composite sample was filtered through a burnt GF-filter under vacuum to remove any solids found in the water sample. In brief, the extraction was conducted by percolating 500 mL of each composite sample

through an Oasis WAX cartridge (Waters, 6 cc, 150 or 500 mg). Before percolation was initiated 100 µl (20 pg L^{-1}) internal standard containing PFASs was added to each sample. Also the cartridges were preconditioned with 4 mL 0.1 % ammonium hydroxide in methanol, 4.0 mL methanol and 4.0 mL Millipore water. After conditioning, the samples were gradually loaded through the cartridges, at a flow of about 1 drop per second and in case the cartridges clogged, a gentle vacuum was applied. After percolation of the sample volume, each cartridge was cleaned with 25 mM ammonium acetate buffer (pH 4) and vacuum suction was left on to ensure that as much liquid as possible was removed from the cartridges. As a final step the cartridge was centrifuged at 3000 rpm for 2 min before being stored in the freezer at -15^{o}C until elution.

The PFASs retained in the cartridges were then eluted by first applying 6 mL of methanol and as a final step adding 6 mL of 0.1 % ammonium hydroxide in methanol. The eluted mixtures were collected in 15 mL PP-bottles. Each elution mixture was then evaporated to about 0.5 mL under a N_2 (g) stream in a N_2-evaporator. The samples were then transferred to 2 mL amber vials. The walls of the 15 mL PP-bottles were cleaned with about 1 mL methanol to ensure that all the PFASs were transferred to the amber vials. The volume of the amber vials was then regulated to exactly 1 mL before the concentration of PFASs in the samples could be analyzed. The analyses were done in a high performance liquid phase chromatography coupled to a mass spectrometer (HPLC-MS/MS). The analyses were done by personnel at SLU according to the procedure described in Ahrens *et al.* (2009).

3.5.2 ANALYSIS OF PFASs IN THE SOLID PHASE

PFASs adsorbed to the filter material were extracted from filters GAC1, GAC2, Bark1 and Bark2 used for the last period of filtration (C2), and from unused filter material (activated carbon, bark 2-5 mm, bark 5-7 mm) to detect any potential contamination from the filters themselves. The filter samples were stored in the freezer for more than 48 hours before analysis. For extraction, samples of 4.5-5 g from each material (7 samples) were transferred to 50 mL PP-tubes and then soaked in 2 mL 100 mM NaOH (80/20, NaOH/Millipore water) for 30 min. After soaking, 20 mL of MeOH and 100 µl of PFAS internal standard were added to each sample. The samples were then shaken on an action-wrist shaker for 1 h at 200 rpm. After the samples were shaken the tubes were centrifuged for 15 min at 3000 rpm. The supernatant form each sample was then transferred to another 50 mL PP-tube in which the extraction was repeated. As a final step, the samples were soaked in 1 mL of 100 mM NaOH (80/20, NaOH/Millipore water) for 30 min and 10 mL of MeOH were then added before shaking the samples for 30 min at 200 rpm on an action-wrist shaker. The samples were then again centrifuged for 15 min at 3000 rpm before transferring the supernatant to the previously collected

supernatant. The seven different mixtures were then spiked with 0.1 mL 4 M HCl before they were shaken by hand and then centrifuged at 3000 rpm for 5 min.

Of the extraction mixtures a subsample of 8.1 mL (1/4 of the total supernatant) were transferred to seven 15 mL PP-tubes and were evaporated under N_2-stream until 1 mL of each sample was left. The 1 mL samples were then transferred to a 1.7 mL Eppendorf centrifuge tube that had been prepared with 25 mg ENVI-carb and 50 µl acetic acid. The Eppendorf centrifuge tubes were then centrifuged at 4000 rpm for 15 min. Of each supernatant 0.5 mL were transferred to 1.5 mL amber vials before analysis using HPLC-MS/MS (Ahrens *et al.*, 2009).

3.5.3 QUALITY ASSURANCE

Samples used for analysis of organic pollutants are sensitive for contamination. To detect any potential contamination of the samples the detection limit of the methods (MDL) were calculated. The MDL are calculated using the mean blank concentration (C_{blank}) and the standard deviation (STD_{blank}) of the blank concentration (equation 1). To calculate the MDL, five blanks (for the liquid phase) and unfortunately no blanks for the solid phase, were analyzed and treated in the same way as the extraction following the procedure for PFAS extraction in liquid. Millipore water was used as liquid for three of the blanks while the other two blanks only followed the procedure described insection 3.5.1. The MDL's were calculated according to equation 1 for each specific compound.

$$MDL = C_{blank} + 3 \cdot STD_{blank} \quad (1)$$

The MDL's calculated for each compound varied between 0.039 and 93 ng L^{-1} and are presented inTable 5, where most of the compounds had an MDL in the range of 0.1-1.0 ng L^{-1}. PFBA, PFPeA and PFNA had 22, 93 and 7.6 ng L^{-1} as calculated MDL. The high MDL suggest that there might be a high contamination regarding these compounds.

Table 5. Method detection limit (MDL) in ng L^{-1} for each PFAS compound analyzed in the HPLC-MS/MS for the liquid phase.

PFASs	**MDL (ng L^{-1})**
PFBA	22
PFPeA	93
PFHxA	0.37
PFHpA	1.0
PFOA	0,09
PFNA	7.6
PFDA	0.0081
PFUnDA	2.9
PFDoDA	0.46
PFTriDA	0.075
PFTeDA	0.074
PFHxDA	0.039
PFOcDA	0.11
PFBS	0.86
PFHxS	0.061
PFOS	0.58
PFDS	0.073
FOSA	0.26
EtFOSA	0.11
EtFOSAA	0.12
EtFOSE	0.52
FOSAA	0.11
MeFOSA	0.084
MeFOSAA	0.11
MeFOSE	0.42

3.5.4 STATISTICAL ANALYSIS

To analyze the potential reduction of PFASs achieved in the bark and GAC filters, concentration of each compound in the filters effluent has been normalized to of those compound found in the filter influent, calculated according to equation 2. The reduction of PFASs are presented as average normalized values together with calculated standard deviation (n=2). Potential outliers have been removed.

$$N_i = \frac{\mathrm{C}}{\mathrm{C_{in}}} \qquad (2)$$

To present an overview about how efficient each filter was in removing PFASs, the total reduction was also calculated. The total reduction was calculated according to equation 3, summarizing the total concentration of PFASs collected in the filter effluent (C_{tot}) normalized to the total concentration of PFASs in the influent ($C_{in,tot}$).

$$N_{tot} = \frac{\mathrm{C\,tot}}{\mathrm{C_{in,tot}}} \qquad (3)$$

4 RESULTS

4.1 ESEM ANALYSIS

The ESEM scan of the GAC sample showed large dark colored areas, indicating lots of pores (Figure 5). The different sizes of the dark areas indicate a variety of pore sizes.

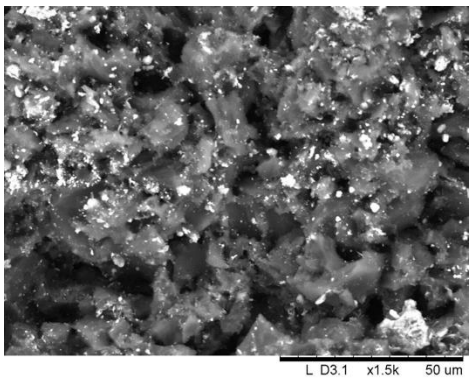


Figure 5. Depiction of the surface area of a GAC sample.

The ESEM scan of the bark sample showed lots of small dark areas, indicating that bark contains lots of smaller pores (Figure 6).

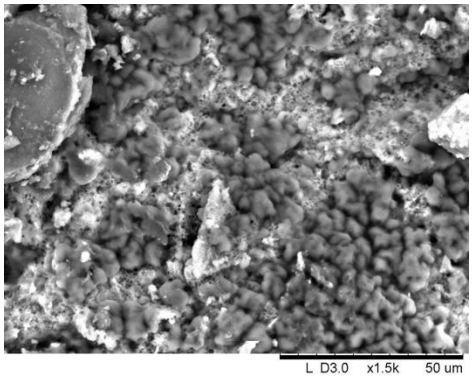


Figure 6. Depiction of the surface area of a bark sample.

4.2 CHARATERIZATION OF WASTEWATER

In general, the COD levels were reduced in both the GAC and the bark filters; however the results were somewhat conflicting between the periods (Table 6). The COD levels varied between 9.1 and 33 mg L^{-1} in the filter influent over the four experimental periods and were reduced for the majority of the periods with the exception of period A2 and C2. The effluent of the GAC filters during period A2 showed an increase of 34 mg L^{-1} while bark showed a 4 mg L^{-1} increase during period C2 (Table 6).

Table 6. COD levels in mg L^{-1} ± the standard deviation in the influent (n=2), effluent from the bark and GAC filters (n=4) and blanks (n=1) with correlating period and date.

Period		**A2**	**B1**	**C1**	**C2**
Date		17-mar	31-mar	20-apr	26-apr
COD					
Influent	mg L^{-1}	33±2.8	9.1±0.071	37	28±19
GAC	mg L^{-1}	67±17	6.5±0.45	<10	20±4.9
Bark	mg L^{-1}	27±15	8.0±0.65	11	32±4.2
Blank	mg L^{-1}	<10	1.2	<10	<10

The results of TOT-N were inconsistent between the different periods, showing either an increase or a decrease in TOT-N levels (Table 7). Concentrations of TOT-N were effectively reduced in the GAC effluent during B1 (3 mg L^{-1}) and C1 (0.9 mg L^{-1}) while showing an increase in TOT-N levels during period A2 (5.2 mg L^{-1}) and C2 (0.7 mg L^{-1}) (Table 7). The bark filters showed a decrease in TOT-N

levels during period C1 (0.5 mg L^{-1}) and C2 (0.6 mg L^{-1}) while showing an increase during period A2 (3.9 mg L^{-1}) and C2 (25 mg L^{-1}) (Table 7).

Table 7. TOT-N levels in mg L^{-1} ± the standard deviation in the influent (n=2), effluent from the bark and GAC filters (n=4) and blanks (n=1) with correlating period and date.

Period		**A2**	**B1**	**C1**	**C2**
Date		17-mar	31-mar	20-apr	26-apr
TOT-N					
In	mg L^{-1}	2.3±0.14	13±3.5	6.4±0.14	7.5±0.49
GAC	mg L^{-1}	7.5±2.1	10	5.5±0.096	8.2±0.80
Bark	mg L^{-1}	6.2±1.8	38±4.8	5.9±0.48	6.9±0.43
Blank	mg L^{-1}	1.3	<10	1.5	1.6

The concentration of TSS in the influent was between 0.0-0.30 mg L^{-1}. For most of the occasions the TSS levels were fully removed in both the GAC and the bark filters (Table 8).

Table 8. Mean TSS concentration ± the standard deviation in the influent (n=2), effluent from the bark and GAC filters (n=4) and blanks (n=1) levels in mg L^{-1} for with correlating period and date.

Period		**A2**	**B1**	**C1**	**C2**
Date		17-mar	31-mar	20-apr	26-apr
TSS					
In	mg L^{-1}	0.074±0.10	2.0±2.8	3.0±1.4	0.0
GAC	mg L^{-1}	0.0	0.0	3.6±3.7	0.0
Bark	mg L^{-1}	0.0	0.0	0.0	0.0
Blank	mg L^{-1}	0.0	0.0	0.0010	0.0

4.3 PFAS CONCENTRATION AND COMPOSITION PROFILE

This section presents the concentration and composition of PFASs in the influent and effluent from the GAC and bark filter. Since several compounds were not detected in this experiment (3.5.3) the coming sections will present the concentration and potential reduction of PFHxA, PFHpA, PFOA, PFDA, PFDoDA, PFTeDA, PFBS, PFHxS, PFOS, FOSA and 6:2FTS. The settings regarding GAC filters are presented in

Table 2 and regarding the bark filter is presented in Table 3.

4.3.1 PFASs IN THE INCOMING WATER

The analysis of the filter influent showed a variation in total concentration between the periods (26-45 ng L^{-1}) (Table 9). Of the entire experimental period (A1-C2) A2 displayed the highest concentration with 45 ng L^{-1} while the remaining periods showed a concentration of 26-30 ng L^{-1}. Of all the compounds PFHxS, PFHxA, PFOS and PFOA were the PFASs that showed the highest mean concentration, which was between 4 and 7.6 ng L^{-1}, while other PFASs occurred in concentrations of between 0.0 and 2.2 ng L^{-1}.

Table 9. Concentration of PFAS in the incoming water for each of the different weeks and periods.

Name		**In-A1**	**In-A2**	**In-B1**	**In-C1**	**In-C2**
PFHxA	ng L^{-1}	5.6	8.0	6.6	6.1	6.0
PFHpA	ng L^{-1}	1.4	1.3	<1.0	1.1	1.3
PFOA	ng L^{-1}	4.2	4.6	4.0	3.9	3.6
PFDA	ng L^{-1}	0.45	1.5	0.7	0.54	0.33
PFUnDA	ng L^{-1}	<2.9	3.02	<2.9	<2.9	<2.9
PFDoDA	ng L^{-1}	<0.46	3.9	0.98	0.75	<0.46
PFTeDA	ng L^{-1}	0.28	0.61	0.070	0.13	<0.07
PFBS	ng L^{-1}	<0.86	<0.86	2.2	2.1	1.9
PFHxS	ng L^{-1}	10.0	13	7.2	7.8	7.9
PFOS	ng L^{-1}	6.9	8.1	5.2	5.3	4.6
FOSA	ng L^{-1}	0.31	0.5	0.31	0.30	<0.26
6:2 FTSA	ng L^{-1}	0.72	1.1	1.3	0.95	0.91
ΣPFAS	ng L^{-1}	30±3.3	45±0.45	29±3.8	29±4.0	26±0.17

PFOS, PFHxS, PFHxA and PFBS displayed the highest variation in the influent water, indicating a difference of concentration between the periods (A1-C2) (Figure 7). The other PFASs analyzed displayed slighter discrepancies between periods, indicating a more coherent concentration over the entire experimental period (A1-C2).

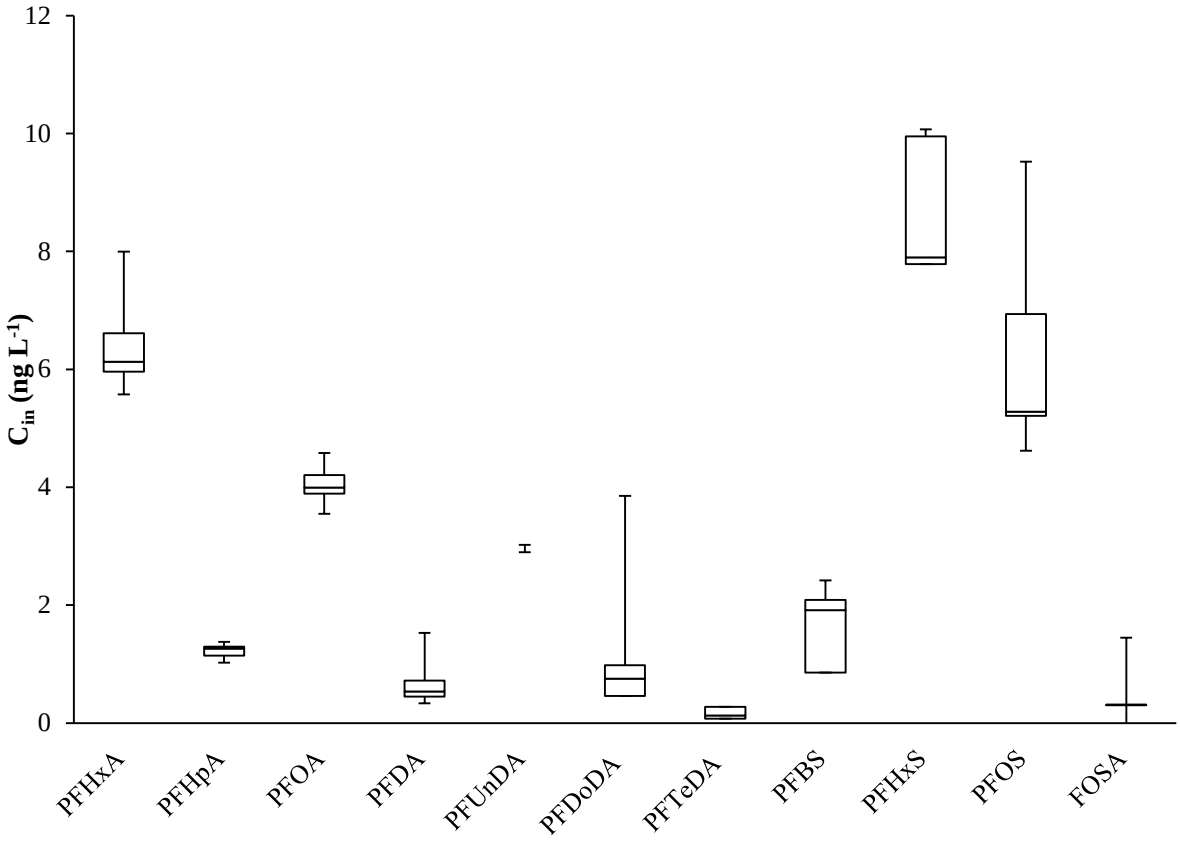


Figure 7. Box-and-whisker plot of different PFAS compounds in the inflow to the filters. The horizontal line inside the boxes represents median, and lower and upper boundary of the boxes represent the lower and higher quartile. Whiskers show the variability from outside the quartiles.

4.3.2 PFASs IN THE EFFLUENT OF THE GAC FILTERS

The GAC filters effluent showed a low total PFAS concentration of 2.9-7.7 ng L^{-1}, were the majority of PFASs were found below 1.0 ng L^{-1} during the entire experimental period; however some differences in concentrations were detected between the periods (Table 10). The total concentration of PFASs was 7.3 ng L^{-1} and 7.7 ng L^{-1} for period A1 and period C2, respectively, while period A1, B1 and C1 that showed a total PFAS concentration of around 3 ng L^{-1} respectively in the filter effluent, indicating a difference in removal of PFASs between these periods. Of the PFASs analyzed were found to be below 1.0 ng L^{-1} for the majority of the experimental periods (Table 10).

Table 10. The mean concentration ± standard deviation (ng L^{-1}) of PFASs in the effluent from GAC filters for each week and period as well as age and flow-rate are presented. The weekly sum of all the compounds during the entire are also calculated.

Period		**GAC-A1**	**GAC-A2**	**GAC-B1**	**GAC-C1**	**GAC-C2**
Flow	L d^{-1}	60	10	30	30	45
PFHxA	ng L^{-1}	1.6	0.67±0.20	0.71±0.20	0.53	1.8±0.15
PFHpA	ng L^{-1}	<1.0	<1.0	<1.0	<1.0	<1.0
PFOA	ng L^{-1}	0.83	0.42±0.13	0.42	0.32±0.083	0.89±0.067
PFDA	ng L^{-1}	0.24	0.023±0.012	0.040±0.045	0.032±0.035	0.10±0.089
PFUnDA	ng L^{-1}	<2.9	<2.9	<2.9	<2.9	10.8±11.2
PFDoDA	ng L^{-1}	0.82	<0.46	0.051	<0.46	1.4±1.3
PFTeDA	ng L^{-1}	0.37	0.091±0.024	0.15±0.10	0.076	<0.074
PFBS	ng L^{-1}	1.5	<0.86	<0.86	<0.86	<0.86
PFHxS	ng L^{-1}	1.2	0.84±0.42	0.54±0.014	0.46±0.14	1.2±0.037
PFOS	ng L^{-1}	0.77	<0.58	<0.58	0.99±0.25	1.9±0.037
FOSA	ng L^{-1}	<0.26	1.1	0.79	0.52±0.36	0.38±0.17
6:2 FTSA	ng L^{-1}	<0.42	<0.42	<0.42	<0.42	<0.42
ΣPFAS	ng L^{-1}	7.3±0.57	3.1±0.69	3.1±0.26	2.9±0.31	7.7±0.75

In general there was a considerable difference between the composition profile for each respective period, indicating that the different experimental circumstances for each period may have affected the removal of PFASs (Figure 8). For instance period A1 showed an even distribution of PFASs while period C2 showed an extremely high portion of PFUnDA (Figure 8).

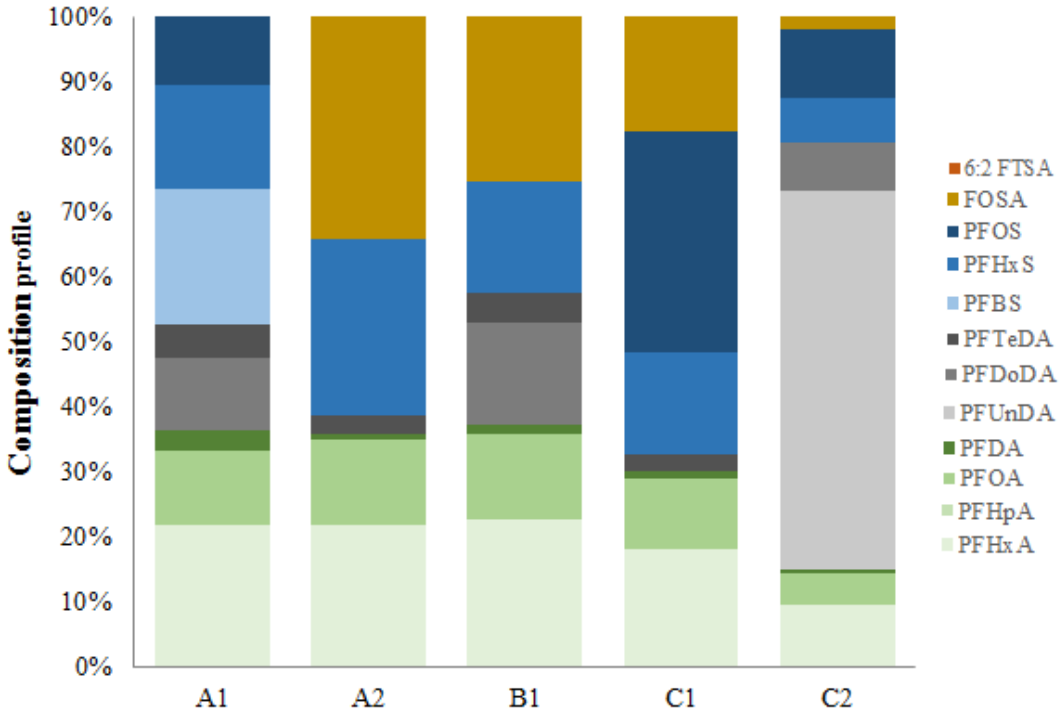


Figure 8. Composition profile (n = 2) of the PFAS from the GAC effluent samples for each period of the experimental period.

4.3.3 PFASs IN THE EFFLUENT OF THE BARK FILTERS

There was a substantial difference in total PFAS concentration between the experimental periods found in the bark effluent, showing a total PFAS concentration ranging from 16-42 ng L^{-1} for the experimental periods (A1-C2) (Table 11). Period A1 displayed a total concentration of 42 ng L^{-1} while the other periods showed a total concentration of 16-27 ng L^{-1}. In addition to the variation in total PFAS concentration the concentration of each compound did also display variations (Table 11). PFHxA, PFOA, PFHxS, PFOS and FOSA showed a mean concentration of between 2.0 and 8.3 ng L^{-1} while the remaining compounds were found bellow or around 1 ng L^{-1} (Table 11).

Table 11. The mean concentration ± standard deviation of each PFAS from the effluent of the two bark columns for each week and period as well as age, flow-rate are presented. The weekly sum of all the compounds during the entire are also calculated.

Name		**Bark-A1**	**Bark-A2**	**Bark-B1**	**Bark-C1**	**Bark-C2**
Paricle size	mm	2-5	2-5	2-5	5-7	5-7
Flow	L d^{-1}	60	10	30	30	45
PFHxA	ng L^{-1}	8.6	<0.37	<0.37	6.9±0.41	6.4±0.26
PFHpA	ng L^{-1}	2.9	<1.0	<1.0	1.2±0.21	1
PFOA	ng L^{-1}	4.7	3.9±0.075	2.9±1.5	4.0±0.18	3.4±0.20
PFDA	ng L^{-1}	0.56	0.22±0.028	0.21±0.16	0.29±0.046	0.26±0.064
PFUnDA	ng L^{-1}	<2.9	<2.9	<2.9	<2.9	<2.9
PFDoDA	ng L^{-1}	<0.46	<0.46	<0.46	<0.46	<0.46
PFTeDA	ng L^{-1}	0.095	<0.074	<0.074	<0.074	<0.074
PFBS	ng L^{-1}	<0.86	1.4±0.076	1.5±0.85	1.9±0.20	2.4±0.21
PFHxS	ng L^{-1}	12	10±0.061	5.6±0.85	7.8±0.20	6.3±0.21
PFOS	ng L^{-1}	7.0	5.0±0.15	3.2±1.8	4.9±0.58	5.4±0.49
FOSA	ng L^{-1}	5.3	2.7±3.3	1.4±1.5	0.54±0.40	0.48±0.25
6:2 FTSA	ng L^{-1}	0.90	0.57±0.22	1.3±0.79	1.2±0.45	1.1±0.24
ΣPFAS	ng L^{-1}	42±3.8	24±2.9	16±1.7	29±2.7	27±2.4

Overall, the composition of PFASs in the GAC effluent were similar during the course of the experiment, however some variations between the periods were detected. Period A2 and B1 showed similar composition profiles in comparison to each other, while period A1, C1 and C2 also showed a similar composition profiles (Figure 9). The difference in composition profile indicate a distinction in removal efficiency of PFASs between period A2 and B1 in comparison to period A1, C1 and C2 (Figure 9).

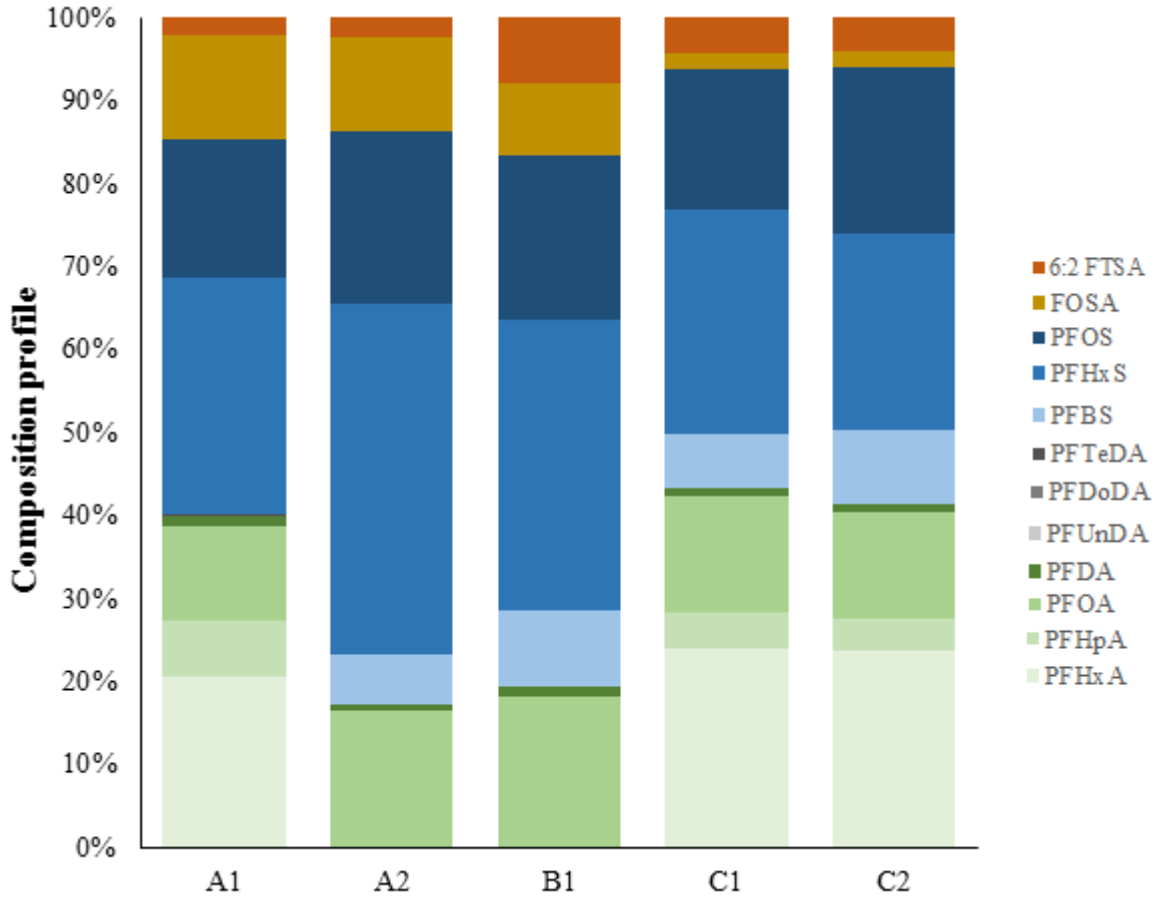


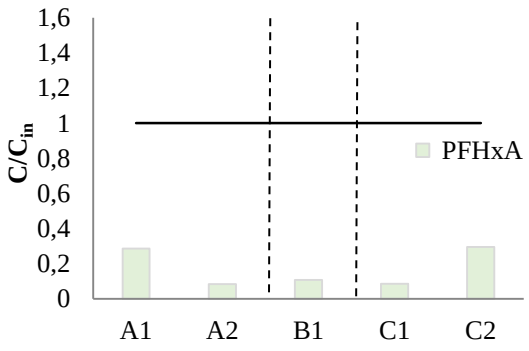
Figure 9. Composition profile (n = 2) of the PFAS from the bark effluent samples for each period of the experimental period.

4.4 REMOVAL OF PFASs

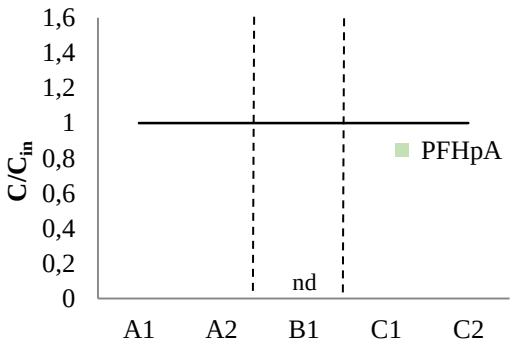
4.4.1 REMOVAL OF PFASs IN THE GAC FILTERS

The GAC filters showed a high reduction of PFCAs of 40-100% throughout the entire experiment (period A1-C2), however some differences in removal efficiency were found between the periods (A1-C2) (Figure 10. A-G). The results suggest that the removal of PFCAs increase with low flowrate (10-30 L d^{-1}) (Figure 10. A-G). Generally, period A2 (10 L d^{-1}), B1 (30 L d^{-1}) and C1 (30 L d^{-1}) showed a higher reduction of PFCAs in comparison to period A1 and C2, as were found for PFHxA, PFDA and PFOA (Figure 10. A, C, D).

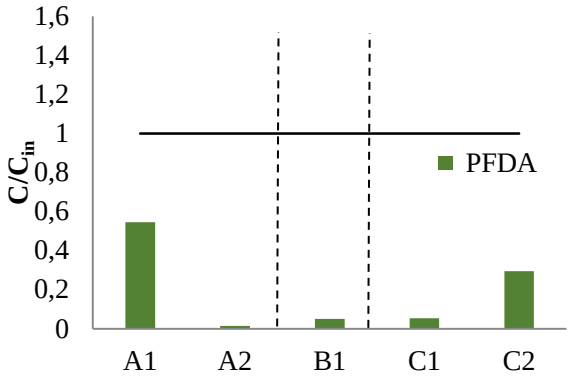
A)



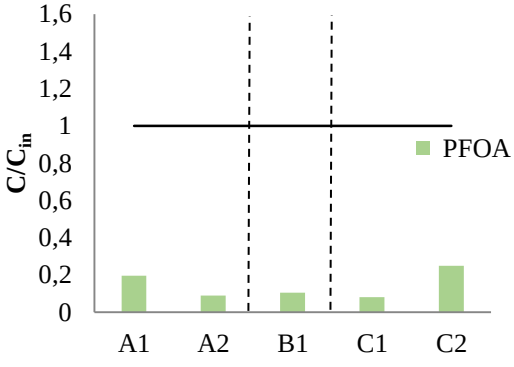
B)



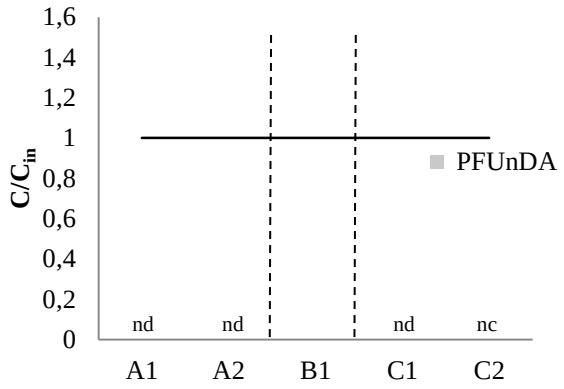
C)



D)



E)



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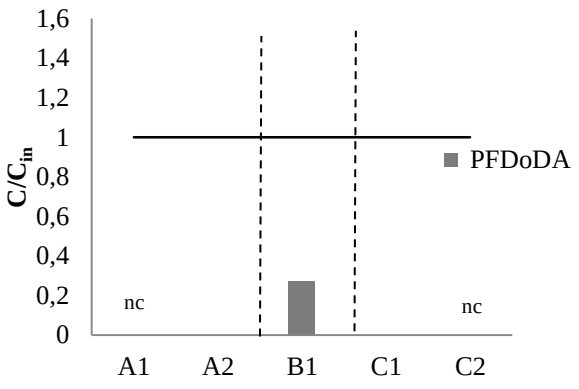


G)

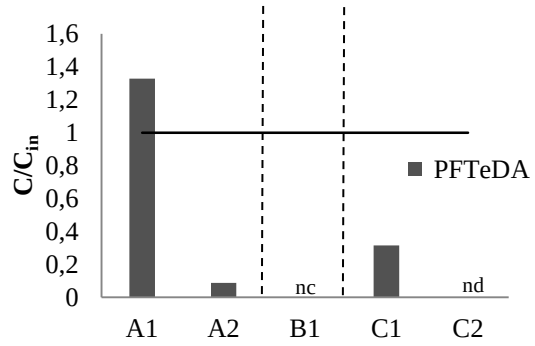
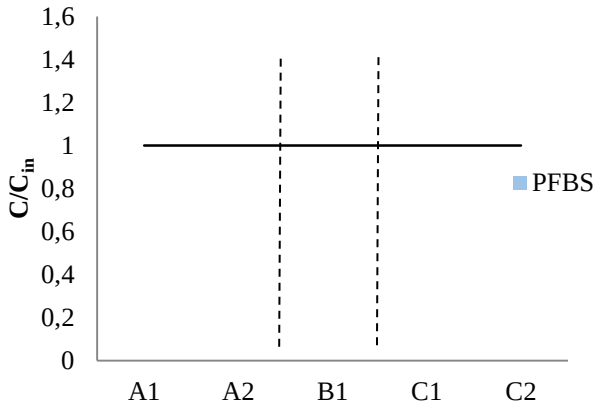


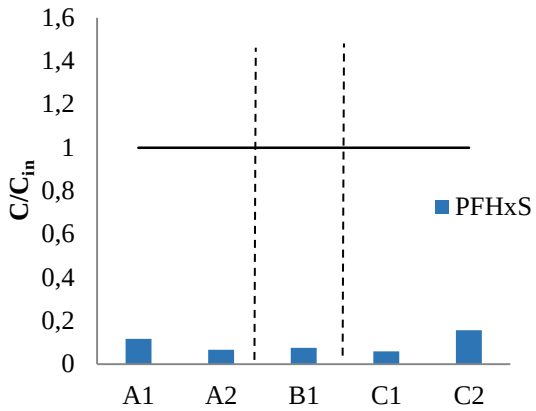
Figure 10. Removal of individual PFCAs in the GAC filters comparing incoming concentrations (C_{in}) and outgoing concentrations (C). nd = not detected in either influent or effluent, nc = only detected in effluent, values below 1 represents decreasing concentrations and above 1 represents increasing concentrations, hence100% removal is indicated when no bar or abbreviation (nc or nd) is shown.

GAC filters effectively removed PFSAs up to 60-100% throughout the experiment; however the results indicate that removal efficiency increase with lower flow-rate (Figure 11. A-C). Period A2(10 L d^{-1}), B1 (30 L d^{-1}) and C1 (60 L d^{-1}) showed a higher reduction of PFSAs compared to period A1(60 L d^{-1}) and C2 (40 L d^{-1}) (Figure 11. B-C).

A)



B)



C)

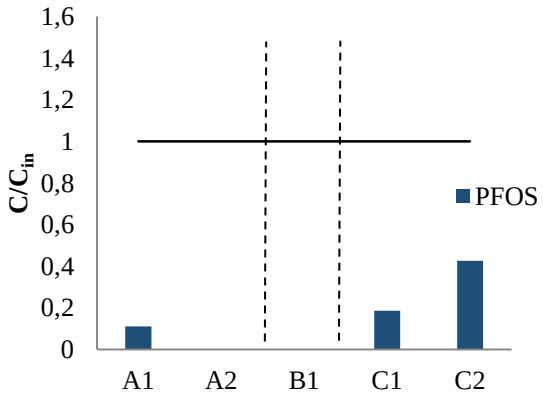


Figure 11. Removal of individual PFSAs in the GAC filters comparing incoming concentrations (C_{in}) and outgoing concentrations (C). nd = not detected in either influent or effluent, nc = only detected in effluent, values below 1 represents decreasing concentrations and above 1 represents increasing concentrations, hence100% removal is indicated when no bar or abbreviation (nc or nd) is shown.

FOSA concentration showed increase in the filter effluent of 10-35% during A2, B1 and C1 while FOSA were fully reduced during period A1 (Figure 12. A). 6:2 FTSA were fully removed during all experimental periods (Figure 12 B).

A) B)

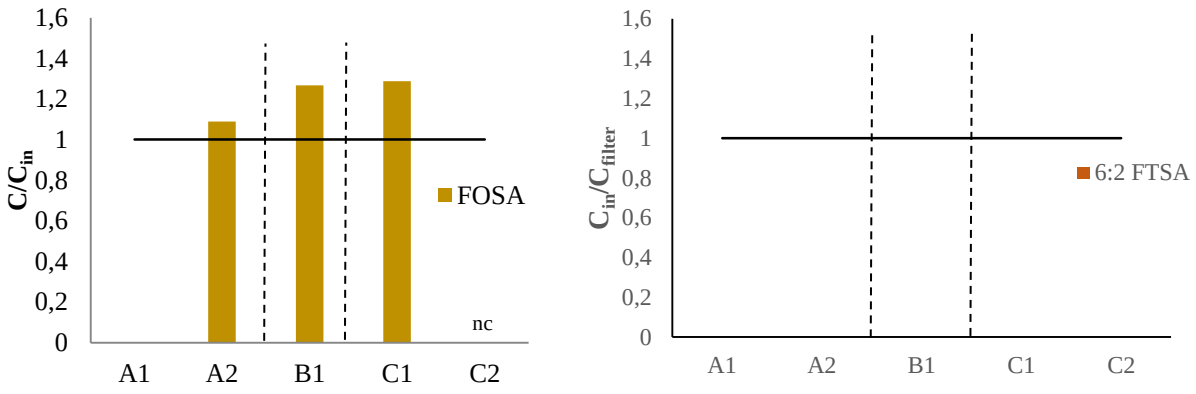
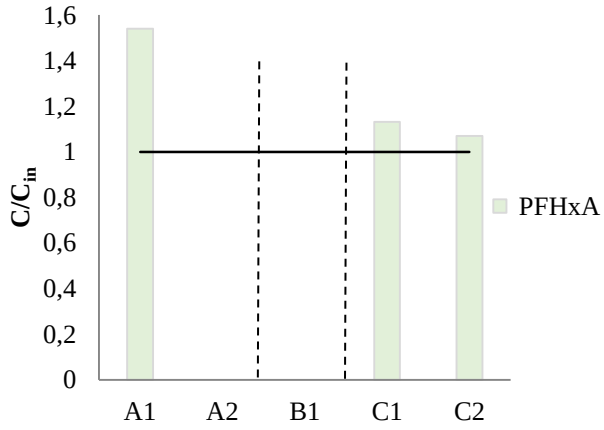


Figure 12. Removal of individual FOSA and 6:2 FTSA in the GAC filters comparing incoming concentrations (C_{in}) and outgoing concentrations (C). nd = not detected in either influent or effluent, nc = only detected in effluent, values below 1 represents decreasing concentrations and above 1 represents increasing concentrations, hence100% removal is indicated when no bar or abbreviation (nc or nd) is shown.

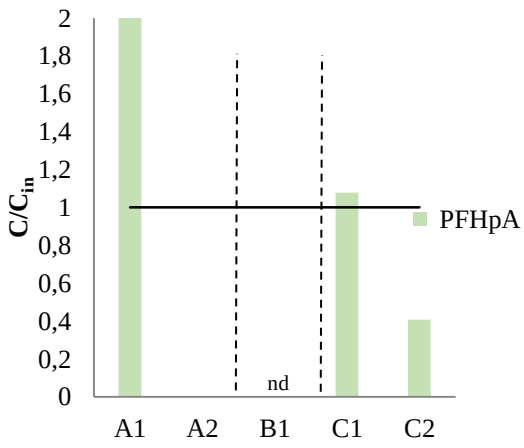
4.4.2 REMOVAL OF PFASs IN THE BARK FILTERS

The bark filters displayed inconsistent removal PFCAs between the experiment periods, therefore indicating that the removal of PFCAs depend on the bark particle size and flow rate (Figure 13. A-G). For instance period A1, with bark particle of size 2-5 mm and flow of 60 L d^{-1}, showed an increase of 15-100% in the bark effluent for the majority of the PFCAs while Period A2 and B1, with a bark particle of size 2-5 mm and flow of 10-30 L d^{-1}, showed a decrease of 20-100% of PFCAs (Figure 13. A-G). Period C1 and C2, with particle size 5-7 mm and flow of 30-40 L d^{-1}, on the other hand showed inconsistent results of little decrease, or in-fact an increase, of PFCAs in the bark effluent (Figure 13. A-D). The results regarding bark filters suggest that removal of PFCAs increase with low flow conditions (10-30 L d^{-1}) and a particle size of 2-5 mm, as were found for the majority of PFCAs during period A2 and B1 (Figure 13. A-G).

A)



B)



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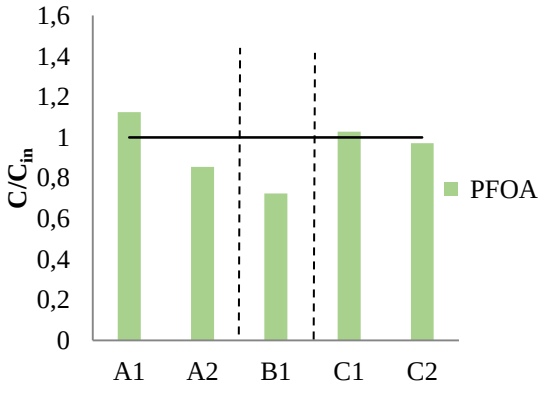
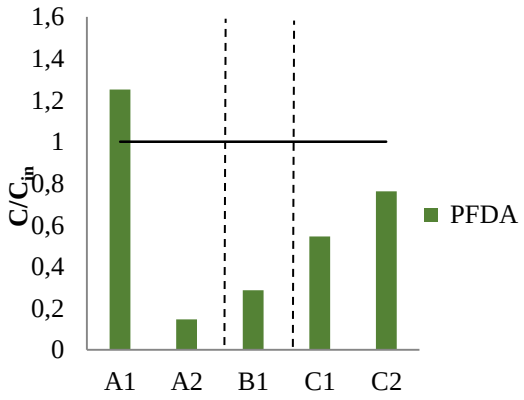
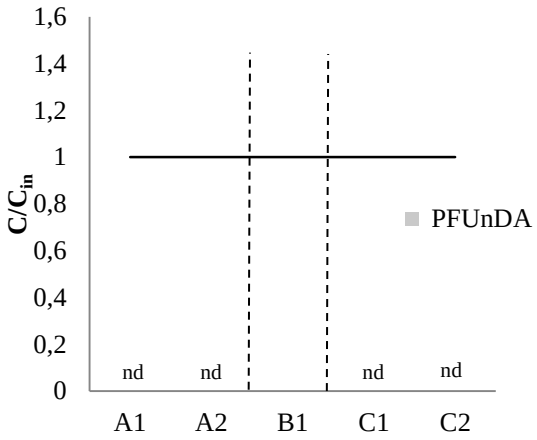


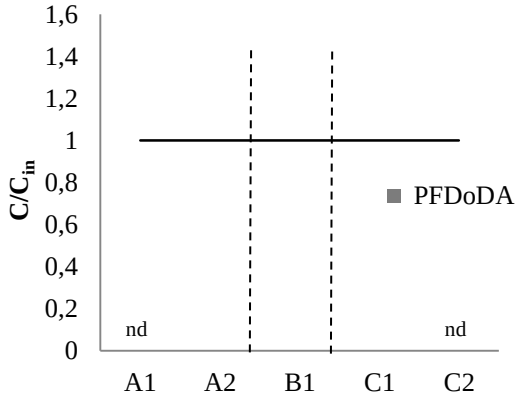
D)



E)



F)



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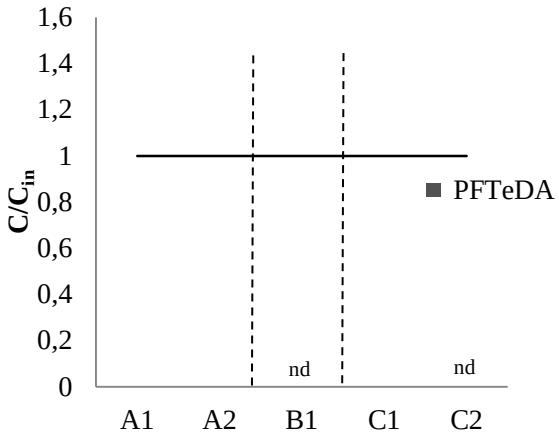

Figure 13. Removal of individual PFCAs in the Bark filters comparing incoming concentrations (C_{in}) and outgoing concentrations (C). nd = not detected in either influent or effluent, nc = only detected in effluent, values below 1 represents decreasing concentrations and above 1 represents increasing concentrations, hence100% removal is indicated when no bar or abbreviation (nc or nd) is shown

The removal efficiency of PFSAs in the bark effluent was inconsistent and appears to depend on the bark particle size and flow rate used for each specific period (Figure 14. A-C). The effluent from the bark filters during period A1 showed inconsistent results of either a decrease or increase of PFSAs (Figure 14 A-C). In contrast did period A2 and B1 show a decrease of 20-100% of PFSAs while period C1 and C2 showing little effects of reduction (Figure 14 A-C). The removal of PFSAs seem to increase under low flow conditions (10-30 L d^{-1}) and smaller particle size (2-5 mm), as were found during period A2 and B1 (Figure 14 A-C).

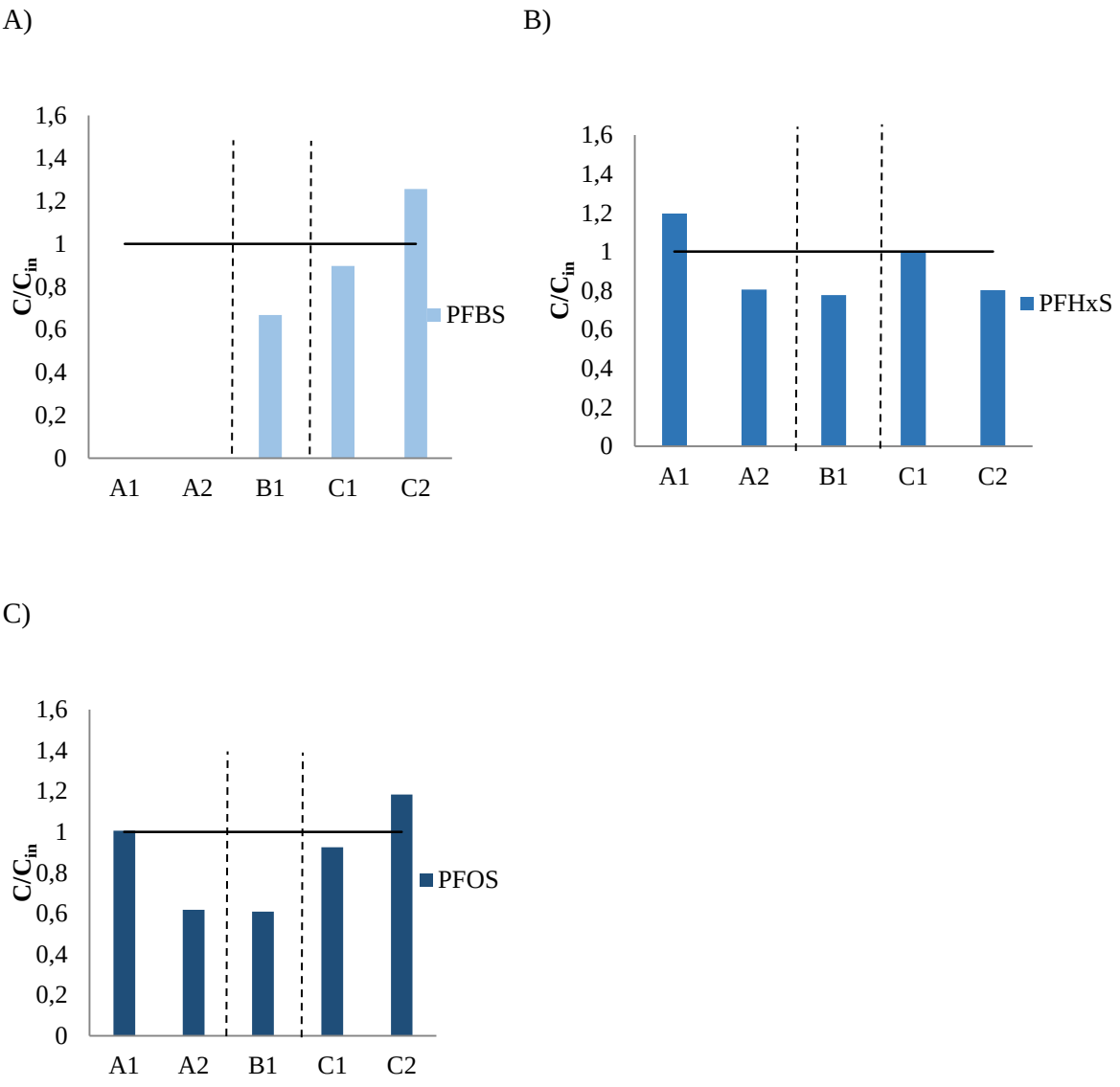

Figure 14. Removal of individual PFSAs in the Bark filters comparing incoming concentrations (C_{in}) and outgoing concentrations (C). nd = not detected in either influent or effluent, nc = only detected in effluent, values below 1 represents decreasing concentrations and above 1 represents increasing concentrations, hence100% removal is indicated when no bar or abbreviation (nc or nd) is shown.

Bark showed inconsistent removal efficiency of FOSA and 6:2 FTSA between the different periods. FOSA showed an increase during period C1 but were fully reduced during period A1 and B1 while period A2 had a 70% removal of FOSA (

Figure 15. A). 6:2 FTSA showed some increase during period A1, C1 and C2 while 6:2 FTSA were reduced during period A2 (

Figure 15. A).

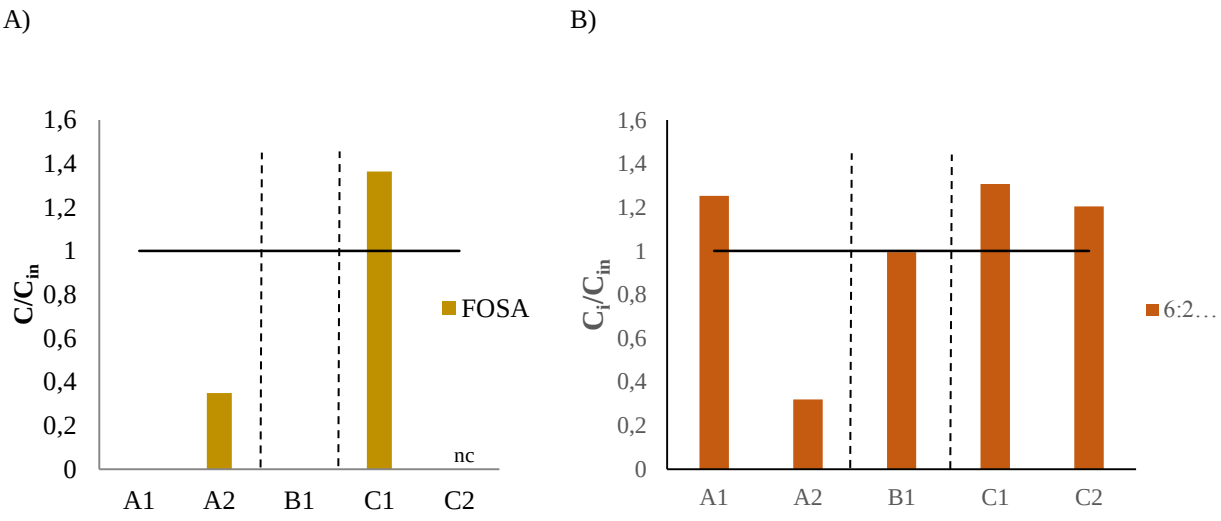

Figure 15. Removal of individual FOSA and 6:2 FTSA in the Bark filters comparing incoming concentrations (C_{in}) and outgoing concentrations (C). nd = not detected in either influent or effluent, nc = only detected in effluent, values below 1 represents decreasing concentrations and above 1 represents increasing concentrations, hence100% removal is indicated when no bar or abbreviation (nc or nd) is shown.

4.4.3 EFFECTS OF FLOW-RATE AND PARTICLE SIZE ON REMOVAL OF PFASs

The GAC filters were more effective in removing PFASs in comparison to the bark filters; however both filter types were more efficient in removing PFASs during low flow conditions, 10-30 L d^{-1} (Figure 16). Both the GAC and the bark filters achieved a high PFAS removal of 90-95% and 40-45% respectively when the flow rate was 10-30 L d^{-1}. However, in contrast to the GAC filters, that were effective in removing PFASs of 71-75% even under high flow conditions (40-60 Ld^{-1}), the bark filters were depending on both a low flow-rate and small particle size for achieving any removal of PFASs (Figure 16). For instance did the bark filters display a 40% increase during period A1, with a flow-rate of 60 L d^{-1} and a particle size of 2-5 mm, while period C1 and C2, with a flow of 30-40 L d^{-1} and particle size of 5-7 mm, showed no effects of PFAS removal (Figure 16).

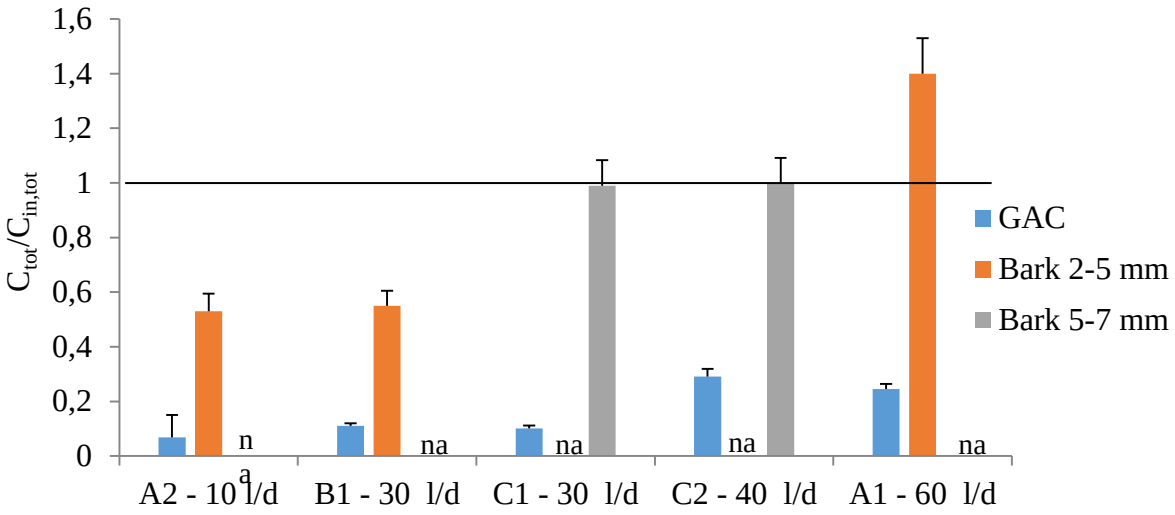

Figure 16. Reduction of the ΣPFASs are presented as normalized values ($C_{tot}/C_{in,tot}$) for the GAC, Bark 2-5 mm and Bark 5-7 mm for each respective flow-ra te. The line at 1 represents the influent concentration, a lower or higher value represents a reduction or increase of each compound. GAC was tested for all periods while bark (2-5 mm) was tested for period A2, B1 and A1 and bark (5-7) was tested for period C1 and C2. na = not available

A correlation between flow-rate and removal of PFASs was found for both the bark (2-5 mm) and the GAC filters, while no correlation between PFAS removal were found for bark filters with a particle size of 5-7 mm (Figure 17). The GAC filters showed a more efficient removal of PFASs with lower flow-rate. Bark, with particle size of 2-5 mm, showed a considerably increased removal of PFASs with decreasing flow-rate. Bark, with particle size of 5-7 mm, on the other hand showed no correlation between flow-rate and removal of PFASs (Figure 17).

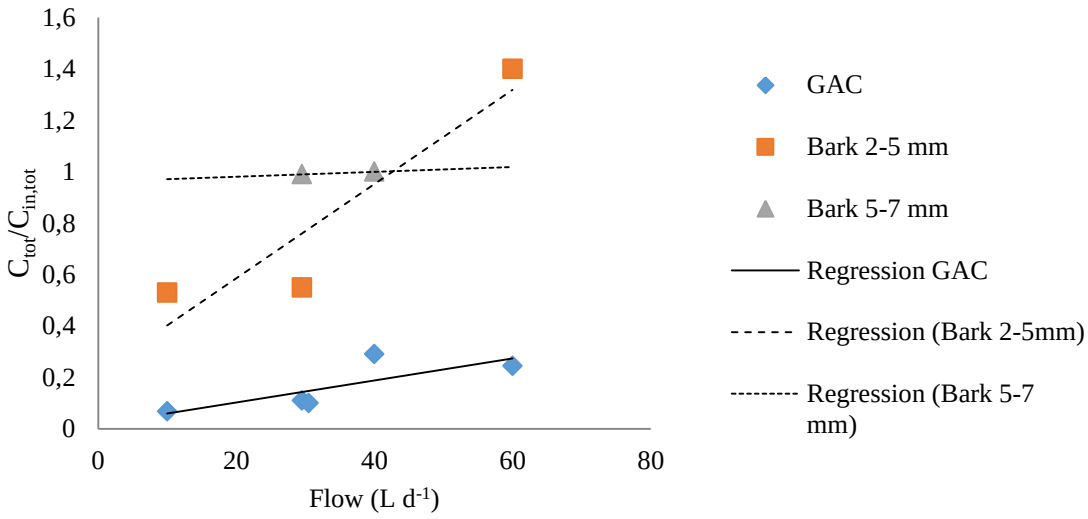

Figure 17. Correlation between removal of the ΣPFASs and flow presented as normalized values ($C_{tot}/C_{in,tot}$) for the GAC, Bark 2-5 mm and Bark 5-7 mm.

4.5 ADSORPTION OF PFASs TO THE GAC AND THE BARK FILTERS

The adsorption of PFASs to the GAC filters indicate that the adsorption capacity of PFASs were greater when using GAC filters in comparison to bark filters; also the clean GAC and bark material showed little effects of PFAS contamination (Table , Figure 18). The GAC filters used for period C2 displayed a PFAS adsorption of 0.048-1.2 ng g^{-1} while the bark filters for the same period on the other hand indicated little or no adsorption of PFASs (Table , Figure 18).

Table 12. Different PFASs in ng g^{-1} (dry weight) found adsorbed to clean GAC, Bark (2-5 mm) and Bark (5-7 mm) and also GAC and Bark (5-7 mm) from period C2.

Filter type		GAC	Bark	Bark	GAC	Bark
Period		-	-	-	C2	C2
Time used	days	0 (clean)	0 (clean)	0 (clean)	7	7
Particle size	mm	2	5-7	2-5	2	5-7
PFHxA	ng g^{-1}	<0.37	<0.37	<0.37	1.0±0.033	<0.37
PFHpA	ng g^{-1}	<1.0	<1.0	<1.0	<1.0	<1.0
PFOA	ng g^{-1}	<0.090	<0.090	<0.090	0.63±0.011	0.0081
PFDA	ng g^{-1}	<0.0081	<0.0081	<0.0081	0.048±0.011	0.011±0.011
PFUnDA	ng g^{-1}	<2.9	<2.9	<2.9	<2.9	<2.9
PFDoDA	ng g^{-1}	<0.46	<0.46	<0.46	<0.46	<0.46
PFTeDA	ng g^{-1}	<0.074	<0.074	<0.074	<0.074	<0.074
PFBS	ng g^{-1}	<0.86	<0.86	<0.86	0.61±0.61	<0.86
PFDS	ng g^{-1}	<0.073	<0.073	<0.073	<0.073	<0.073
PFHxS	ng g^{-1}	0.069	<0.61	<0.61	1.2±0.0074	<0.61
PFOS	ng g^{-1}	0.63	0.62	<0.58	1.1±0.23	0.41±0.41
FOSA	ng g^{-1}	<0.26	<0.26	<0.26	<0.26	<0.26
6:2 FTSA	ng g^{-1}	<0.42	<0.42	<0.42	<0.42	<0.42
ΣPFAS	ng g^{-1}	0.69±0.17	0.62±0.17	0.0	4.6±0.47	0.42±0.11

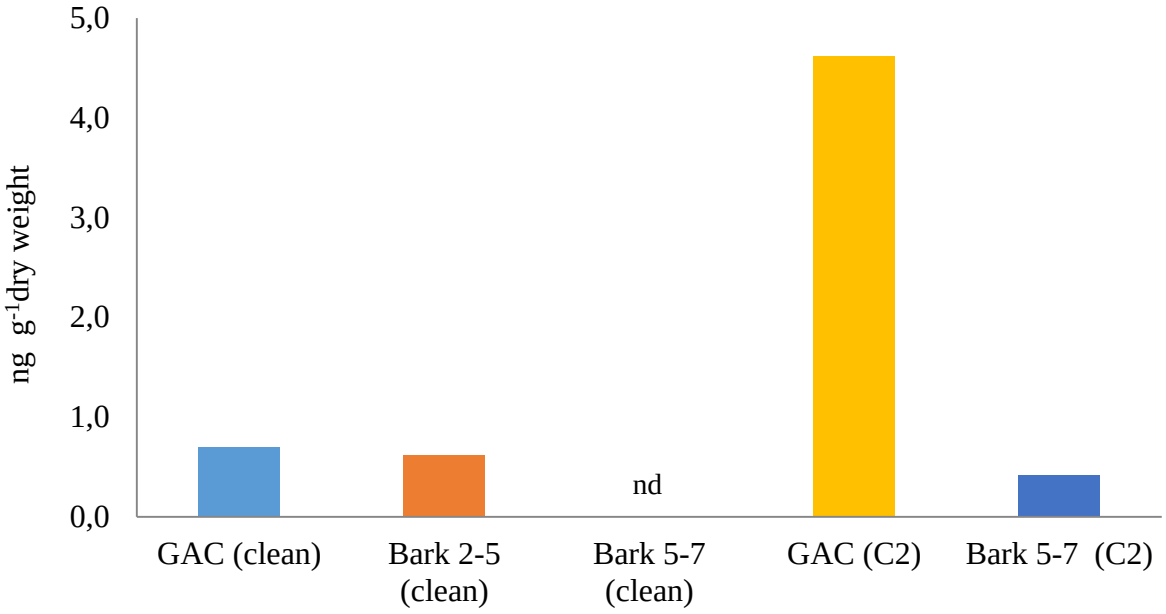

Figure 18. The total PFASs in ng g^{-1} (dry weight) found adsorbed to the filters regarding clean GAC, Bark (2-5 mm) and Bark (5-7 mm) and also GAC and Bark (5-7 mm) from period C2. nd = not detected.

5 DISCUSSION

5.1 EXPERIMENT ROBUSTNESS

The experiment conducted in this study did unfortunately suffer several modifications as a result of filter clogging. Clogging is a common problem in filter-bed type wastewater techniques, due to the accumulation of particles inside the filters (Svenskt Vatten AB, 2013). In this experiment, the problem of clogging occurred mainly in the bark filters, with the particle size of 2-5 mm, while the GAC filters only showed some indication of clogging. Since the filters clogged the filter beds were replaced with new material on three occasions during the experiment. In addition to replacing the filters other experimental factors had to be adjusted to prevent the filters from being clogged again.

Adapting flow and increasing the particle size of bark was necessary to hinder further clogging of the filters, however, changing experimental circumstances may affect the results, making the comparison between the periods (A1-C2) uncertain. The total removal efficiency for each filter-type presented in Figure 16 displays a clear distinction between the different periods (A1-C2), indicating that flow-rate and particle size have an important impact on the removal of PFASs. However, since the filters were clogged, the sampling size for each period was small (n=1), therefore it is difficult to draw any definite conclusion on what effects the flow and particle size may have on the reduction of PFASs. Therefore the results should only be seen as indications.

Several studies have also shown that PFAS reduction may be affected by different parameters, such as the concentration of DOM, which unfortunately was not analyzed, due to the time-limited nature of this project (Appleman *et al.*, 2013). An elevating concentrations of DOM has the potential to hamper the filters capacity of PFAS adsorption (Çeçen & Aktaş, 2011; Rahman *et al.*, 2014). Since the flux of DOM through Kungsängsverket presumably was quite substantial, and might variate between the experimental periods, it cannot be delimited that concentrations of DOM may have affected the filters capacity of adsorbing PFASs in this study (Hansen *et al.*, 2010; Rahman *et al.*, 2014).

5.2 CHARACTERIZATION OF WASTEWATER

The analysis of COD, TOT-N and TSS was made to provide further understanding of the filters impact on treating wastewater. The results presented in section 4.2 shows that the GAC and bark filters were efficient in removing TSS from the wastewater (Table 8), while filters had varied effects on COD and TOT-N concentrations

COD levels were reduced for the majority of the periods in this study, however some inconsistencies between the periods was found, causing difficulties when evaluating the filters effects on COD levels in wastewater (Table 6). The GAC filters showed an increase in COD levels during period A2 while they showed a reduction of 39-73% for the remaining periods (Table 6). The bark filters on the other hand showed an increase in COD levels during period C2 of 16% while it showed a decrease of 12-70% during remaining periods (Table 6). Studies made by Dalameh *et al.* (2010, 2012) and Muhammad *et al.* (2012, 2013) have found that COD are effectively removed from both bark and GAC filters, which corresponds well with the results for the majority of periods in this study. However, due to the small sampling size of this study (n=4) and since there were some inconsistencies in COD levels between the periods for both the GAC and the bark filters, it is difficult to evaluate what effects GAC and bark has on COD levels in this study. Similar problems were also detected in the TOT-N analyses.

The results regarding TOT-N levels from the GAC and bark filters were inconsistent throughout the experiment (Table 7). The GAC filters reduced TOT-N levels during period B1 and C1 respectively while they showed a substantial increase during period A2 and C2 (Table 7). The bark filters on the other hand exhibited a decrease of TOT-N during period C1 and C2 while TOT-N levels increased substantially during period A2 and B1 (Table 7). Since the TOT-N results were inconsistent between the experimental periods, it is difficult to establish what effects the two filter materials have on TOT-N concentrations. In contrast to the results in this study however, other studies have found that GAC and bark are effective in reducing TOT-N levels in wastewater (Muhammad *et al.*, 2012, 2013; Dalameh *et al*, 2010, 2012). Why the results regarding TOT-N, as well as COD, differ between this study and studies by Muhammad (2012, 2013) and Dalahmeh (2012) are difficult to establish, but several factors could have caused the inconsistencies found in this results.

One possible factor that might have affected the results was the potential reduction of COD and TOT-N in the influent wastewater samples, which may have occurred due to the unfavorable sampling method. In this study the influent water samples were collected the day before analyses, which could

cause a reduction of both COD and TOT-N in the influent samples (Ibanez, 2007). In order to hinder any potential reduction precautionary measures were applied, such as acidifying and storing the samples at 2 ^{o}C, however it cannot be delimited that reduction of COD and TOT-N has occurred. Therefore, if reduction of COD and TOT-N has occurred in the influent samples, the samples may have provided inaccurate results. Even though the sampling may have affected the results other factors, such as the small sampling size, may have affected the results as well.

Since the aim of this study was to compare the filters effects on the reduction PFASs the analysis of COD, TOT-N and TSS could only be made on four occasions in this study. Since the sampling size was small and the results for both the COD and TOT-N were inconsistent between the periods no conclusions can be made about what actual effects the filter types have on COD and TOT-N levels. Therefore further studies are needed to conduct more comprehensive analysis on what effects GAC and bark have on COD and TOT-N levels using treated wastewater.

5.3 REMOVAL EFFICENCY OF PFASs

5.3.1 REMOVAL EFFICENCY OF PFASs FROM THE GAC FILTERS

The results gained in this experiment supports that GAC filters remove PFASs efficiently in wastewater (Çeçen & Aktaş, 2011). Throughout the experiment the total reduction of the PFASs was calculated to be 71-93%, which is similar to what has been achieved in other related studies (Hansen *et al.*, 2010, Rahman *et al.*,2014) (Figure 16). However other studies on this topic have found that PFASs with increased carbon chain length (C>6) have been more efficiently reduced in GAC filters in comparison to shorter-chained PFASs (Eschauzier *et al.*, 2012; Rahman *et al.*, 2014; Lidegren, 2015). This study, in contrast to other related studies, could not find any distinction in removal of PFASs from the GAC filters based on the compounds carbon chain length, presumably since several shorter-chained PFASs was not detected (Figure 10-Figure 13). For instance PFBA (C=3) and PFPeA (C=4) had a high calculated MDL, therefore these compounds could not be detected (Table 5). Consequently, no major differences between the carbon-chain length and the removal of PFASs could be found, which otherwise would be expected (Hansen *et al.*, 2010). Even though GAC filters generally have been found effective in removing PFASs, studies have found that different experimental factors, such as flow-rate and run-time of the filters, have an effect on the GAC filters removal efficiency of PFASs.

The results in this study showed that a high removal of PFASs in the GAC filters was correlated to a low flow rate (Figure 16). Period A2 (10 L d^{-1}), B1 (30 L d^{-1}) and C1 (30 L d^{-1}) demonstrated the highest total reduction of PFASs, with up to a 90-93% decrease, while the period A1 (60 L d^{-1}) and

C2 (40 L d^{-1}) with higher flow rate were less efficient in reducing PFASs, with up to 71-75% removal (Figure 16). It has been shown in related studies that low flow rate stimulates removal of organic compounds since the retention time increase. Since adsorption is the dominant removal process of PFASs when using GAC filters in treating waste water a long retention stimulates adsorption of PFASs (Çeçen & Aktaş, 2011). In this study for instance did period A1 have a retention time of 21 minutes d^{-1} and a 71% removal of al PFASs while period A2 on the other hand showed a more efficient removal of PFASs, with a retention time of 128 min d^{-1} and a 93 % removal of all PFASs. Similarly, other studies have found that low flow rate, and thus an increased retention-time, stimulates adsorption of PFASs to the GAC filters (Çeçen & Aktaş, 2011; Eschauzier *et al.* 2012). Along with retention time, do other factors correlated to the flow-rate, such as pore water velocity; also affect the adsorption efficiency of the activated carbon filters. The pore water velocity defines the flow of water through the pores of the GAC filter and depends on the porosity and the specific flow of water through the GAC filter bed. It has been found that a lower pore water velocity, which correlates to a low flow rate and low porosity, stimulates a more efficient removal of PFASs (Hansen *et al.*, 2010). Unfortunately however was the porosity of the GAC filters in this study not available, but since the same particle size were used throughout the study the porosity is presumed to be the same throughout the study, therefore the difference in pore water velocity depends mainly on the flow rate. Therefore, since the pore water velocity in this study is proportional to the flow-rate, the high removal of PFASs during period with a low flow-rate (10-30 L d^{-1}) is assumed to be a result of an increased retention time, rather than the pore water velocity in this example, however if the porosity were to altered it would have been possible that the pore water velocity would affect the removal efficency as well. In contrast to the relationship between flow-rate and removal of PFASs in the GAC filters other experimental factors, such as run-time, were not as easily evaluated.

Several studies have found that GAC filters become depleted in time, this fact however was difficult to evaluate in this study, since the filters had to be replaced due to clogging (Çeçen & Aktaş, 2011). Since the filters had to be replaced, the filters were only in service for a maximum of 1-2 weeks; therefore it became unfeasible to analyze what effects increasing run-time of the filters have on removal of PFASs (

Table 2). Other studies have found that GAC filters becomes depleted after 1 year in service, therefore the short run-time of the filters in this experiment is presumed to have had little effect on the GAC filters removal efficiency of PFASs (Takagi *et al.* 2011). Overall the GAC filters showed an efficient removal of PFASs, yet an increase of several PFASs (i.e FOSA and PFTeDa) was found throughout the experiment, which could be a result of several factors (e.g degradation of precursors).

Several compounds, mainly FOSA, showed an increase in the GAC filter effluent, and could be the result of the degradation of so-called precursors (Figure 12 A). Since the WWTPs stimulates biological degradation, precursors may degrade, causing an increase of PFASs in wastewater (Sinclair & Kannan, 2006; Zhang *et al.*, 2013). The increase of PFASs in this study however could be a result of accumulation of biofilm inside the GAC filters, which, similar to the treatment methods at WWTPs, also could stimulate degradation of precursors. In fact Velten *et al.* (2011) found in a small scale experiment that an increase of biofilm could be detected shortly after the GAC filters had been installed, therefore potentially stimulating biological degradation of precursors. Unfortunately, the amount of precursors, nor the amount of biofilm, was analyzed in this study; therefore other factors may have caused an increase of PFAS concentration in the filter effluent, such as potential contamination of the samples.

Contamination is a concern when analyzing organic compounds, and may have occurred during the laboratory analysis. To detect any contamination of the samples MDL was calculated for each compound; therefore any contamination should have been accounted for (Table 5). In addition to calculating the MDL, clean GAC filter material were analyzed to detect any potential contamination from the filter material. However, low concentrations of PFASs were found in clean GAC material, therefore delimiting the GAC filters as a potential source of PFASs (Table 12, Figure 18). Since MDL was calculated and clean material was analyzed, the degradation of precursors in the influent is assumed be the most likely source of PFAS increase. Generally however, only a few PFASs increased in the GAC filter, therefore it can be concluded that the GAC filters in this experiment were effective in reducing PFASs (Figure 12).

5.3.1 REMOVAL EFFICENCY OF PFASs FROM THE BARK FILTERS

The bark filters showed varying results regarding the removal of PFASs between the periods (A1-C2), indicating that experimental circumstances, such as flow-rate and particle size, as well as the run-time (time after installation), have an impact on the removal of PFASs (Figure 16). Unfortunately, since the bark filters had to be replaced at two occasions due to clogging, the effects of the bark filters run-time on the removal of PFASs was difficult to analyze. However, since the run-time for each period was short (maximum of 2 weeks), the effects of run-time is presumed to have little effects on the bark filters removal efficiency of PFASs, therefore the variations in removal efficiency between the periods is presumed to depend mainly on flow-rate and particle size (Takagi *et al.*, 2011).

The results showed that the high removal of PFASs in the bark filters was correlated to a low flow-rate and small particle size of the bark filters, presumably due to an increased retention time as well as an decrease in pore water velocity (Figure 13,

Figure 15). During period A2 and B1, with a flow rate of 10 and 30 L d^{-1}, respectively, and a bark particle size of 2-5 mm, PFASs showed an effective removal of up to 40-45% (Table 3, Figure 16). Since the flow-rate was low (<30 L d^{-1}) the retention time in the filters was high for period A2 (128 min d^{-1}) and B1 (43 min d^{-1}), therefore promoting adsorption of PFASs to the filter material (Figure 16), which also have been found in other related studies using GAC filters in treating PFAS (Hansen *et al.*, 2010; Çeçen & Aktaş, 2011; Eschauzier *et al.*, 2012). Similarly to high retention time, do a small particle size increase the adsorption capacity due to an increase in specific area due to a lower porosity, which also have been found to improve removal of PFASs in related studies using activated carbon (Appleman *et al.*, 2013). It is presumed that the adsorption capacity in activated carbon filters, both granular (GAC) and powdered (PAC), depends largely on the pore water velocity inside the filters, which depends on the porosity of the filter bed(Çeçen & Aktaş, 2011). However since the porosity is not available in this study, fort neither the 2-5 mm and 5-7 mm filters, it becomes difficult to fully evaluate the importance of pore water velocity on the removal of PFASs, therefore it can only be assumed that bark filters show similarities to GAC filters in this regard, which the results indicate. In contrast to period A2 and B1, period C1 and C2 showed low removal of PFASs, presumably due to the particle size (5-7 mm).

The results during period C1 (30 L d^{-1}) and C2 (40 L d^{-1}), showed a low removal efficiency of PFASs (Figure 13-

Figure 15), presumably due to the large particle size (5-7 mm) (Table 3). Since the bark particle size was larger during period C1 and C2 in comparison to the filters used during period B1 (2-5 mm), the adsorption capacity during period C1 and C2 was lower as well in comparison to period B1, consequently resulting in a lower removal of PFASs (Figure 16). Also, since the flow rate, and retention time during period C1 (30 L d^{-1}) and C2 (40 L d^{-1}) was similar to period B1 (30 L d^{-1}), it becomes evident that porosity have an impact on PFAs removal, since period B1 showed a 40 % removal of all PFASs whilst period C1 and C2 showed no overall removal of PFASs. As previously mentioned, other related studies on activated carbon have shown that a smaller particle size have an impact on the adsorption capacity of PFASs due to the specific area increase with decreasing particle size, and therefore it may be assumed that bark filters would show similar tendencies as well, thus a lower porosity would result in a lower removal of PFASs. The dominant force behind this result is presumed to be the difference in pore water velocity, which correlates to the specific flow and porosity of the filters. In this experiment since the porosity is the main difference between period B1

and C1 and C2, it becomes apparent that porosity and pore water velocity have an impact on PFAS removal, even though the specific porosity of the bark filters was not available in this study (Appleman *et al.*, 2013; Rahman *et al.*, 2014).

Period A1, with a flow-rate of 60 L d^{-1} and particle size of 2-5 mm, had a 40% increase of the total amount of PFASs, which could depend on a combination of different factors, such as the degradation of precursors as well as a high flow-rate (Figure 13-

Figure 15). The degradation of precursors is a common problem in WWTPs, therefore it may cause an increase of PFASs. Since the removal of PFASs in the bark filters in this study is correlated to the flow-rate (Figure 17), the high flow-rate during period A1 may have resulted in low adsorption of PFASs, therefore the degradation of precursors could result in an net-increase of PFASs in the bark effluent (Table 3) (Sinclair & Kannan, 2006; Zhang *et al.*, 2013). In fact other small-scale studies have found that there is an abundance of bacterial cultures inside the bark filters when treating wastewater, therefore the biofilm accumulated in this study may potentially have stimulated microbiological degradation of precursors (Dalameh *et al.* 2014). Unfortunately, neither the amount of precursors nor biofilm was analyzed in this study, therefore other factors, such as potential contamination of the samples, could have caused an increase of PFASs in the filter effluent as well.

PFAS blank contamination is a risk during the experiment and sample preparation. Procedure blanks were used to calculate the MDL to account for blank contamination during the sample preparation. In addition, clean bark filters were analyzed, in order to detect if the filters were contaminated with PFASs. Only a small amount of PFASs were detected in the clean bark (2-5, 5-7 mm) (Figure 18), therefore contamination from the filter itself can be excluded.

5.4 COMPARISION BETWEEN THE GAC AND THE BARK FILTERS

Bark has similar physical properties as GAC and therefore it becomes interesting to evaluate its potential in removing PFAS from waste water. In this study however, GAC proved to be more efficient in reducing PFASs than the bark filters (Figure 16), presumably due to difference in adsorption capacity depending on the pore structure of the filters. According to the ESEM scan's the GAC were the more porous of the two materials, therefore achieving a higher adsorption of PFASs in comparison to the bark filters (Figure 5, Figure 6). Unfortunately the porosity of the bark particles was inaccessible therefore the specific area cannot be calculated, however the specific area of GAC can vary between 500 to 1500 m^2 g^{-1}, which presumably is greater than that of the bark filters (Çeçen & Aktaş, 2011).

Both the GAC and the bark filters showed a correlation between flow rate and PFAS removal (Figure 17). The highest PFAS removal was during period A2, with a flow rate of 10 L d^{-1}, when GAC and bark showed a reduction of 95% and 45%, respectively (Figure 16). However, while bark was only efficient when the flow-rate was lower than 30 L d^{-1} and the particle size was 2-5 mm the GAC filters showed an effective removal of PFASs during all periods (Figure 16). Therefore, the results indicate that bark was more dependent on a low flow rate to achieve an effective removal of PFASs than the GAC filters (Figure 16). The correlation between a low flow rate for both the GAC and the bark filters and higher adsorption of PFASs is presumed to be a result of mainly an increased retention but also potentially an increased pore-water velocity. Both the GAC and the bark filters removal of PFASs were largely affected by the retention time but as the results showed for the bark filters, when comparing periods with a larger (5-7 mm) bark particle size to periods with smaller (2-5 mm) bark particle size, it becomes evident that pore water velocity have an impact on the removal efficiency of the filters (Figure 17). Since the small particle size decrease the porosity the pore water velocity decrease as well, which have been proven to promote adsorption (Çeçen & Aktaş, 2011). In addition the bark filters were more sensitive to clogging then the GAC filters, consequently it is difficult to establish the potential use of bark filters as a wastewater treatment technique.

While GAC is a common wastewater treatment technique bark filters are not, therefore the potential use of bark in WWTPs is not fully established. The results in this study however showed that bark filters were effective removal of PFASs under low flow conditions, unfortunately the bark filters were sensitive to clogging, therefore using bark in WWTPs might be problematic. Even though the potential cost of bark filters is considerably lower than for instance GAC, maintenance cost could be substantial due to the clogging issues. Based on these results, bark could pose as an alternative in small WWTPs in rural communities in third world countries where price is the main limitation. Therefore further studies are needed to provide deeper understanding of the potential use of bark as a wastewater treatment technique (Dalahmeh *et al.*, 2012, 2014).

6 CONCLUSIONS

According to the results in this study, GAC was more effective in removing PFASs from wastewater in comparison to bark. Also a correlation between high removal efficiency and low flow-rate were found regarding both the GAC and the bark filters, presumably due to an increased retention time that stimulates adsorption of PFASs. Of the two materials was bark most dependent on a low flow-rate to achieve an efficient removal of PFASs (Figure 17). The results also indicate that pore water velocity is an important factor when removing PFASs through adsorption in filter-bed-type waste water treatment techniques. Furthermore the results showed that bark particle size had an impact on the results, where for instance no net-reduction of PFASs could be detected with bark particle size of 5-7 mm (Figure 17). The bark filters also showed an increase of several PFASs, which is presumed to depend on the degradation of precursors (Figure 16). In addition, GAC filters were less sensitive to clogging in comparison to the bark filters, which would be problematic if the bark filters were to be used in full-scale.

Even though the GAC filters were more effective than bark filters in removing PFASs from wastewater, the bark filters, with a small particle size (2-5 mm), were effective in reducing PFASs under low flow conditions (<30 L d^{-1}). Bark may therefore pose as an alternative method in treating PFAS contaminated waters in small-scale, given the water contained a low amount of solids, which otherwise could clog the filters. It would be recommended to further study the potential of bark as an adsorbent of PFASs in laboratory-scale in order to minimize uncertainties and to study the PFAS removal in a confined and controllable environment. Also further studies are needed to establish to what extent flow rate, pore water velocity and retention have on adsorption of PFASs as well as what effects bark has on the degradation of precursors.

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8 APPENDIX

8.1 FILTERS PHYSICAL PROPERTIES

Table. A displays the weight properties of each layer and Table. B shows the weight properties of each respective layer in the GAC and bark filters.

Table. A Weight of each layer in the column experiment.

Weight properties		**GAC 1**	**GAC 2**	**Bark 1**	**Bark 2**
Column	kg	0.32	0.31	0.33	0.32
Drainage layer 1	kg	0.0071	0.0075	0.0081	0.0061
Column + Drainage layer 1	kg	0.39	0.39	0.41	0.38
Filter bed	kg	0.40	0.40	0.17	0.17
Column + Drainage layer 1 + Filter bed	kg	0.79	0.79	0.58	0.54
Drainage layer 2	kg	0.054	0.051	0.052	0.067
Total weight	kg	0.85	0.84	0.63	0.61

Table. B Length of each layer in the column experiment.

Lenght properties		**GAC 1**	**GAC 2**	**Bark 1**	**Bark 2**
Radius	m	0.00225	0.00225	0.00225	0.00225
Column	m	1.058	1.065	1.064	1.058
Drainage layer 1	m	0.031	0.03	0.03	0.032
Column + Drainage layer 1	m	1.027	1.035	1.034	1.026
Filter bed	m	0.5	0.5	0.5	0.5
Column + Drainage layer 1 + Filter bed	m	0.527	0.535	0.534	0.536
Drainage layer 2	m	0.003	0.003	0.0029	0.0031
Total lenght	m	0.497	0.5	0.505	0.505

Table. C presents the calculated porosity that were attained. Due to leakage this experiment can only be seen as an approximation of the water holding capacity and porosity. According to Table C both filters seemed to have fairly similar water holding capacity, the total collected volume were higher for Bark indicating that the Bark filter has a slightly lower water holding capacity therefore potentially lower adsorption capacity of PFASs.

Table. C Results from the experimental analysis of porosity and water holding capacity for GAC and Bark 2-5 mm.

		GAC1	GAC2	Bark 1	Bark 2
Particle size		2	2	2-5	2-5
Length column	m	1.058	1.065	1.064	1.058
Total length	m	0.497	0.5	0.505	0.505
Height (m)	m	0.561	0.56	0.559	0.553
Radie (m)	m	0.0225	0.0225	0.0225	0.0225
Volume column (l)	l	1.7	1.7	1.7	1.7
Volume filter bed (l)	l	0.89	0.89	0.89	0.88
Volume added water (l)	l	0.41	0.35	0.455	0.5
Volume (1 minute)	l	0.31	0.29	0.40	0.43
Volume (30 min)	l	0.0090	0.0090	0.045	0.019
Volume (6h)	l	0.012	0.014	0.0060	0.0030
Volume (30 h)	l	0.0030	0.0020	0	0
Total collected volume	l	0.33	0.31	0.45	0.45
Pore volume		0.41	0.35	0.455	0.5
Porosity		0.46	0.39	0.51	0.57

8.2 DETAILED SAMPLING PLAN

For each of the weekly samples from the filters roughly 200 mL were added from each sampling day, so that L liter merged sample could be detained (Table. D). For the incoming water there were six sampling days so roughly 167 were added from each sampling point. Due to some malfunctioning of the setup for the first week W1 of A1, not all the water could be collected as according to the description that was previously mentioned. Some problems with collecting water also occurred during the second week W2 of A2. Table. D**Fel! Hittar inte referenskälla.** and Table. F shows the number of sampling days and what sampling days each merged weekly sample contained (W1, W2, W3, W5 and W6). Each day are named i.e. D1, which refers to day 1 of the entire experimental period. The weekend samples are named i.e. D9-D11 which indicates the day of when the sampling started, in this case D9, and when it ended, which for this example were D11.

Table. D Volume from each daily sample that creates the merged weekly sample from each filter.

		A1	**A2**	**B1**	**C1**	**C2**
		W1	**W2**	**W3**	**W5**	**W6**
		2/3-7/3	11/3-18/3	31/3-6/4	13/4-19/4	20/4-27/4
In	mL d^{-1}	250	167	167	167	167
A1	mL d^{-1}	333	167	200	200	200
A2	mL d^{-1}	333	167	200	200	200
B1	mL d^{-1}	250	167	200	200	200
B2	mL d^{-1}	333	167	200	200	200

Table. E The number of samples that conduct the merged weekly samples for W1 and W2 during period A1 and A2.

	A1		**A2**	
	W1		**W2**	
	Samples	**Days**	**Samples**	**Days**
In	4	D1, D2,D3, D6	6	D8, D9, D12, D13, D14, D15
A1	3	D1, D3-5, D6	6	D8, D9-D11, D12, D13, D14, D15
A2	3	D1, D3-5, D6	6	D8, D9-D11, D12, D13, D14, D15
B1	4	D1, D2, D3-5, D6	6	D8, D9-D11, D12, D13, D14, D15
B2	3	D1, D2, D6	6	D8, D9-D11, D12, D13, D14, D15

Table. F The number of samples that conduct the merged weekly samples for W3, W5 and W6 during period B1, C1 ar

B1	**C1**	**C2**
W3	**W5**	**W6**

	Samples	Days	Samples	Days	Samples	Days
In	6	D16, D17, D18, D19-D20, D21, D22	6	D23, D24, D25, D26-D27, D28, D29	6	D30, D31, D32, D33-D34, D35, D36
A1	5	D16, D17, D18-D20, D21, D22	5	D23, D24, D25-D27, D28, D29	5	D30, D31, D32-D34, D35, D36
A2	5	D16, D17, D18-D20, D21, D22	5	D23, D24, D25-D27, D28, D29	5	D30, D31, D32-D34, D35, D36
B1	5	D16, D17, D18-D20, D21, D22	5	D23, D24, D25-D27, D28, D29	5	D30, D31, D32-D34, D35, D36
B2	5	D16, D17, D18-D20, D21, D22	5	D23, D24, D25-D27, D28, D29	5	D30, D31, D32-D34, D35, D36

8.3 REDUCTION OF PFASs IN GAC AND BARK EFFLUENT

To visualize reduction or increase from the GAC filters normalized values are presented in Table. G for each period with correlating flow-rates and particle sizes. Period A2, B1 and C1 showed a similar reduction in most of the compounds to around a 85-100% decrease, with exception from PFDoDA and PFTeDA which had a reduction of 73 and 69% during period B1 and C1. PFUnDA and PFBS were not detected during period A2 while PFHpA and PFTeDA were not detected during period B1 and PFUnDA were not detected during period C1. FOSA also showed a increase of 10, 30 and 30% during period A2, B1 and C1. Period C2 and A1 with a flow rate of 40 and 60 L d^{-1}, showed also a similar reduction to around 70 and 85% in most of the compounds with the exception of PFDA, which showed a decrease of 45% during period C2 and PFOS, which showed a 57% decrease during period A1. PFTeDA also showed a 30 % increase during period A1. Period C2 also had a increase of PFUnDA, and PFDoDA, but showed no concentration in the influent while PFTeDA were not detected in either the influent or the effluent. Period A1 did also have a increase of PFDoDA and PFBS which also only were noted in the filter effluent. PFTeDA were not detected during period C2 and PFUnDA were not detected during period A1.

Table. G Mean reduction (n=2) for each PFAS achieved from the GAC filters presented as normalized values (N) for each correlating period, flow rate and particle size.

Period		A2	B1	C1	C2	A1
Flow	L d^{-1}	10	30	30	40	60
PFHxA		0.083±0.026	0.11±0.030	0.086±0.026	0.29±0.026	0.29

PFHpA	0	nd	0	0	0
PFOA	0.090±0.028	0.10±0.00067	0.081±0.019	0.25±0.019	0.2
PFDA	0.015±0.0080	0.050±0.070	0.054±0.26	0.29±0.26	0.55
PFUnDA	nd	0	nd	nc	nd
PFDoDA	0	0.27±0.39	0	nc	nd
PFTeDA	0.088±0.12	nc	0.31	nc	1.3
PFBS	nd	0	0	0	nd
PFHxS	0.067±0.033	0.075±0.0019	0.059±0.0047	0.16±0.0047	0.12
PFOS	0	0	0.19±0.22	0.43±0.22	0.11
FOSA	1.1±1.5	1.3±1.8	1.3	nc	0
6:2 FTSA	0	0	0	0	0
∑PFASs	0.069±0.082	0.11±0.010	0.10±0.011	0.29±0.028	0.25±0.019

To visualize reduction or increase from the Bark filters normalized values are presented in Table. H for each period with correlating flow-rate and particle size. Periods A2 and B1 showed a similar reduction up to 70-100% regarding PFHxA, PFHpA, PFDA, PFUnDA, PFDoDA, PFTeDA and FOSA while there were a 15-40% decrease regarding PFOA, PFHxS. 6:2 FTSA differed between the two periods showing a 68% decrease period A2 and no reduction during period B1. PFUnDA and PFBS were not detected during period A2 while PFHpA and PFTeDA were not detected during period B1. The highest reduction for the different compounds during period C1 and C2 was PFDA, which showed a 45 and 25% reduction respectively. PFHxA, FOSA and 6:2 FTSA showed an increase of between 10 and 40% during C1 and C2 while PFHpA and PFBS both showed an increase and decrease between the two periods. Regarding the other compounds during period C1-C2 there were only a small reduction of up to 10% or no sdifference noted over the entire two periods. PFUnDA were not detected during period C1 while PFUnDa, PFDoDA, PFTeDA were not detected in either influent or the effluent while FOSA only were detected in the effluent during period C2. Period A1 showed a increase regarding PFHxA, PFHpA, PFOA, PFDA, PFHxS and 6:2 FTSA of between 10 and 110%. PFTeDA and FOSA showed a reduction of 75 and 100% respectively while PFUnDA, PFDoDA and PFBS were not detected during period A1.

Table. H Mean reduction (n=2) for each PFAS compound achieved from the Bark filters presented as normalized values (N) for each correlating period, flow rate and particle size.

Period		**A2**	**B1**	**C1**	**C2**	**A1**
Flow	L d^{-1}	10	30	30	40	60
Particle size	mm	2-5	2-5	2-5	5-7	5-7
PFHxA		0	0	1.1±0.067	1.1±0.044	1.5
PFHpA		0	nd	1.1±0.19	0.41±0.058	2.1
PFOA		0.85±0.016	0.72±0.38	1.0±0.047	0.97±0.055	1.1
PFDA		0.15±0.018	0.29±0.23	0.55±0.087	0.76±0.19	1.3
PFUnDA		nd	0	nd	nd	nd
PFDoDA		0	0	0	nd	nd
PFTeDA		0	nd	0	nd	0.34
PFBS		nd	0.67±0.39	0.90±0.098	1.3±0.11	nd
PFHxS		0.80±0.0048	0.78±0.35	1.0±0.0031	0.80±0.039	1.2
PFOS		0.62±0.018	0.61±0.34	0.92±0.11	1.2±0.11	1
FOSA		0.35±0.49	0	1.4±1.9	nc	0
6:2 FTSA		0.32±0.45	0.99±0.62	1.3±0.48	1.2±0.37	1.3
∑PFASs		0.53±0.065	0.55±0.059	0.99±0.093	1.0±0.092	1.4±0.13

8.4 PFAS RAW DATA

Table. I presents the raw data from PFAS analysis with correlating experimental settings as well as period and week.

Table. I Raw data concentration for all PFASs over the entire experimental period.

	Period	Week	Run time	Particle size	Flow	PFHxA	PFHpA	PFOA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	6:2 FTSA
			w	mm	L d^{-1}												
Inflow	A1	1	1	-	60	5.6	1.4	4.2	0.45	0	0	0.28	0	9.9	6.9	0.31	0.72
GAC	A1	1	1	2	60	1.6	0	0.83	0.24	0	0.82	0.37	1.5	1.2	0.77	0	0
Bark	A1	1	1	2-5	60	8.6	2.9	4.7	0.56	0	0	0.095	0	12	7.0	0	0.90
Inflow	A2	2	0	-	10	8.0	1.3	4.6	1.5	3.0	3.9	0.61	0	13	8.1	0.49	1.1
GAC	A2	2	2	2	10	0.52	0	0.32	0.031	0	0	0.11	0	0.54	0	0	0
GAC	A2	2	2	2	10	0.81	0	0.51	0.014	0	0	0	0	1.1	0	1.1	0
Bark	A2	2	2	2-5	10	0	0	4.0	0.20	0	0	0	1.9	10	4.9	0.34	0
Bark	A2	2	2	2-5	10	0	0	3.9	0.24	0	0	0	0	10	5.1	0	0.73
Inflow	B1	3	0	-	30	6.6	0	4.0	0.72	0	0.98	0	2.2	7.2	5.2	0.31	1.3
GAC	B1	3	1	2	30	0.85	0	0.42	0.071	0	0.53	0.22	0	0.55	0	0	0
GAC	B1	3	1	2	30	0.57	0	0.42	0	0	0	0	0	0.53	0	0.79	0
Bark	B1	3	1	2-5	30	0	0	1.8	0.090	0	0	0	0.87	3.8	1.9	0	0.72
Bark	B1	3	1	2-5	30	0	0	4.0	0.32	0	0	0	2.1	7.4	4.4	0	1.8
Inflow	C1	5	0	-	30	6.1	1.1	3.9	0.54	0	0.75	0.13	2.1	7.8	5.3	0.30	0.95
GAC	C1	5	1	2	30	0.53	0	0.38	0.058	0	0	0.079	0	0.56	0.81	0.78	0
GAC	C1	5	1	2	30	0.53	0	0.26	0	0	0	0	0	0.36	1.2	0	0
Bark	C1	5	1	2-5	30	7.2	1.1	4.1	0.26	0	0	0	1.7	7.8	4.5	0	1.6

Bark	C1	5	1	2-5	30	6.7	1.4	3.9	0.33	0	0	0	2.0	7.8	5.3	0.82	0.92
Inflow	C2	6	0	-	45	6.0	1.3	3.5	0.33	0	0	0	1.9	7.9	4.6	0	0.91
GAC	C2	6	2	2	45	1.6	0	0.94	0.16	19	2.3	0	0	1.3	2.6	0.50	0
GAC	C2	6	2	2	45	1.9	0	0.84	0.036	0	0	0	0	1.2	1.2	0	0
Bark	C2	6	2	2-5	45	6.6	0	3.6	0.30	0	0	0	2.6	6.1	5.8	0.31	0.86
Bark	C2	6	2	2-5	45	6.2	1.0	3.3	0.21	0	0	0	2.3	6.5	5.1	0.65	1.3

8.5 RAW DATA CONVENTIONAL ANALYSIS

Raw data from the COD, TOT-N and TSS analysis are presented in Table. J, Table. K and Table. L correspondingly. Yellow marked values are outliers that were removed.

Table. J COD in mg L^{-1} for correlating period, week day and date

		A2	**B1**	**C1**	**C2**
Week		W2	W3	W5	W6
Day		D15	D2	D21	D27
Date		17-mar	31-mar	20-apr	26-apr
In.1	mg L^{-1}	31	9	165	41
In.2	mg L^{-1}	35	9.1	37	14
A1.1	mg L^{-1}	82	5.9	<10	23
A1.2	mg L^{-1}	76	6.4	<10	325
A2.1	mg L^{-1}	44	7	<10	87
A2.2	mg L^{-1}	65	6.5	<10	16
B1.1	mg L^{-1}	14	8.4	<10	88
B1.2	mg L^{-1}	24	7.8	<10	128
B2.1	mg L^{-1}	121	8.5	11	29
B2.2	mg L^{-1}	44	7.1	<10	35
Blank	mg L^{-1}	5<10	1.2	<10	<10

Table. K TOT-N in mg L^{-1} for correlating period, week day and date

		A2	**B1**	**C1**	**C2**
Week		W2	W3	W5	W6
Day		D15	D2	D21	D27
Date		17-mar	31-mar	20-apr	26-apr
In.1	mg L^{-1}	2.2	10	6.5	7.8
In.2	mg L^{-1}	2.4	15	6.3	7.1
A1.1	mg L^{-1}	8.7	<10	5.4	7.6
A1.2	mg L^{-1}	7.9	<10	5.5	7.6
A2.1	mg L^{-1}	9.1	<10	5.6	8.1
A2.2	mg L^{-1}	4.4	10	5.4	9.3

B1.1	mg L^{-1}	5.3	45	5.5	6.8
B1.2	mg L^{-1}	14.1	34	6.1	7.1
B2.1	mg L^{-1}	8.3	37	6.4	7.4
B2.2	mg L^{-1}	5	36	5.4	6.4
Blank	mg L^{-1}	1.3	<10	1.5	1.6

Table. L TSS in g L^{-1} for correlating period, week day and date

		A2	**B1**	**C1**	**C2**
Week		W2	W3	W5	W6
Day		D15	D2	D21	D27
Date		17-mar	31-mar	20-apr	26-apr
In.1	g L^{-1}	0.0015	0.0040	0.0040	-0.0020
In.2	g L^{-1}	0	0	0.0020	0.0010
A1.1	g L^{-1}	0.0030	-0.0035	0.0015	-0.0070
A1.2	g L^{-1}	-0.0070	0	-0.0054	-0.0085
A2.1	g L^{-1}	-0.0030	-0.00050	-0.0035	-0.0090
A2.2	g L^{-1}	0.0050	-0.0060	-0.0070	-0.0080
B1.1	g L^{-1}	-0.001	-0.0040	-14	-0.014
B1.2	g L^{-1}	-0.004	-0.0050	-0.0102	-0.0060
B2.1	g L^{-1}	-0.45	0.0075	-0.0030	-0.014
B2.2	g L^{-1}	0.0035	-0.0015	0.0039	-0.0071
Blank	g L^{-1}	-0.0093	-0.0030	0.0010	-0.0010