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Evaluation of a bark adsobent for removal of pharmaceuticals from wastewater

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ABSTRACT

During and after medical treatment, pharmaceutical compounds as well as their metabolites and conjugates are excreted from the users through urine and feces. The pharmaceuticals end up in wastewater treatment plants, which are not designed to deal with this kind of organic micro-pollutant. Eventually the pharmaceuticals end up in the environment where they can have adverse physiological and behavioral effects on aquatic life and could contribute to the spread of antibiotic resistance among microorganisms. Adsorption to activated carbon is an established method for removal of pharmaceuticals from wastewater. It is however quite expensive and it is of interest to identify cost-effective alternatives. One possible alternative is bark, which is a common by-product from forest industry and has a complex microstructure and high porosity compared to many other naturally occurring materials.

In order to investigate the potential of using bark to remove pharmaceuticals from municipal wastewater four column filters were built, two with activated carbon and two with bark. They were used in an experiment conducted at Kungsängsverket, the largest wastewater treatment plant in Uppsala municipality. The objectives were to assess pharmaceutical concentrations in treated wastewater at Kungsängsverket and to compare the performance of bark and activated carbon filters under different loading rates. During this time the filters were run at different loading rates and two different types of bark was used. 24 common pharmaceuticals from different therapeutic groups were targeted.

The pharmaceutical concentrations measured at Kungsängsverket were generally low, but mean concentrations of five pharmaceuticals (atenolol, metoprolol, furosemide, hydrochlorothizide and diclofenac) exceeded 250 ng/l. Out of these, four have been shown to have adverse effects on aquatic life and it would be preferable if they were not released into the recipient.

Bark was not as good at removing pharmaceuticals from wastewater as activated carbon was, but decent removal rates were achieved for several compounds. The removal rates of either filter type did not seem to be significantly impacted by variations in loading rate or bark size. The concentrations of a few compounds increased after treatment with the bark filters and the reason for this is not clear. One possibility is interference from other organic substances in the wastewater or the bark, but determining the reason for this increase should be a priority for any further research on the subject.

Another problem encountered during the project that is likely to pose a problem for future implementation is that the bark filters were very sensitive to clogging. Running the filters at full scale would require frequent back-washing which would be a disadvantage from both economical and practical reasons.

Keywords: wastewater treatment, pharmaceuticals, activated carbon, bark, adsorption

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REFERAT

Läkemedel är utformade för att vara resistenta mot biologisk nedbrytning och vid medicinering utsöndrar användaren de aktiva substanserna i princip onedbrutna. Läkmedlen hamnar efter utsöndring i avloppsreningsverken som inte är anpassade för att ta hand om den här typen av organiska föroreningar. De följer därför med det renade avloppsvattnet ut i recipienten och vidare i naturen. I dagsläget har läkemedel hittats i ytvatten, sediment, grundvatten och jord; vilket är oroande eftersom flera läkemedel har negativa effekter på vattenlevande organismer och kan bidra till spridning av antibiotikaresistens.

Det behövs särskilda reningstekniker för att rena läkemedel från avloppsvatten och en effektiv sådan är adsorption till aktiverat kol. Aktivt kol är dock dyrt och det finns därför intresse för att hitta alternativa material som ger god effekt till ett lägre pris. Ett alternativ skulle kunna vara bark som är en vanlig restprodukt från skogsindustrin med en komplex mikrostruktur och stor porositet jämfört med många andra naturliga material.

För att undersöka om den här potentialen verkligen fanns gjordes ett försök på Kunsgängsverket i Uppsala. Fyra kolumnfilter byggdes; två med aktivt kol och två med tallbark. Målet var dels att undersöka hur mycket läkemedel som fanns i avloppsvattnet som renats på Kungsängsverket, och dels att jämföra läkemedelsreningen för de två filtertyperna. Under försöket kördes filtren med olika avloppsvatten-belastning och dessutom undersöktes två sorters bark med olika partikelstorlek. Tjugofyra olika läkemedel från flera terapeutiska grupper så som smärtstillande, vätskedrivande, anti-depressiva och beta-blockerare undersöktes.

Läkemedelskoncentrationerna som uppmättes på Kungsängsverket var generellt låga, men fem substanser stack ut: atenolol, metoprolol, furosemid, hydroklortiazid och diclofenac. Av dessa fem har fyra bekräftats ha negativa effekter på vattenlevande organismer och det skulle vara önskvärt att de inte släpptes ut i Kungsängsverkets recipient Fyrisån.

Avloppsvattenbelastning och storlek på barkpartiklarna verkade inte ha någon större påverkar på reningseffektiviteten. Bark är inte ett lika bra material som aktivt kol för att rena läkemedel från avloppsvatten, trots att reningseffektiviteten var bra för flera substanser. Det är framförallt två problem som påverkar möjligheten att kunna använda barkfilter för att rena läkemedel ur avloppsvatten. De analyserade koncentrationerna av flera läkemedel ökade när vattnet passerade genom barkfiltren och anledningen är inte känd. En möjlig orsak är störningar under analysen från organiska föreningar i avloppsvattnet eller i barken ger en falsk ”ökning” under analysen. Att ta reda på orsaken till den observerade ökningen bör vara en prioritet för framtida forskning på området.

Det andra problemet som upptäcktes var att barkfiltren är känsliga för igensättning av slam. Om barkfilter skulle implementeras i full skala skulle det krävas frekvent backspolning för att hindra filtren från att sättas igen vilket skulle vara en nackdel av både praktiska och ekonomiska skäl.

Nyckelord: avloppsvattenrening, läkemedel, aktivt kol, bark, adsorption

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PREFACE

This thesis corresponds to 30 credits has been made as the final part of the Master Programme in Environmental and Water Engineering at Uppsala University and the Swedish University for Agricultural Sciences. The project has been a collaboration between Swedish University for Agricultural Sciences and IVL Swedish Environmental Research Institute. The supervisor of this project has been Sahar Dalahmeh, researcher at the Department of Energy and Technology at the Swedish University for Agricultural Sciences. Håkan Jönsson, Professor at the Department of Energy and Technology at the Swedish University for Agricultural Sciences, has been the subject reviewer and the examiner was Anna Sjöblom, Senior Lecture at the Department of Earth Sciences at Uppsala University. Christian Baresel has been the contact at IVL Swedish Environmental Research Institute.

I want to thank everyone mentioned above for your kind help in bringing this project from start to finish, your help and advice has been very valuable. I would like to thank Jörgen Magnér and Linda Örtlund at IVL for the help with the analysis of the pharmaceuticals and Erik Cato at Kungsängsverket for allowing us to run the experiment there.

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POPULÄRVETENSKAPLIG SAMMANFATTNING

Världen konsumerar mediciner som aldrig förr och konsumtionen väntas bara öka de närmaste åren när fler och fler läkemedel blir tillgängliga på den globala marknaden. Men det finns ett stort problem: läkemedel är utformade för att vara svårnedbrytbara vilket innebär att de inte bryts ner i kroppen i någon större utsträckning. Vid behandling hamnar läkemedlen eller deras eventuella nedbrytningsprodukter i avloppet och så småningom i ett reningsverk. Avloppsreningsverken är inte utrustade för att ta hand om läkemedel och andra liknande föroreningar. Beroende på det enskilda läkemedlets egenskaper kan det skiljas från vattnet tillsammans med fast material genom sedimentation eller brytas ned under den biologiska reningen. Men många läkemedel följer med det renade avloppsvattnet ut till sjöar och vattendrag och sprids vidare i miljön.

Närvaron av läkemedel i miljön är oroande av flera anledningar. Antibiotika i miljön kan dels skada naturliga samhällen av bakterier, svampar och andra mikroorganismer, dels bidra till spridning av antibiotikaresistens. I de fall läkemedelsrester spridit sig till grundvatten kan det finnas en risk att det hamnar i dricksvatten. Dessutom är det bevisat att flera läkemedel har negativa effekter på vattenlevande organismer. Dessa effekter är oftast kroniska snarare än akuta, vilket innebär att de uppstår efter exponering för låga koncentrationer under lång tid och de kan därför vara svåra att upptäcka.

För att förhindra att läkemedel kommer ut i naturen krävs särskilda reningstekniker i avloppsreningsverken. En etablerad metod som ger mycket goda resultat är adsorption, eller bindning, till aktiverat kol. Kolet har behandlats för att göra det mer poröst och öka den specifika arean vilket innebär att mycket föroreningar kan binda till materialet. Aktivt kol är dock dyrt och det finns därför intresse för att hitta alternativa material som ger god effekt till ett lägre pris. Ett möjligt alternativ skulle kunna vara bark som är en vanlig restprodukt från skogsindustrin med och är väldigt poröst jämfört med många andra naturliga material.

Syftet med projektet var att undersöka om bark verkligen har potential för att kunna användas för att rena läkemedelsrester från avloppsvatten. Ett försök gjordes på Kungsängsverket i Uppsala där fyra filter byggdes och testades, två med aktivt kol och två med tallbark. Under försöket kördes filtren med olika avloppsvattenbelastning och två sorters bark undersöktes. Koncentrationer av tjugofyra olika läkemedelssubstanser mättes före och efter filtren för att kunna beräkna reningsgraden. Läkemedlen tillhörde olika behandlingsgrupper så som smärtstillande, vätskedrivande, anti-depressiva medel och beta-blockerare. Målen var att:

- Undersöka hur mycket läkemedel som fanns i avloppsvattnet som renats på Kungsängsverket.
- Jämföra reningsgraden för aktivt kolfilter och barkfilter.
- Undersöka om belastning och storlek på barkstorlek påverkar reningsgraden

Koncentrationerna av läkemedel som uppmättes på Kungsängsverket var generellt låga och vid en jämförelse med andra svenska reningsverk låg de uppmätta halterna under medel. Fem substanser stod dock ut med höga koncentrationer över 250 ng/l: två beta-blockerare, två vätskedrivare och ett smärtstillande. Av dessa fem har alla utom ett bekräftats ha negativa effekter på vattenlevande organismer och det skulle vara önskvärt att de inte släpptes ut i Fyrisån med det renade vattnet från Kungsängsverket.

Reningsgraden för filtren med aktivt kol var mycket god, i de flest fall över 90 % med mycket små variationer mellan veckor med olika belastning. Barkfiltren hade en lägre reningseffektivitet, men även för dessa filter var skillnaderna i reningsgrad mellan veckor med olika belastning och barktyper mycket små. För flera läkemedel var barkfiltrens reningsgrad god, vissa läkemedelskoncentrationer minskade dock inte alls medan några andra ökade. Detta är ett allvarligt problem som påverkar möjligheten att använda barkfilter för att rena läkemedelsrester ur avloppsvatten. Skälet till denna ökning är höljt i dunkel. En möjlighet är att det rör sig om en falsk ”ökning” på grund av störningar från andra föreningar i avloppsvattnet eller i barken. Att ta reda på orsaken till den observerade ökningen bör vara en prioritet för framtida forskning på området.

Under projektet upptäcktes även att barkfiltren var känsliga för igensättning av slam. Om barkfilter skulle implementeras i full skala skulle det krävas frekvent rengöring för att hindra filtren från att sättas igen vilket skulle vara ohållbart av både praktiska och ekonomiska skäl. Dessa två problem visar på att bark inte är ett lika bra material för att rena läkemedel från avloppsvatten som aktivt kol.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variances
BOD_5	Biochemical oxygen demand over 5 days
BOD_7	Biochemical oxygen demand over 7 days
COD	Chemical oxygen demand
DDD	Defined daily doses
GAC	Granular activated carbon
HPLC-MS/MS	High-performance liquid chromatography coupled with tandem mass spectrometry
IS	Internal standard
IVL	IVL Swedish Environmental Research Institute
LOD	Limit of detection
LOQ	Limit of quantification
MF	Microfiltration
MQ	Milli-Q
NF	Nanofiltration
PAC	Powdered activated carbon
PhAC	Pharmaceutically active compound
POP	Persistent organic pollutant
RO	Reverse Osmosis
SLU	Swedish University for Agricultural Sciences
SPE	Solid phase extraction
SSRI	Selective serotonin reuptake inhibitor
TOC	Total organic carbon
Tot-N	Total nitrogen
Tot-P	Total phosphorous
TSS	Total suspended solids
UF	Ultrafiltration
WWTP	Wastewater treatment plant

1. INTRODUCTION

Medicine has come a long way since the first synthetic drug was introduced in 1869 (Jones, 2011). Today thousands of pharmaceutical compounds are used around the world and that number is expected to increase (IMS Institute, 2015). In order to remain stable before treatment, and in the patients' bodies during treatment, these compounds are often designed to be resistant to biological transformation. However, this means that some of the pharmaceuticals are not easily degraded in the wastewater treatment plants where the compounds end up after excretion (Swedish Environmental Protection Agency, 2008). The pharmaceuticals follow outflowing water into the recipients where they can have adverse effects on the aquatic life. Another cause for concern is the potential risk to human health in case of contamination of drinking or irrigation water as well as increased antibiotic resistance among pathogens (Jones et al., 2003, 2005a).

Thus, there is a need for complementary treatment methods that offer efficient removal of pharmaceuticals while being cost-effective. Adsorption to activated carbon is one of the most effective methods of removing pharmaceutical compounds from wastewater to date. The carbon has been specially treated to increase the porosity and the specific surface area, which allows for considerable removal rates of many substances (Swedish Environmental Protection Agency, 2008). Activated carbon is however quite expensive and it is of interest to identify cost-effective alternatives (Homem and Santos, 2011). This project has been an attempt to investigate the potential of bark as an alternative adsorbent of pharmaceuticals for treated municipal wastewater. The project has been a collaboration between Swedish University for Agricultural Sciences (SLU) and IVL Swedish Environmental Research Institute (IVL).

1.1 AIM

The aim of the project has been to examine the potential of bark as an adsorbent material for removal of pharmaceuticals from treated wastewater in comparison to granular activated carbon (GAC). The specific objectives were:

- Assess the concentrations of selected pharmaceuticals in wastewater treated at Kungsängsverket wastewater treatment plant (WWTP) in Uppsala
- Assess the performance of bark filters in removal of pharmaceuticals from the treated wastewater at Kungsängsverket under different loading rates and using two bark types with different particle sizes
- Compare the performance of bark filters with that of granular activated carbon (GAC) filters regarding pharmaceutical adsorption

The approach used to achieve the objectives was by installing bark and GAC filters which were fed continuously with treated wastewater at Kungsängsverket. Concentrations of 24 pharmaceutical target analytes in filter inflow wastewater and effluent were determined and the reduction of pharmaceuticals from the municipal wastewater was assessed during the first 1-2 weeks of the filter service life. The experiment was run for six weeks in total (2/3-26/4 2016). The results were compared to pharmaceutical reduction of achieved with GAC filters that were operated in parallel to the bark filters.

1.2 LIMITATIONS

This project has focused on the first two weeks of filter service life for two reasons. The efficiency of GAC filters, and likely bark filters, decrease with time and because of this the highest removal rates are found early on. The second reason was practical; the filters had to be repacked with new material and loading rates changed because of frequent problems with clogging and overflowing.

2 BACKGROUND
2.1 PHARMACEUTICALS
2.1.1 In society
The world is consuming more pharmaceuticals than ever and the market is expanding. In 2014, the revenues in the worldwide pharmaceutical market exceeded 1 trillion US dollars, compared to 390.2 billion US dollars in 2001 (Statista, www). The market is expected to increase by approximately 30% to 1.4 trillion dollars in 2020 and the amount of doses per year is expected to increase to 4.5 trillion, where the largest increases can be found in emerging markets like India, China, Brazil and Indonesia (IMS Institute, 2015).

The number of pharmaceutically active compounds (PhACs) available to the world's population is ever increasing. According to recent estimations, there will be 943 so-called "New Active Substances" that have been introduced during the previous 25 years on the worldwide market in 2020 and populations around the world will have access to most of these substances. Many of the breakthroughs expected in the next few years concern treatment of heart disease, autoimmune diseases, hepatitis C and several forms of cancer (IMS Institute, 2015).

It is however important to keep in mind that PhACs are not the only organic micropollutant in water that need to be considered. In fact they only make up a small part of the 50,000-100,000 synthetic chemicals that are estimated to be commercially available (Platt McGinn, www). Apart from medications, humans also consume stimulants, sweeteners and parabens. Other important groups with significant effects on the environment and human health include pesticides, perfluoroalkyl substances (PFASs) and plasticizers.

In 2014, the total amount of pharmaceuticals sold in Sweden was 1,728 defined daily doses (DDD) per 1,000 inhabitants, which corresponded to a total sales value of 37,829 million SEK excluding VAT. This was an increase by approximately 300 DDD/1,000 inhabitants from 2002 and most of this took place between 2002 and 2009 (eHälsomyndigheten, 2015). The large amount of pharmaceuticals sold is a natural consequence of the fact that medicine is the most prevalent treatment in the Swedish healthcare system (Swedish National Board of Health and Welfare, 2016). On the Swedish market, there are approximately 7,600 pharmaceutical products and 1,200 active substances, most of which are intended for human use. There are many gaps of knowledge regarding environmental effects, largely due to lack of data needed for risk assessment (Björlenius et al., 2010).

Around 66% of the population used at least one prescription pharmaceutical in 2015. The corresponding percentage for women was 74% compared to 58% for men. The largest differences in pharmaceutical use between the sexes were found for contraceptives, painkillers, antidepressants, anti-ulcer agents and soporifics where women consumed more. These numbers have remained more or less the same for the last few years. Doctors prescribe less antibiotics and more anti-ulcer agents. The use of the effective treatment of hepatitis C which was introduced in 2014 continued to increase (Swedish National Board of Health and Welfare, 2016).

Some measures have been taken in order to reduce the use of pharmaceuticals, including reviews of patients' medicine use and more ordinations regarding lifestyle changes. The public are encouraged to return leftover medication to pharmacies for destruction and a system for environmental classification of pharmaceuticals has been introduced as an aid to doctors (Björlenius et al., 2010).

2.1.2 In the environment

As many pharmaceuticals are not removed during wastewater treatment, they will be released into the environment along with the treated wastewater. Pharmaceutical compounds have been found in surface water, sediment, groundwater and soil (Fatta-Kassinos et al., 2011). The presence of pharmaceuticals in natural environments is a cause for alarm, especially since there are knowledge gaps regarding their effects on various organisms. Three areas of concern are physiological and behavioral effects on aquatic life, potential threats to drinking water and possible development and spreading of antibiotic resistance among microorganisms (Jones et al., 2003).

Several pharmaceuticals have been proven to have negative effect on aquatic organisms (Table 1). These effects are rarely acute but rather chronic in nature, meaning that the symptoms are only exhibited after long-time exposure at either high or low concentrations. One major uncertainty when it comes to pharmaceuticals in the environment is the fact that very little is known about how different compounds interact with each other. The synergistic and antagonistic effects the compounds can have on each other is popularly referred to as “the cocktail effect” (Vasquez et al., 2014).

The negative effect from pharmaceuticals on aquatic organisms depends on the compound in question. For example, natural estrogen as well as artificial hormones from contraceptives and other endocrine disrupting substances can cause hermaphroditism, delayed development of eggs and changes in male sex organs for fish (Björlenius et al., 2010). In Table 1, environmental effects from the pharmaceutical compounds studied in this project are presented. It is important to note that the absence of a description of environmental effects for some compounds simply means that no studies describing specific effects have been found. It does not imply that there are no environmental risks associated with the compound in question.

Table 1. Effects on aquatic environment from target compounds.

Compound	Function	Effects on aquatic environment	Reference
Amlodipine	Calcium channel blocker: lowers blood pressure by widening blood vessels	Inhibition of regenerative properties of *Hydra vulgaris*	(Pascoe et al., 2003)
Atenolol	Beta-blocker: treatment of cardiac arrhythmias and hypertension (high blood pressure)	Reduction of the amount of red blood cells and glucose in rainbow trout blood plasma	(Steinbach et al., 2014)
Bisoprolol	Beta-blocker: treatment of cardiac arrhythmias and hypertension (high blood pressure)	-	
Caffeine	Central nervous system stimulant	-	
Carbamazepine	Treatment of epilepsy and neuropathic pain	Damage to liver, kidneys and gills of fish, Inhibition of emergence of *Chironomus riparius*, Inhibition of enzyme activity in fish liver cells	(Laville et al., 2004; Oetken et al., 2005; Triebskorn et al., 2007)
Citalopram	Antidepressant (SSRI)	Reduced amount of neonates per female in *Ceriodaphnia dubia*	(Henry et al., 2004)
Diclofenac	Nonsteroidal anti-inflammatory drug (NSAID): anti-inflammatory, analgesic, antipyretic	Damage to liver, kidneys and gills of fish, Inhibition of enzyme activity in fish liver cells	(Triebskorn et al., 2007)
Fluoxetine	Antidepressant (SSRI)	Reduced activity in Amphipoda, Inhibition of enzyme activity in fish liver cells, Reduced amount of broods per female in *Ceriodaphnia dubia*	(De Lange et al., 2009; Henry et al., 2004; Laville et al., 2004)
Furosemide	Diuretic: Prevent fluid build-up, treatment of high blood pressure	Inhibition of growth in crustaceans, rotifers and bacteria + potentially mutagenic photoproduct	(Isidori et al., 2006)
Hydrochlorothiazide	Diuretic: Prevent fluid build-up, treatment of high blood pressure	-	
Ibuprofen	Nonsteroidal anti-inflammatory drug (NSAID): anti-inflammatory, analgesic, antipyretic	Reduced activity in Amphipoda, Inhibition of growth in duckweed and stimulation of cyanobacteria growth	(De Lange et al., 2009; Laville et al., 2004; Pomati et al., 2004)
Ketoprofen	Nonsteroidal anti-inflammatory drug (NSAID): anti-inflammatory, analgesic, antipyretic	-	
Metoprolol	Beta-blocker: treatment of cardiac arrhythmias and hypertension (high blood pressure)	Damage to liver, kidneys and gills of fish	(Triebskorn et al., 2007)
Naproxen	Nonsteroidal anti-inflammatory drug (NSAID): anti-inflammatory, analgesic, antipyretic	-	
Oxazepam	Benzodiazepine: treatment of anxiety, insomnia and alcohol withdrawal	Behavioral changes in European perch	(Brodin et al., 2013)
Paracetamol	Analgesic	-	
Propranolol	Beta-blocker: treatment of cardiac arrhythmias and hypertension (high blood pressure)	Weak inducer of enzyme activity in fish liver cells	(Laville et al., 2004)
Ramipril	Angiotensin-converting-enzyme inhibitor: treatment of hypertension (high blood pressure)	-	
Ranitidine	Anti-ulcer agent: decreases stomach acid production	Inhibition of population growth in crustaceans and rotifers	(Isidori et al., 2008)
Risperidone	Antipsychotic: schizophrenia, bipolar disorder, autism-related irritability	-	
Sertraline	Antidepressant (SSRI)	Reduced amount of neonates per female in *Ceriodaphnia dubia*, Accelerated development rate and reduced feeding rated of tadpoles	(Conners et al., 2009; Henry et al., 2004)
Simvastatin	Lipid-regulator: decreases elevated lipid levels	-	
Terbutaline	β2 adrenergic receptor agonist: “reliever” for asthma symptoms, delay pre-term labor	-	
Warfarin	Anticoagulant	-	

Although the environmental risks associated with pharmaceutical compounds are significant, the general public tends to be more concerned with human exposure (Jones et al., 2005b). As the need for direct and in-direct water reuse increases globally, the question becomes more relevant. Acute effects as a result of the presence of pharmaceuticals and their metabolites in drinking water are extremely unlikely due to low concentrations (Jones et al., April 2005b). However, very little is known about chronic effects caused by long-time exposure to sub-therapeutic concentrations of PhACs and how the different compounds might interfere with each other. In a possible but unlikely scenario, sub-therapeutic concentrations of pharmaceuticals in drinking water might interfere with medication treatments. The presence of pharmaceuticals and their metabolites in drinking water most likely poses no risk for healthy adults, but there could be variations in sensitivity and dose responses due to gender, maturation, vulnerable life stages (i.e. pregnancy) and allergies (Jones et al., April 2005b).

In addition to having a negative impact on natural microbial communities, the spreading of antibiotics in nature could contribute to increased antibiotic resistance. Today antibiotic resistant strains of pathogenic bacteria have been found in wastewater and WWTPs, some of which are multi-resistant. This type of microorganism strains have also been found in different environmental compartments, like surface waters and soils (Kümmerer, 2003). The increase of antibiotic resistant microorganisms is usually considered a result of increased use of antibiotics in society, particularly irresponsible use like unnecessary prescriptions and use without prescriptions (Jones et al., 2003)

The presence of microorganisms that are resistant or multi-resistant to antibiotics is worrying since gene transfer between microorganisms means that the resistant genes could be spread further. Surface waters could also act as a reservoir and source of these resistant genes (Jones et al., 2003). Large amounts of antibiotics are also used in animal husbandry and in many countries this by far exceeds the human use. The fact that the concentrations of antibiotics in wastewaters and recipients are significantly lower than the therapeutic dose does not mean that the conditions for spread of antibiotic resistant genes are negatively affected. On the contrary, these low concentrations are believed to be important for spreading and maintaining antibiotic resistance (Gullberg et al., 2011).

2.2 REMOVAL OF PHARMACEUTICALS FROM WASTEWATER

2.2.1 Behavior of pharmaceuticals in wastewater treatment

During and after medical treatment, pharmaceutical compounds as well as their metabolites and conjugates are excreted from the users through urine and feces. The PhACs eventually end up in the wastewater treatment plants, which are not designed to deal with this kind of organic micropollutant. Although the concentrations will be reduced in the wastewater treatment processes for most pharmaceuticals substances, this depends greatly on the physiochemical properties of the compounds and the treatment train of the WWTP in question (Swedish Environmental Protection Agency, 2008).

The removal paths for organic pollutants are evaporation to air, sorption to particles and subsequent sedimentation and biological transformation (Björlenius et al., 2010). Since very few pharmaceuticals are volatile, the removal through evaporation is negligible in practice and will not be described further. In Sweden, treatment at municipal WWTPs usually consists of three steps in series: mechanical treatment where larger waste and particles are removed, biological treatment for removal of organic material (and sometimes nitrogen) and chemical precipitation of phosphorous with sedimentation between the different treatment steps (Svenskt Vatten AB, 2013).

Sorption of PhACs to particles can take place as either absorption where aliphatic and aromatic groups interact with sludge fat fractions and lipophilic cell membranes, or adsorption where positively charged compounds interact with negatively charged microorganism surfaces (Ternes et al., 2014). Removal by sorption and sedimentation occurs mainly at the presedimentation and at the biological treatment steps (Björlenius et al., 2010). Removal of pharmaceuticals through biological transformation is likely a result of co-metabolism or mixed substrate growth since the concentrations of PhACs in the wastewater are low (Ternes et al., 2014). In the case of co-metabolism, the degradation or partial transformation is a result of broad-acting enzymes acting on a primary substrate and the PhACs are not used as a carbon source. For mixed substrate growth, the PhACs are used as a carbon and energy source and complete degradation is likely. However, a primary substrate is still needed to support the microbial community (Ternes et al., 2014).

Important factors that influence the degradation of PhAcs include sludge age, redox conditions and pH. The pH of the wastewater and the pKa of the pharmaceuticals affect their distribution between water and sludge particles (Björlenius et al., 2010). The availability of oxygen, nitrate and other oxidizing compounds affect the degradation ability of the micro-organisms (Ternes et al., 2014). A factor that influences the biological transformation of PhACs in WWTP is the sludge age. An increase in sludge age means that microorganisms with slower growth have time develop and that the microbial community can become acclimatized to the present compounds (Jones et al., 2005a).

The presence of biological removal of nitrogen by nitrification/denitrification in the treatment train has proven to have a positive influence on the removal of PhACs. A likely reason for this is that, besides the increased sludge age, the sequence of aerated and non-aerated zones means that the compounds are exposed to a wide range of microorganisms and redox potentials, which allows for sequential transformation (Jones et al., 2005a).

The removal of pharmaceuticals has been shown to vary greatly between substances. Joss et al. (2005) studied the removal of seven pharmaceutical compounds in biological wastewater treatment and found that the removal of some substances like carbamazepine was insignificant (<10%) while others, like ibuprofen, were almost completely removed from the wastewater with low effluent concentrations as a result. A recent evaluation of the reduction of pharmaceuticals in Swedish WWTPs with biological nitrogen removal found that approximately 25% of the detected pharmaceuticals were removed to a high degree (>75%) and 25% were removed to a moderate degree (30-75%). Approximately 25% were removed to a limited degree (<30%) or not at all, while the concentrations of the last quartile increased. While the 25% that were removed to a high degree could probably be removed completely by optimizing existent technology, complementary treatment methods are needed in order to deal with the remainder (Hörsing et al., 2014).

The reason for the “negative removal” was likely the transformation in the WWTP of pharmaceutical conjugates and metabolites back to the parent compound. This kind of transformation between parent compounds and their derivatives can take place during complex metabolic processes like those in the human body and in the biological treatment step in WWTPs. It is also possible that there is some release of certain compounds, e.g. antibiotics and other macrolides, from feces with increasing concentrations being measured as a result (Jelic et al., 2011).

2.2.2 Complementary wastewater treatment technologies

As established in Section 2.1.2, there is a need for complementary treatment in order to remove pharmaceuticals and their metabolites from wastewater. The available treatment technologies can be divided into four groups: oxidation, photolysis, membrane filtration and adsorption. In this section, some of these methods will be presented. There is also a section discussing the potential use of bark as an adsorbent material for the removal of pharmaceuticals from wastewater.

Oxidation with ozone

Advanced oxidation methods are characterized by the formation of hydroxyl radicals. This section contains a brief description of the most common advanced oxidation method: ozonation.

Ozone is a strong oxidizing agent that has the potential to degrade most organic compounds to carbon dioxide and water under suitable conditions. Ozone oxidizes organic material either by acting directly on nucleophilic molecules or indirectly through formation hydroxyl radicals. The degradation is affected by the concentrations of organic matter, suspended solids, chlorine, carbonate and bicarbonate as well as pH and temperature (Homem and Santos, 2011). If the conditions are nonoptimal, like in the case of wastewater treatment with temperatures between 10-20°C and neutral pH, the required dose for a complete degradation will be very high (Swedish Environmental Protection Agency, 2008).

Ternes et al. (2003) investigated ozone's degradation of antibiotics, β-blockers, anti-inflammatory drugs, lipid regulator metabolites and anti-epileptics as well as contrast media, musk fragrances and estrone (natural estrogen). After exposure to ozone levels of 10-15 mg/l for 18 minutes all pharmaceutical levels were below the level of detection. Baresel et al. (2016) investigated the removal of 42 pharmaceuticals from municipal wastewater at Linköping WWTP using ozonation between bio-sedimentation and post-denitrification processes. They found that most substances were removed at an ozone dose of 5 mg O3/l, with no ecotoxicological effects.

Degradation rates can vary since ozone is a so-called selective oxidizer which degrades compounds by attacking functional groups like amino-groups, benzene rings and functional groups containing sulphur. The characteristics of the water determine which functional group will be reacting with the ozone (Swedish Environmental Protection Agency, 2008). It has also been shown that while the removal rates of the parent compound are often quite good, the degradation is generally not complete because of less than optimal conditions. Depending on the properties of the parent compound, the toxicity of the metabolites can increase, decrease or remain unchanged (Homem and Santos, 2011).

One of the advantages of ozonation is that the method is applicable for varying flow rates and wastewater composition (Homem and Santos, 2011). The water treated with ozonation is also disinfected, which is another advantage (Baresel et al., 2015). Disadvantages include the high costs associated with equipment and maintenance, high demand for energy and limitations regarding mass transfer between gas and liquid phase (Homem and Santos, 2011). The main disadvantages with ozonation are that the degradation is often not complete and that the metabolites may be toxic. Certain compounds are resistant to ozonation and and will remain even at high dosages (Baresel et al., 2015).

Membrane filtration

Pharmaceuticals can also be separated from wastewater by filtration through a semipermeable membrane. Membranes can be divided into four different categories depending on the pore size. The categories, presented in order of decreasing pore size are: microfiltration, (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Of these categories NF-filtration is the one deemed most suitable for removal of PhACs and other micro-pollutants from waste water. This is because the pores of MF- and UF-filters are too large and allow many compounds to pass through. The pores of RO-membranes on the other hand are too small and other molecules like salt are separated as well. RO membranes have the highest energy consumption and cost of all four membrane categories (Swedish Environmental Protection Agency, 2008).

Yoon et al. (2007) investigated the removal of 27 pharmaceuticals, personal care products and endocrine disruptors achieved by UF and NF. They found that the removal rates when using NF ranged between 30 and 90% for most compounds. This result was considered to be quite good, especially when compared with UF where only a few compounds had removal rates >30%. The same study suggests that hydrophobic adsorption is crucial for the removal and that size exclusion may only become the dominant removal mechanism after steady-state operation is achieved. As a result of this, hydrophobic compounds are more easily removed through membrane filtration than polar and volatile compounds. But while the molecular properties of the compounds that are to be removed influences how well the compound will be separated, the characteristics of the membrane and the water that is to be treated are of greater importance (Snyder et al., 2007).

Effective removal of PhACs and other micro-pollutants can be achieved using membranes requiring high-pressure like NF. Since the membranes can be stacked vertically this type of treatment method is suitable in situations where available space is limited. To protect NF- and RO-membranes from clogging, extensive pre-treatment is required and membranes operating at lower pressures, i.e. MF and UF, are very suitable for this purpose (Snyder et al., 2007). One disadvantage with NF membranes includes the high costs and energy consumption resulting from the high pressure used. There is also need for further treatment of the membrane permeate since there is no destruction of separated pollutants in the process (Swedish Environmental Protection Agency, 2008).

Adsorption to activated carbon

Adsorption is the adhesion of compounds originally found in a fluid medium, e.g. liquid or gas, to a solid surface or concentration of compounds in the interface between two fluid phases (Cecen and Aktas, 2012). The phases involved can be almost any combination of liquid, gas and solid: liquid-solid, gas-solid, gas-liquid and liquid-liquid. In the case of wastewater treatment adsorption takes place between a liquid phase (water) and a solid phase (in this case carbon). The adsorption is determined by two factors: the water solubility of the compounds that are to be removed and the electrical attraction between the compounds and the adsorbent surface. There are two types of adsorption: a strong adsorption of hydrophobic compounds and a weaker adsorption induced by van der Waal forces or chemical interaction (Cecen and Aktas, 2012). Activated carbon has a predominately negatively charged surface area. The surface area of activated carbon is >1000 m2/g and the pH is approximately 10.4 (Dalahmeh et al., 2012).

Adsorption to activated carbon is an established method for removal of organic micro-pollutants that is widely used in both industry and treatment of drinking water and wastewater.

This treatment method takes advantage of the large specific surface area that is a consequence of the extremely porous microstructure of specially treated (activated) carbon. This area is usually between 800 and 1,200 m2/g, which makes activated carbon unrivaled when it comes to the amount of active sites available for adsorption (Swedish Environmental Protection Agency, 2008).

Manufacturing of activated carbon consists of two steps: carbonization and activation. During the carbonization step raw materials with naturally high carbon content (e.g. coal, lignite, wood and peat) are pyrolyzed at a temperature of 400-600°C without access to oxygen. The microporous structure of the activated carbon is formed during the activation step. The carbon can be activated through either thermal activation with steam at a temperature >800° or chemical activation through impregnation with chemicals like phosphoric acid, potassium hydroxide and zinc chloride. Note that the impregnation takes place before the carbonization of the raw material (Cecen and Aktas, 2012).

There are two types of activated carbon: powdered activated carbon (PAC) and granular activated carbon (GAC). The average size of a PAC particle is 15-25 µm and because of the small size, PAC is usually added to the wastewater treatment process as a "feed chemical" either in the activated sludge process or in a separate treatment step. Later, it needs to be separated from the treated water. The size of GAC particles is between 0.2 and 5 mm which makes them suitable as filter materials which the water passes through (Cecen and Aktas, 2012).

The characteristics of the compounds that are to be removed and adsorbent properties like surface area, porosity and pore diameter are important factors that determine the adsorption efficiency. Another factor that influences the adsorption of micro pollutants is the content of dissolved organic matter in the water since it blocks micro-pores and thus competes with micro pollutants for the adsorption sites (Homem and Santos, 2011).

Removal of pharmaceuticals through adsorption to activated carbon has shown good results for both PAC and GAC. Snyder et al. (2007) examined the GAC filter removal of various micro pollutants, including pharmaceuticals. They found that the removal rates exceeded 90% for most compounds and similar removal rates have been observed in other studies. A study by Ek et al. (2014) investigated the removal of seven common pharmaceuticals from municipal wastewater using three serial-operated GAC-filters. The removal rates of these compounds ranged between 90 and 98%. It is worth noting that for treatment with GAC there is some risk for break-through of water soluble compounds since they are not as strongly bound as hydrophobic compounds. This can be remediated through regular regeneration or replacement of the filter material (Snyder et al., 2007). In time, biological transformation of pharmaceuticals and their metabolites will become possible as microbial communities get established in the filters.

One main advantage of adsorption as a removal process for pharmaceutical compounds is the fact that there is no formation of potentially toxic or carcinogenic metabolites. This is however coupled to one main disadvantage of the process; there is no degradation, only concentration. This means that the treatment process produces a solid waste with high concentrations of pharmaceuticals that needs to be disposed, e.g. through incineration (Homem and Santos, 2011). For GAC, thermal regeneration is an alternative to disposal. The regeneration process is however complicated and requires a lot of energy (Snyder et al., 2007).Since the cost for active carbon can be quite high and the regeneration process can be complicated there is considerable interest in finding cheaper alternatives to GAC. Studies have been done on waste

products from industry and agriculture like shells of hazelnuts, coconuts, walnuts, almonds etc. These materials have usually been activated in order to increase adsorption potential (Homem and Santos, 2011).

Potential of bark as an adsorbent material

In the previous section it was established that there is an interest for alternative adsorbent materials which could become viable and economical alternatives to activated carbon. The most interesting raw materials that have been investigated are waste products from agriculture and other industries. One material that might have potential as an adsorbent is bark, which is a porous material with a complex microstructure compared to many other naturally occurring materials (Dalahmeh et al., 2012). It has also been used for sorption of metals (Gundogdu et al., 2009). and degradation of organic compounds (Chosova et al., 2014). However, activated carbon and other man-made/synthetic materials are even more porous and thus have a larger surface area and adsorption potential. Since bark is a natural material that is not necessarily treated, it is possible that there are microorganisms present in the material which means that there is potential for biological degradation of organic compounds that could somewhat compensate for the smaller surface area (Dalahmeh, 2016). The surface area of pine bark is approximately 0.734 m2/g and its pH is approximately 5.1 (Dalahmeh et al., 2012).

Bark is a common by-product from forest industry such as saw-mills and pulp industries. Today, most of the bark is incinerated in order to recover energy and reduce the volumes put on landfills. Other uses for bark include soil conditioner and insulation for earthwork done at low temperatures (Carlsson, 2005). There is an interest from bark-producing businesses to find new applications for bark in order to create new markets and make revenue (Carlsson, 2005). According to the European Union's waste hierarchy the most desirable way to deal with waste is to reduce the amount of waste produced, followed by reuse, recycling, recovery of energy and lastly disposal. If bark can be used as an adsorbent this would mean that there is a way to reuse the waste before incinerating it.

The fact that bark can adsorb pollutants is not new information. It has been documented that atmospheric deposition of heavy metals can be assessed from concentrations in bark due to the adsorption of metals from the air (Kuang et al., 2007). Bark can also adsorb heavy metals like cadmium, lead, copper and nickel from water matrixes (Al-Asheh and Duvnjak, 1997; Gundogdu et al., 2009). Only a few studies concerning the removal of organic pollutants could be found and none of these included pharmaceuticals. One, however, investigated if biologically and chemically treated bark could be used to remove hydrocarbons from wastewater and it was found possible to remove 97% (Haussard et al., 2001). Another study aimed to investigate the potential of removing persistent organic pollutants (POPs) using bark, and focused on the pesticides lindane and heptachlor. The removal efficiency attained was 80.6% and 93.6% respectively (Ratola et al., 2003). From these studies it seems as though bark has the potential to remove organic pollutants from water.

Researchers at SLU have investigated the possibility of using bark filters to treat greywater in order to achieve irrigation quality. They found that the removal rates for common wastewater parameters were quite good: 98% of BOD5 was removed as well as ca 74% of COD and 97% of Tot-P. However, the removal of Tot-N was only 19%. The fact that the removal efficiency of COD was much lower than for BOD5 was believed to be due to the leaching of organic acids from the bark (Dalahmeh et al., 2012).

3. MATERIALS AND METHOD

3.1 KUNGSÄNGSVERKET

The experiment was conducted at Kungsängsverket, the largest wastewater treatment plant in Uppsala municipality. Approximately 171 400 persons are connected to Kungsängsverket and the amount of water treated during 2015 amounted to 17.9 million m3 of municipal wastewater (Uppsala Vatten och Avfall AB, 2015). The wastewater undergoes mechanical, biological and chemical treatment at the WWTP before it is released to Fyrisån. A principle sketch of the treatment is shown in Figure 1.

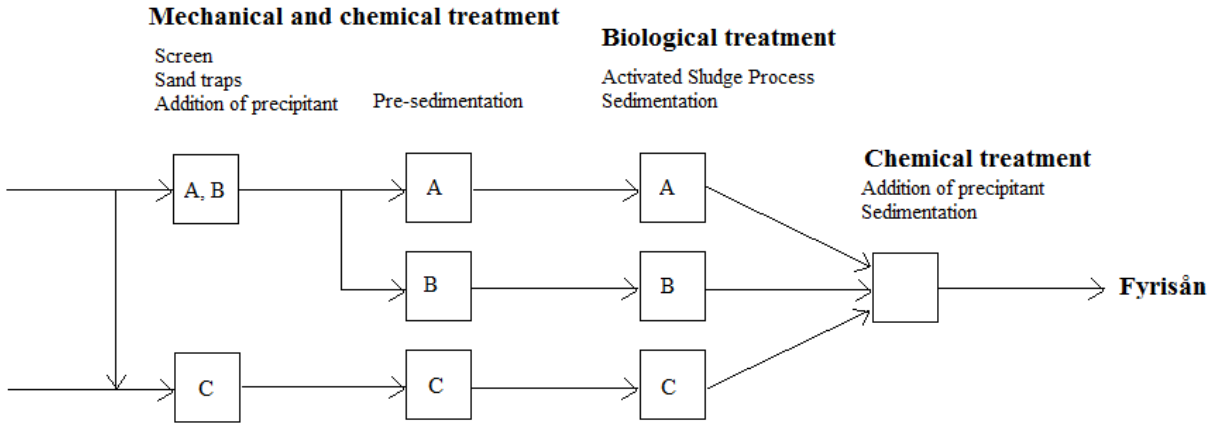

Figure 1. Principle sketch of the treatment train at Kungsängsverket. Adapted from (Uppsala Vatten och Avfall AB, 2015). Used with permission from Uppsala Vatten och Avfall.

In the mechanical treatment larger waste such as paper, plastic, rags etc. are removed using a screen. Heavier particles such as sand are removed in aerated sand traps before a precipitant (iron chloride) is added and particles are removed in a sedimentation step before the biological treatment (Uppsala Vatten och Avfall AB, 2015). In the biological treatment dissolved organic material is removed in the activated sludge process, where the wastewater is mixed with microorganisms (activated sludge). As the microorganisms grow and reproduce, the organic matter in the wastewater is degraded. Nitrogen is also removed from wastewater using biological processes by optimizing the conditions for the transformation of ammonia to nitrate (nitrification) and the transformation of nitrate to nitrogen gas (denitrification) (Svenskt Vatten AB, 2013).

At Kungsängsverket there are three lines of biological treatment with some differences between them: A, B and C. Descriptions of the treatment in lines A and C will be omitted since all water used in the experiment originated from line B. This line contains multiple nitrification and denitrification zones and water from the mechanical treatment is added gradually into the different denitrification zones. After the biological treatment, the water is led to sedimentation zones where the sludge is removed from the treated water. Some of the sludge is removed from the process while the rest is pumped back to the first denitrification zone. In line B, a sub-stream of the sludge is treated anaerobically before being returned to the treatment process to promote biological removal of phosphorous (Uppsala Vatten och Avfall AB, 2015).

In the final treatment step iron chloride is added to remove the remaining phosphorous by precipitation and sedimentation with lamella, which allows for a large effective sedimentation

area. Any remaining sludge flocks from the biological treatment are also removed in this step. The water is then released into the recipient (Uppsala Vatten och Avfall AB, 2015).

The efficiency for the removal of the four main pollutant parameters biological oxygen demand (BOD7), total organic carbon (TOC) and total phosphorous (Tot-P) during 2015 were all above 90% while the removal efficiency of total nitrogen (Tot-N) was 80% (Table 2) (Uppsala Vatten och Avfall AB, 2015).

Table 2. The removal efficiency for BOD7, TOC, Tot-N and Tot-P at Kungsängsverket. Used with permission from Uppsala Vatten och Avfall.

Pollutant	Removal efficiency
BOD7	99%
TOC	94%
Tot-N	80%
Tot-P	99%

3.2 SET-UP AND FILTER CONSTRUCTION

When deciding where to set up the filters there were some factors that needed to be taken into account, primarily logistics and the water quality of what would become the incoming water in the experiment. Two different locations were considered (Figure 2)

- Just after the chemical treatment and sedimentation (Location 1)
- Right after the biological treatment in line B (Location 2)

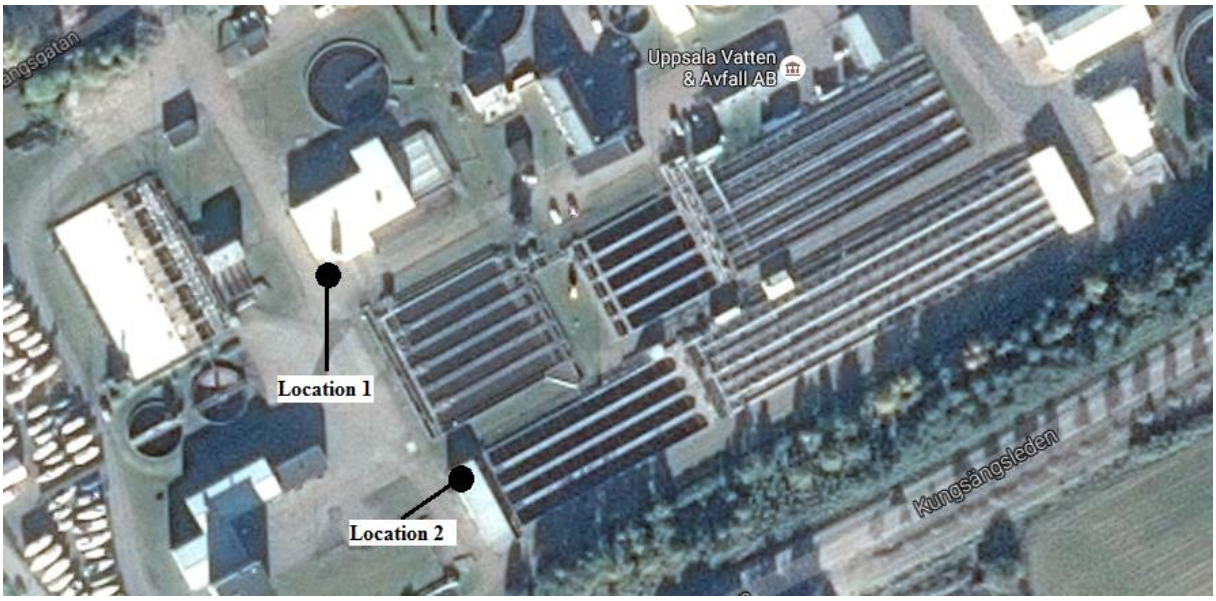

Figure 2. Aerial view of Kungsängsverket (Google Earth, 2016) with the two locations considered for the experiment marked: Location 1 adjacent to the chemical treatment/sedimentation and Location 2 adjacent to line B of the biological treatment.

Since Location 1 is situated after the final treatment step the water would have low levels of suspended solids and other pollutants which would mean that the risk of the filters clogging would be small. However, it was not possible to set up the filters within any existing buildings. To set up the experiment outdoors was unsuitable because of the risk of negative impact from low and high temperatures, rain and wind. Due to time and budget constraints, it was not possible to rent a mobile space such as a container.

At Location 2, it was possible to set up the experiment indoors, adjacent to the sampling station for line B in the biological treatment. According to personnel at Kungsängsverket the concentrations of suspended solids were usually low at this stage in the treatment and should not be very different from the levels at Location 1. Location 2 was therefore deemed to be the more suitable location for the set-up.

Four column filters (4.5cm diameter and 50 cm height) were built with two columns for GAC (A1, A2) and two columns for pine bark (B1, B2). Three separate filter sets were used. The media particle size distribution was determined using sieve analysis. Surface topography and composition of bark and GAC were investigated using an energy dispersive scanning-electron microscope. The activated carbon used in the filters was granulated activated carbon (GAC) from VWR with a particle size of 2-4 mm. Two types of pine bark were used. The bark used in the first two filter sets was procured from Clean by Cortex (CBC), with particles of 0-6 mm with a shifting towards smaller factions. The bark used for the third set of filters was more homogenous in size and had larger particles, 5-7 mm in diameter. It was obtained from Rimbo Jord (Rimbo, Sweden).

The filter media were packed in grey plastic pipes (4.5cm diameter and 110 cm height). The filters were made up of three layers: (i) 3 cm drainage layer made of course gravel placed at the bottom of the column (ii) the actual filter layer 50 cm of the filter media (activated carbon or bark) and (iii) 3 cm water distribution layer consisting of coarse gravel and placed at the top surface of the filter. Before packing the filters, the water pipes and stop-ends were rinsed with methanol three times from both ends. For the first filter sets, the packed filters were washed with 14.9 l MilliQ-water over the course of 6 days. For the other two filter sets, this washing was omitted due to lack of time.

Some characteristics of the filters are presented in Table 3. Porosity was calculated using Equation 1, where the particle density was assumed to be 1340 kg/m3 for the bark and 1900 kg/m3 for the GAC (Dalahmeh et al., 2012). The empty bed contact time (EBCT) was calculated using Equation 2. Loading rates used for the calculation are presented in Table 4. For the sake of the calculation, it was assumed that the filters were loaded continuously during the day. In reality the filters were loaded 20 times a day for an amount of time that depended on the loading rate. The time between loading occasions never exceeded 1 hour.

$$p = 100 \cdot \left(1 - \frac{\rho_B}{\rho_p}\right) \qquad (1)$$

p=porosity, ρ_B=filter (bulk) density, ρ_p=particle density

$$EBCT = Vm/Q \qquad (2)$$

Vm=Filter volume, Q=loading rate

Table 3. Filter characteristics.

Filter name	Set	Filter volume, Vm (ml)	Filter density, ρ_B (kg/m^3)	Filter porosity, p (%)	EBCT week 1 (min)	EBCT week 2 (min)	EBCT week 3 (min)	EBCT week 4 (min)	EBCT week 5 (min)	EBCT week 6 (min)
A1	1	794	505	27	19	114	-	-	-	-
A2	1	794	505	27	19	114	-	-	-	-
B1	1	795	211	16	19	114	-	-	-	-
B2	1	794	213	16	19	114	-	-	-	-
A1	2	747	535	28	-	-	108	36	-	-
A2	2	755	530	28	-	-	109	36	-	-
B1	2	755	225	17	-	-	109	36	-	-
B2	2	755	220	16	-	-	109	36	-	-
A1	3	755	532	28	-	-	-	-	36	24
A2	3	763	524	28	-	-	-	-	37	24
B1	3	771	342	26	-	-	-	-	37	25
B2	3	763	261	19	-	-	-	-	37	24

Figure 3 shows a principle sketch of the set-up of the experiment. Water was pumped from the exit channel of line B of the biological treatment once a day. The water was divided between four storage barrels for incoming water, one for each filter. This water was then pumped into the filters using peristaltic pumps 20 times /day evenly distributed throughout the 24 hours. The outgoing water from the filters was divided between collection tanks for sampling and a waste stream, where the surplus was led to a drainage gutter. In Figure 4, the actual set-up of the experiment is shown.

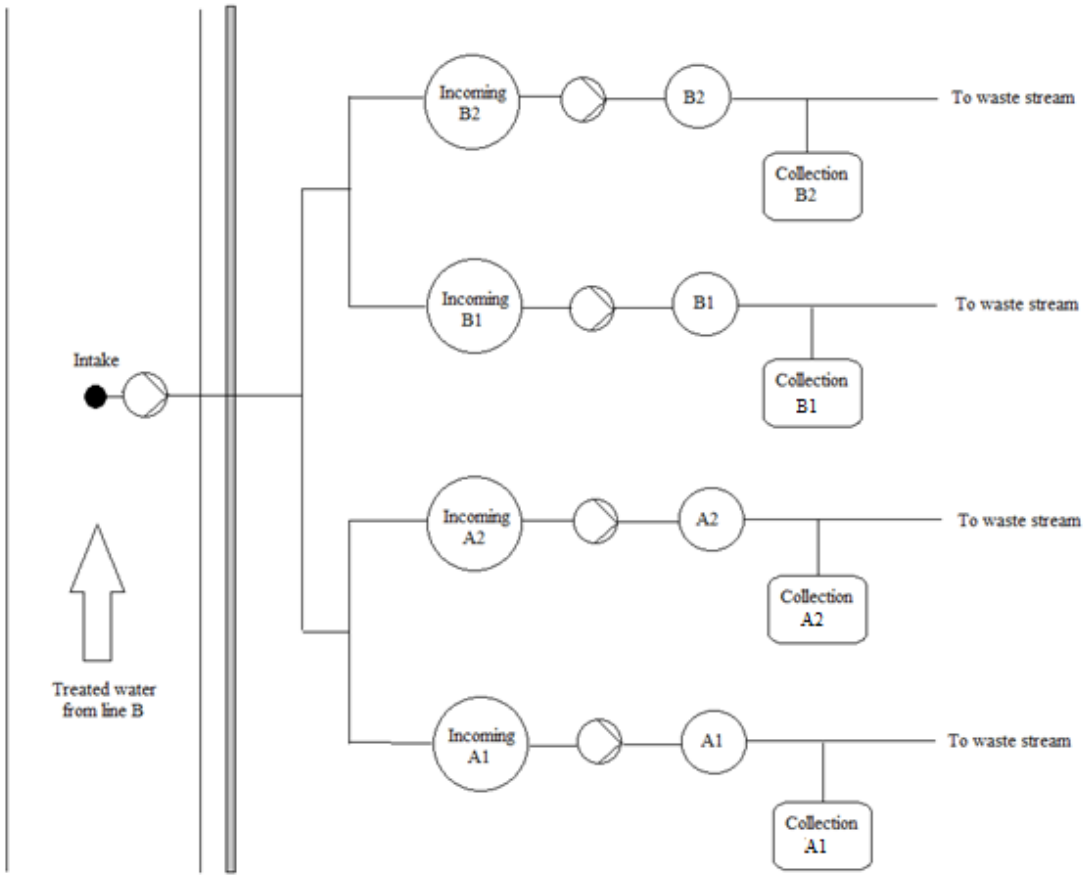

Figure 3. Principle sketch of the experimental set-up which shows the intake of treated wastewater, storage tanks for incoming water, pumps, filters and collection tanks.

Figure 4. The set-up of the experiment: storage barrels for incoming water (black), collection tanks (white) and filters (grey).

There was also a standing water table above the top layer of the filters in order to have a saturated flow of wastewater through the filters. During weeks 1-4 (W1-W4) the level of the water table was of approximately 20 cm above the distribution layer. For the last two weeks of the experiment (W5-W6) it was lowered to approximately 5 cm to reduce the risk of floods in case of clogging. The water level was measured with a yardstick each morning and would rise while the peristaltic pumps were loading the filters only to decrease to the decided level as soon as they shut off. The height of the water table was regulated through adjusting the level of the outlet. A principle sketch of the filters' construction is shown in Figure 5.

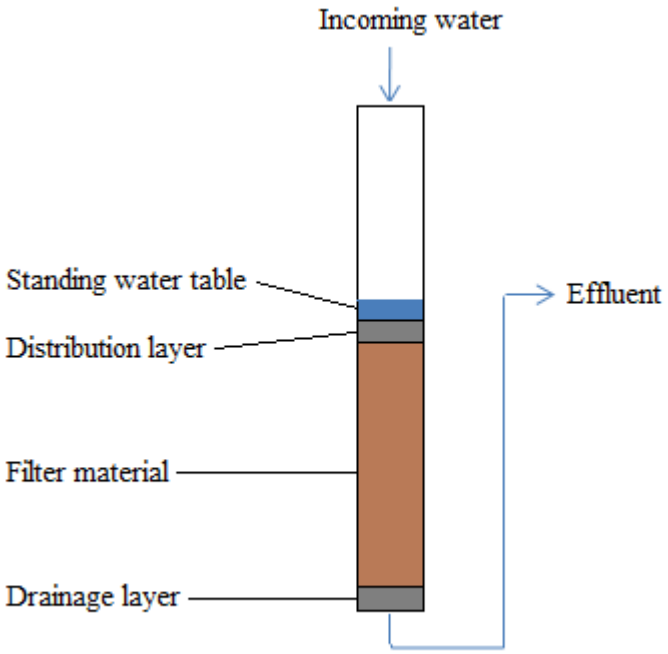

Figure 5. Principle sketch of filters.

3.4 LOADING CONDITIONS AND SAMPLING

The experiment was run for six weeks in total (2/3-26/4) where three sets of filters were operated, each running for two weeks (Table 4). The filters were fed continuously with treated wastewater with saturated down-flow regime. The filters were operated under four loading rates, under which the filters were fed continuously for periods of 1-2 weeks (Table 4). The filters were repacked with fresh material between week 2 and 3 and between week 4 and 5. The reason for running the filters for such a short time at each loading rate was the fact that there were considerable problems with clogging, which are presented in Chapter 4.1.

Table 4. Information about the running of the filters.

Week number	Dates	Filter set	Loading rate
1	2/3-8/3	1	60 l/day
2	10/3-16/3	1	10 l/day
3	30/3-5/4	2	10 l/day
4	6/4-12/4	2	30 l/day
5	13/4-19/4	3	30 l/day
6	20/4-26/4	3	45 l/day

Samples of incoming water and outgoing water from the four filters were taken daily, except during the weekends. Water from the entire weekend was collected and sampled on Mondays.

The sampling bottles had a volume of 1 l and two samples were taken from incoming water (IN) and water treated by filters A1, A2, B1 and B2. Before sampling, the bottles were rinsed twice with the water that was to be sampled, and when bottles had to be reused they were rinsed with methanol and washed in a dishwasher between usage. Samples of the incoming water (IN) were collected daily from each feeding barrel and all IN samples were mixed at equal proportions to prepare two representative daily samples. All samples were transported to SLU and stored at 2°C until extraction

During each week of running the filters, five samples were obtained for each of A1, A2, B1 and B2 and six samples for incoming water. During the weekend composite samples of Friday, Saturday and Sunday were collected for A1, A2, B1 and B2, but for IN the Friday sample was taken separately. Weekly composite samples for each of A1, A2, B1, B2 and IN were prepared by mixing equal volumes from each "daily" sample from the week in question for each corresponding filter resulting in two duplicate weekly samples per filter and incoming water with a volume of 1 l each. When pooling the samples the same volume was used for the weekend-samples as well as for the samples from each weekday.

The first week of experiment there was some trouble acquiring enough water because of problems with valve adjustments which resulted in very small collected volumes, Composite samples were therefore made using the available daily samples. The second week, there was no intake of incoming water during the weekend, resulting in a weekly sample consisting of five samples instead of six.

3.5 ANALYSIS

3.5.1 Analysis of pharmaceuticals

Concentrations of 24 different PhACs have been investigated in this study. The compounds were chosen because they are the ones IVL can detect in the instrumental analysis. They cover a wide range of therapeutic applications such as analgesics, antidepressants, beta-blockers, diuretics and lipid regulators (Table 5).

Table 5. Target pharmaceuticals, their function and some characteristics.

Compound	Molecular formula and molecular weight (g/mol)	Function	pK_a	Log K_{ow}
Amlodipine	$C_{20}H_{25}ClN_2O_5$ 409	Calcium channel blocker: lowers blood pressure by widening blood vessels	8.79[A]	3.00[A]
Atenolol	$C_{14}H_{22}N_2O_3$ 266	Beta-blocker: treatment of cardiac arrhythmias and hypertension (high blood pressure)	9.6[A]	0.16[A]
Bisoprolol	$C_{18}H_{31}NO_4$ 325	Beta-blocker: treatment of cardiac arrhythmias and hypertension (high blood pressure)	pK_{a1} = 9.67, pK_{a2} = 14.09[B]	1.87[A]
Caffeine	$C_8H_{10}N_4O_2$ 194	Central nervous system stimulant	14.0[A]	-0.07[A]
Carbamazepine	$C_{15}H_{12}N_2O$ 236	Treatment of epilepsy and neuropathic pain	13.9[A]	2.45[A]
Citalopram	$C_{20}H_{21}FN_2O$ 324	Antidepressant (SSRI)	9.78[B]	3.5[A]
Diclofenac	$C_{14}H_{11}Cl_2NO_2$ 296	Nonsteroidal anti-inflammatory drug (NSAID): anti-inflammatory, analgesic, antipyretic	4.15[A]	4.51[A]
Fluoxetine	$C_{17}H_{18}F_3NO$ 309	Antidepressant (SSRI)	9.8[B]	4.05[A]
Furosemide	$C_{12}H_{11}ClN_2O_5S$ 331	Diuretic: Prevent fluid build-up, treatment of high blood pressure	pK_{a1}= 3.8; pK_{a2}= 7.5[A]	2.03[A]
Hydrochlorothiazide	$C_7H_8ClN_3O_4S_2$ 298	Diuretic: Prevent fluid build-up, treatment of high blood pressure	7.9[A]	-0.07[A]
Ibuprofen	$C_{13}H_{18}O_2$ 206	Nonsteroidal anti-inflammatory drug (NSAID): anti-inflammatory, analgesic, antipyretic	4.91[A]	3.97[A]
Ketoprofen	$C_{16}H_{14}O_3$ 254	Nonsteroidal anti-inflammatory drug (NSAID): anti-inflammatory, analgesic, antipyretic	4.45[A]	3.12[A]
Metoprolol	$C_{15}H_{25}NO_3$ 267	Beta-blocker: treatment of cardiac arrhythmias and hypertension (high blood pressure)	9.6[A]	1.88[A]
Naproxen	$C_{14}H_{14}O_3$ 230	Nonsteroidal anti-inflammatory drug (NSAID): anti-inflammatory, analgesic, antipyretic	4.15[A]	3.18[A]
Oxazepam	$C_{15}H_{11}ClN_2O_2$ 289	Benzodiazepine: treatment of anxiety, insomnia and alcohol withdrawal	pK_{a1}= 1.55; pK_{a2}= 10.9[A]	2.24[A]
Paracetamol	$C_8H_9NO_2$ 151	Analgesic	9.38[A]	0.46[A]
Propranolol	$C_{16}H_{21}NO_2$ 259	Beta-blocker: treatment of cardiac arrhythmias and hypertension (high blood pressure)	9.42[A]	3.48[A]
Ramipril	$C_{23}H_{32}N_2O_5$ 416	Angiotensin-converting-enzyme inhibitor: treatment of hypertension (high blood pressure)	pK_{a1}= 3.75; pK_{a2}= 5.2[B]	2.9[A]
Ranitidine	$C_{13}H_{22}N_4O_3S$ 314	Anti-ulcer agent: decreases stomach acid production	8.08[B]	0.27[A]
Risperidone	$C_{23}H_{27}FN_4O_2$ 410	Antipsychotic: schizophrenia, bipolar disorder, autism-related irritability	8.76[A]	3.49[A]
Sertraline	$C_{17}H_{17}Cl_2N$ 306	Antidepressant (SSRI)	9.85[B]	5.1[A]
Simvastatin	$C_{25}H_{38}O_5$ 419	Lipid-regulator: decreases elevated lipid levels	pKa1= -2.8; pKa2= 14.91[B]	4.68[A]
Terbutaline	$C_{12}H_{19}NO_3$ 225	β2 adrenergic receptor agonist: "reliever" for asthma symptoms, delay pre-term labor	pK_{a1}= 8.86; pK_{a2}= 9.76[B]	0.9[A]
Warfarin	$C_{19}H_{16}O_4$ 308	Anticoagulant	5.08[A]	2.6[A]

[A](The PubChem Project, www), [B](DrugBank, www)

Solid Phase Extraction of pharmaceuticals
PhACs were extracted from A1, B1 and B2 weekly composite samples using solid phase extraction (SPE). The liquid sample passes through a cartridge containing a solid phase sorbent which retains the analytes. They are then removed from the sorbent through elution with a liquid that provides a more desirable environment than the solid phase (Simpson, 2000). Due to budgetary constraints, samples from week 4 as well as all samples from filter A2 were not analysed for pharmaceuticals.

Prior to extraction, 500 ml of the water samples were filtered through glass microfiber filters (0.7 µm, Ø 47 mm, GE Healthcare, Life Science, WhatmanTM). Before filtration, the filtration unit and the glass microfiber filters were heated to 400°C for 8 h and the glassware was cleaned with tap-water and ethanol between samples. Before the SPE, 15 ml 0.1 M Na2EDTA and 25 µl of a 1 ng/µl internal standard solution was added to each sample. The filtered samples were percolated through Oasis HLB 6cc cartridges, which were preconditioned with 6 ml methanol (MeOH) and 6 ml Type 1 ultrapure water (Milli-Q).

The samples were loaded onto the cartridges and the water percolated at flow rate of 1 drop/s. When the samples were totally percolated through the cartridges, the cartridges were rinsed with 6 ml Milli-Q and centrifuged at 2,000 rpm (805 g-forces) for 2 minutes in an Eppendorf 5810 centrifuge to remove excess water. Elution was done using 8 ml MeOH with no vacuum, and the eluate was collected in pre-cleaned PP-plastic tubes before being concentrated by drying under a nitrogen gas stream until approximately 200 µl remained. The samples were transferred to amber HPLC vials, evaporated to complete dryness, and reconstituted with 100 µl MeOH and 400 µl Milli-Q water.

Instrumental analysis
The instrumental analysis of the PhACs was performed by IVL Swedish Environmental Research Institute, using liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). After the liquid chromatography the sample is ionized and passes through a mass filter which separates ion from each other into a collision cell. The sample then passes through a second mass filter before reaching the detector (Grebe and Singh, 2011) The analysis was done on two separate occasions. Samples from week 1, 2 and 3 were analyzed on the first occasion, while samples from week 5 and 6 were analyzed on the second occasion.

A liquid chromatography system with an auto-injector (Shimadzu, Kyotu, Japan) was coupled to an API 4000 triple quadrupole mass spectrometer (MS/MS) (Applied Biosystems, Foster City, USA). For the chromatographic separation a Xbridge C18 reversed phase column (50*3 mm, 5-micron particle size; Water Corporation, Milford, USA) was used. Electrospray ionization was performed in both positive and negative mode. For the instrumental analysis the temperature was 35°C and the flowrate was 0.3 ml/minute. The mobile phased used consisted of 10 mM acetic acid in water (mobile phase A) and methanol (mobile phase B). Initially, the gradient consisted of 100% of mobile phase A and 0% of mobile phase B, but over 11 minutes the percentage of mobile phase B was increased to 95% and maintained on that level for 5 minutes. The mobile phase composition was then returned to the initial state over 1 minute and then maintained for another 4 minutes before the next injection. The total sample run time was 21 minutes.

For the quantification of the pharmaceuticals, an external calibration curve was used for compounds analyzed in positive mode, while compounds analyzed in negative mode were quantified against the ibuprofen internal standard. This had to be done because no internal standard

for positive mode had been added to any samples and the internal standards diclofenac and hydrochlorothiazide were missing in some samples. The lab at IVL determined the amount of pharmaceuticals (ng) in each sample and the concentration in each sample was calculated based on these amounts.

3.5.2 Analysis of wastewater quality parameters

In addition to the PhACs analysis, the wastewater was analyzed to determine the concentrations of chemical oxygen demand (COD), total nitrogen (Tot-N) and total suspended solids (TSS). These background parameters were chosen because they provide insight in any time-based variations of the general pollution level of the wastewater. These analyses were done on daily samples, approximately once a week.

The COD levels were determined using mercury-free COD Cell Tests (ISO 15705) from Merck KGaA. The tests were specified for the range 10-150 mg COD/l.

The determination of the Tot-N consisted of two steps: (i) in the first step, the organic nitrogen in the samples was digested and mineralized into NO_3-N using Crack Set 20 from Merck KGaA. Thereafter, the resulting total NO_3-N concentration was determined using Nitrate Test (ISO 8466-1, DIN 38402 A51) from Merck KGaA and corresponded to the total nitrogen concentration. The test were specified for the range 0.1-25 mg NO_3-N/l.

The concentration of TSS was determined by filtering 200 ml of the sample through glass microfiber filters (0.7 μm, Ø 47 mm, GE Healthcare, Life Science, Whatman^{TM}). Cleaner samples were filtrated first, and the glassware was rinsed with tap-water and ethanol in between samples. The filters had been weighed before the filtration and were then dried at 100°C for 1 h 15 min and allowed to cool in desiccators before being weighed again. The difference in weight between the two weightings was equivalent to the amount of suspended solids dry mass (TSS) caught during the filtration of the 200 ml of water. From this, the TSS concentration in mg/l was calculated.

3.5.3 Statistical analysis

For the statistical analysis of the results the single factor analysis of variances (ANOVA), t-test and F-test of Excel's Analysis ToolPak were used. ANOVA was used when there were more than two samples to be analyzed, while t-test was used when there was only two samples. Prior to the t-tests, an F-test was done in order to know whether to assume equal or unequal variances for the t-test. The statistical analysis was made for the total pharmaceutical removal, (i.e. the mean removal of all pharmaceuticals) and not for the individual compounds.

In order to determine if there was a significant variation in pharmaceutical removal over time, ANOVA was used for the percentage of removal during week 1-6 for all three filters. For the bark filters, this time period was divided in two: week 1-3 and week 5-6, to separate the time periods where different bark sizes were used. In order to determine if there were any significant differences between the two time periods, t-tests were made on the mean percentage removal of these periods

4. RESULTS AND OBSERVATIONS

4.1 OPERATING EXPERIENCES

At the beginning of the experiment there was some difficulty regarding the adjustments of the valves that dividing the flow from the filters between the collection barrels and the waste stream that was leading to the drain. A major consequence was the fact that the collection of treated water was not evenly distributed over the day. This means that the samples may not adequately reflect the whole 24 hour-period. Another problem that followed from the valve adjustments was the fact that the collected volumes were on some occasions extremely small and had to be discarded during the pooling of the weekly samples. If they had been used in the composite weekly samples, the volumes would have been too small for the SPE. Due to technical problems with pump capacity and timers, there was no collection of incoming water during the weekends of the first two weeks (5-6/3 and 12-13/3 respectively). After the first few days the experiment went well and a suitable amount of water was collected each day.

In the early afternoon the 7th of March (approximately 14.00), filter B2 overflowed and the running water short-circuited the timer which controlled the intake of incoming water from the channel. This resulted in a minor flooding of the premises and the experiment had to be briefly suspended. The high water levels were probably a result of clogging due to high levels of sludge in the incoming water during the weekend. Measures were taken to prevent further clogging. Nylon socks were installed where the incoming water entered the storage barrels and at the intake of the peristaltic pumps in the hope that they would act as "pre-filters" and reduce the amount of sludge getting into the filters. The upper layers of the filters were stirred with a metal rod in order to break up any potential clogging mats and the load was lowered from 60 l/day to 10 l/day. This was achieved by running the peristaltic pumps for 10 minutes at a time on 20 occasions evenly distributed over the day. Because of the dramatic decrease of the loading rate, there was no longer any need to divide the flow after the filters and the valves could be omitted. Things worked smoothly at the lower loading rate and no further problems were experienced during this period.

The experiment was cancelled on the 16th of March in anticipation of the Easter week. After Easter the filters were repacked and the experiment restarted on March 30th with a new loading rate of 10 l/day. After running the filters for one week without any incidents the loading rate was increased to 30 l/day by allowing the peristaltic pumps to run for 30 minutes at a time on 20 occasions evenly distributed over the day. On the 11th of April there was another incident where one of the bark filters overflowed due to clogging. The experiment had to be briefly suspended and the filters repacked, this time with coarser bark in B1 and B2. The new filters were run for two weeks with a loading rate of 30 l/day for the first week and 45 l/day for the second week. In conjunction with increasing the loading rate, the upper layers of the filters' potential clogging mats were broken up by stirring the upper layer of the filters with a metal rod.

During the entire project there was concern regarding the levels of sludge and particles in the incoming water. The problems were more prominent during and just after the weekends, and the nylon sock pre-filters didn't seem to have any significant effect as the sludge flocks appeared to reform after passing them. The outgoing water of the bark filters had a slightly yellow tinge and smelled of pine, while the water from the GAC filters was colorless and mostly odorless. Towards the end of the experiment, sludge was noticed in the outgoing water of all filters.

4.2 RESULTS

4.2.1 Surface structure of filter materials

When magnified 300 and 1500 times with an electron microscope, the porous structure of the material is visible (Figure 6). Some kind of contamination containing iron, calcium, silicon, aluminum and magnesium is present in the material and are visible as bright specks. The origin of the contamination is unclear, but its effect on the removal of PhACs was considered to be negligible.

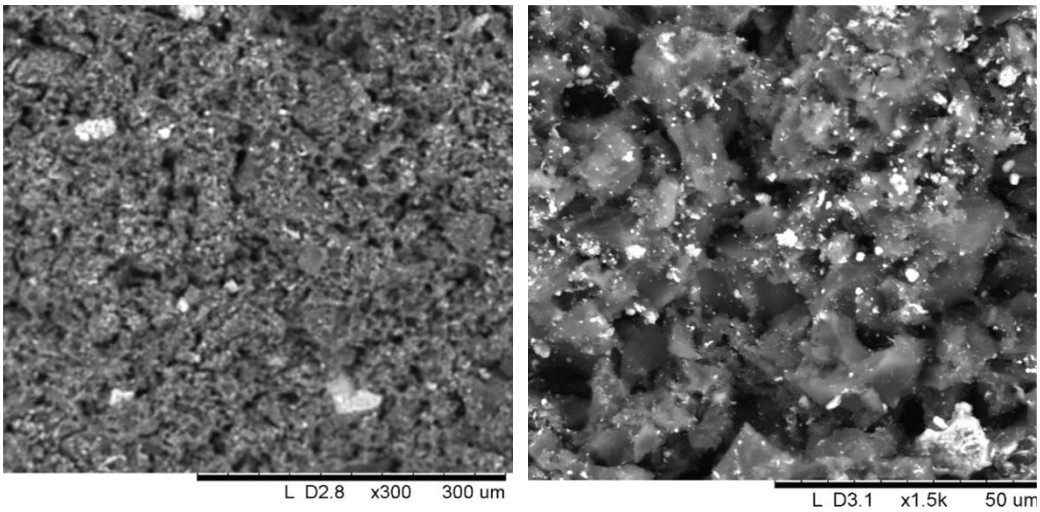

Figure 6. The activated carbon used in the experiment. Left: 300 times magnification. Right: 1,500 times magnification.

The microstructure of the bark differed greatly from that of activated carbon which can be seen in the 300 times magnification (Figure 7, left). In the upper parts of the picture, the usual flaky bark structure can be distinguished while the bottom right corner bears the mark of biological activity in the form of a grainier and more porous structure. The 1,500 times magnification (Figure 7, right) focuses on the area with traces of biological activity. The bark was contaminated with zirconium, a metal that is rather uncommon in nature. Possible sources include alloys on forestry machinery and exhaust fumes from roads in the vicinity of the area where the trees grew. The effect of the zirconium on the removal of PhACs was considered to be negligible.

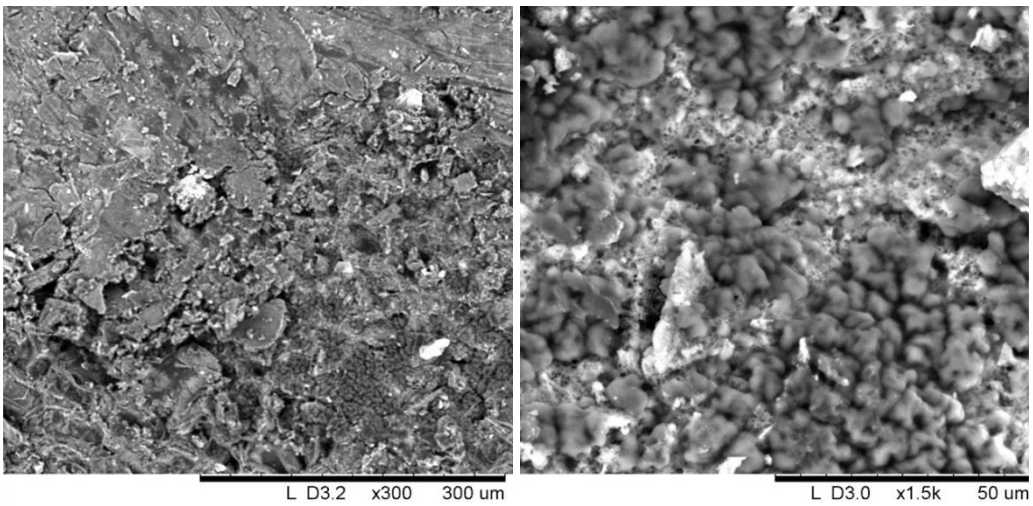

Figure 7. The bark used in the experiment. Left: 300 times magnification. Right: 1,500 times magnification.

4.2.2 Incoming water to filters

Here, the characteristics of the water treated at line B of the biological treatment train at Kungsängsverket are presented. It gives an idea about the amount of pharmaceuticals in the effluent from the wastewater treatment plant and which pharmaceuticals are likely to be found in the recipient. It is important for the purpose of the experiment since this water was used as the influent of the filters.

The concentrations of TSS present in the water to the filters were very low and ranged between 0.0005 and 0.011 mg/l while Tot-N and COD were present in higher concentrations (Table 6). The Tot-N-concentrations ranged between 1 and 7.9 mg/l and COD concentrations ranges between 2.5 and 91 mg/l.

Table 6. Incoming concentrations of wastewater quality parameters.

	W2	W3	W5	W6
Date	2016-03-16	2016-03-30	2016-04-19	2016-04-25
Tot-N [mg/l]	1.0	7.9	4.9	5.9
COD [mg/l]	23.0	2.5	91.0	17.5
TSS [mg/l]	0,011	0,005	0,002	0,001

Nine pharmaceutical compounds were not present in concentrations above the limit of detection (LOD): amlodipine, caffeine, fluoxetine, ketoprofen, paracetamol, risperidone, sertralin, simvastin and warfarin. LOD and quantification (LOQ) for the target compounds are presented in Table 7. The concentrations of the remaining compounds varied greatly; some were present in concentrations <100 ng/l while others were abundant at levels of more than 1000 ng/l (Table 7). The four most common compounds were the beta-blockers atenolol and metoprolol, the anti-inflammatory drug diclofenac and the diuretic hydrochlorothiazide. Ranitidine, terbutaline, naproxen and ramipril were the scarcest compounds of those quantified with mean incoming concentrations <20 ng/l.

There were also differences in how the concentrations of the individual compounds varied over time. The atenolol concentrations were rather stable, with a decreasing trend that amounts to a difference of approximately 115 ng/l or 30% between week 1 and 6 (Figure 8). The decreasing trend of the metoprolol concentration is also evident with a difference of 300 ng/l or 23% between week 1 and 6, despite a noticeable peak during week 5. Diclofenac concentrations had a slightly increasing trend, but were otherwise stable while hydrochlorothiazide concentrations increased considerably. The difference in hydrochlorothiazide concentration amounts to approximately 510 ng/l or 29%, compared with a difference in diclofenac concentration of 44 ng/l or 6%. Furosemide concentration ranged between approximately 500 and 1,000 ng/l with the lowest concentration during week 3 and the highest during week 5. The error bars in the diagram show the standard error.

Table 7. Incoming concentrations of pharmaceuticals and LOD and LOQ for the target pharmaceutical compounds.

Compound	Min [ng/l]	Max [ng/l]	Mean [ng/l]	Standard deviation (5 samples) [ng/l]	LOD [ng/l]	LOQ [ng/l]
Atenolol	249.3	364.8	284.7	46.9	1.5	5.1
Amlodipine	<LOD	<LOD	<LOD	<LOD	0.5	1.7
Bisoprolol	55.5	72.5	60.3	7.0	0.3	0.9
Caffeine	<LOD	<LOD	<LOD	<LOD	37,3	124.0
Carbamazepine	165.4	208.6	190.5	17.7	0.6	1.9
Citalopram	85.6	175.6	135.0	32.8	1.9	6.4
Diclofenac	729.8	813.8	777.9	34.2	42.6	142.0
Fluoxetine	<LOD	<LOD	<LOD	<LOD	0.4	1.2
Furosemide	483.4	1149.2	818.2	278.9	1.8	5.8
Hydrochlorothiazide	1357.9	2261.1	1873.8	368.0	0.4	1.3
Ibuprofen	23.1	52.4	39.8	12.5	2.8	9.2
Ketoprofen	<LOD	<LOD	<LOD	<LOD	48.8	162.6
Metoprolol	967.3	1309.0	1094.1	138.5	0.4	1.4
Naproxen	6.5	21.1	10.5	6.1	0.4	1.3
Oxazepam	111.2	215.3	163.4	44.7	0.6	2.0
Paracetamol	<LOD	<LOD	<LOD	<LOD	21.9	73.0
Propranolol	35.7	61.4	43.7	10.3	0.5	1.6
Ramipril	10.3	25.5	18.5	5.7	0.6	2.1
Ranitidine	9.8	31.0	19.1	8.3	1.6	5.3
Risperidone	<LOD	<LOD	<LOD	<LOD	1.8	6.1
Sertralin	<LOD	<LOD	<LOD	<LOD	0.4	1.3
Simvastatin	<LOD	<LOD	<LOD	<LOD	4.1	13.8
Terbutaline	5.4	12.9	9.6	3.0	0.3	1.0
Warfarin	<LOD	<LOD	<LOD	<LOD	2.0	6.7

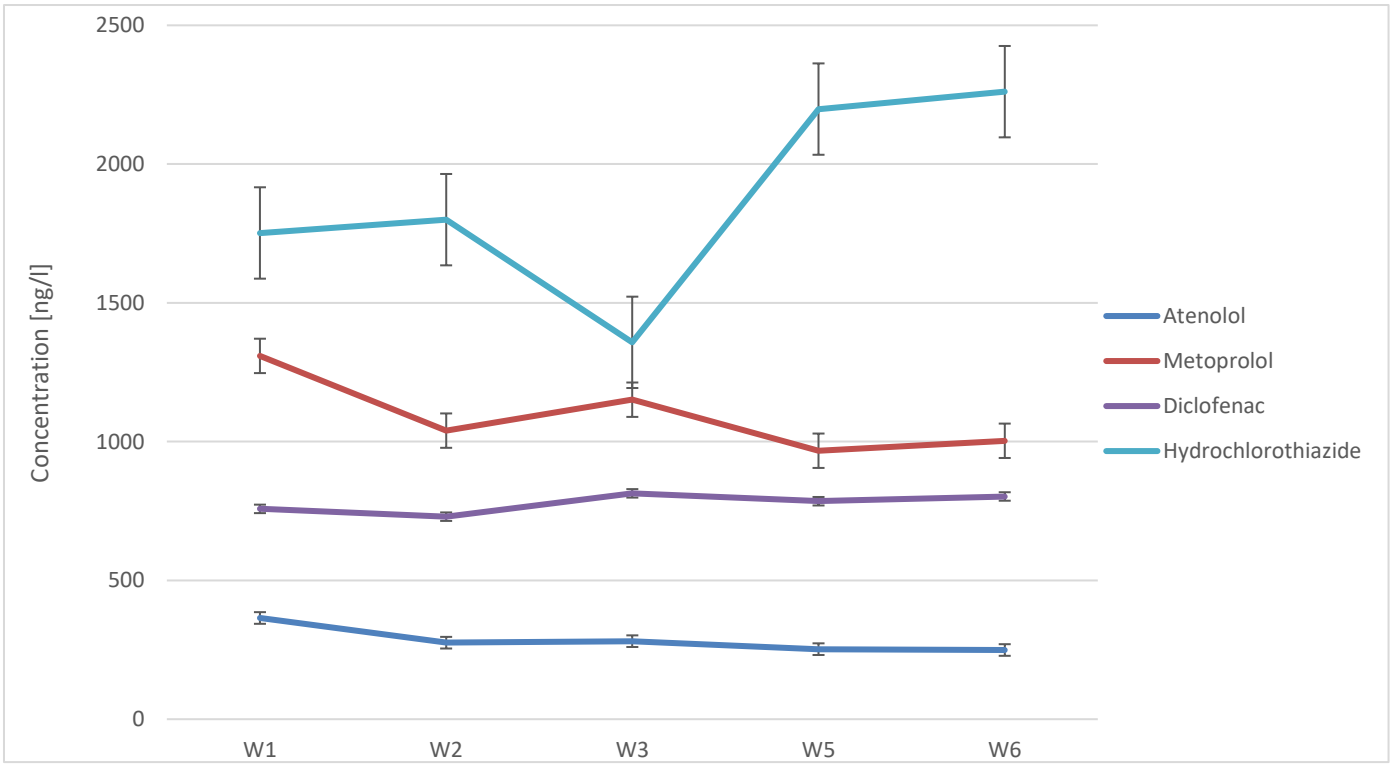

Figure 8. Incoming concentrations of pharmaceuticals.

4.2.3 Comparison of bark and GAC

The removal rates for the wastewater quality parameters varied greatly between different weeks for both GAC and bark filters with Tot-N removal ranging between -600% and 37% and COD between -837% and 100%. Removal rates of TSS were a bit short of 100%, but incoming concentrations were extremely low (Table 8). Mean removal rates for Tot-N and TSS were quite similar between the two filter types, while the difference was greater for COD. The mean removal rates of Tot-N were around -140% for both GAC and bark filters while COD removal was <-200% for GAC and approximately -90% for bark. The mean removal rate of TSS was almost 80% for both GAC and bark filters (Table 9).

Incoming concentrations of fluoxetine for W3 and paracetamol for W1 were lower than the LOQ for the compounds but lower than the LOD in all other samples. When calculating removal rates, LOD values were used for samples with concentrations <LOD and LOQ values for samples with concentrations <LOQ. As a result of this, mean removal rates are more uncertain than for the other compounds, and may not be representative. Excluding fluoxetine and paracetamol, the range in removal rates for the GAC filter was 83-99%. The compound that was removed to the lowest degree was terbutaline while the highest removal rates were achieved for hydrochlorothiazide. The removal rates ranged between -34 and 84% for B1 and -35 and 81 for B2, excluding fluoxetine and paracetamol. For both bark filters, the compound with the lowest removal was hydrochlorothiazide while ranitidine had the highest removal rates (Table 10, Figure 9).

The GAC filters had the highest removal rates while the bark filters were not as effective. Using ANOVA on the mean compound removal (%) of A1, B1 and B2, there was a significant difference between the three filters. Since ANOVA does not say between which samples the significant difference can be found, a t-test was used for the two bark filters. It was concluded that there was a statistically significant difference between the removal rates of the GAC filter and the bark filters.

Table 8. Incoming concentrations and removal of wastewater quality parameters for the filters.

			Tot-N Removal [%]			COD Removal [%]			TSS Removal [%]	
Date	Week	Incoming Tot-N [mg/l]	GAC	Bark	Incoming COD [mg/l]	GAC	Bark	Incoming TSS [mg/l]	GAC	Bark
2016-03-16	W2	1	-600	-586	23	-200	-58	0.011	32	68
2016-03-30	W3	8	37	14	3	100	-430	0.005	75	40
2016-04-19	W5	5	19	11	91	100	100	0.002	100	100
2016-04-25	W6	6	-3	9	17	-837	37	0.001	100	100

Table 9. Mean removal of wastewater quality parameters for the filters.

	Mean removal [%]	
Parameter	GAC	Bark
Tot-N	-137	-138
COD	-209	-88
TSS	77	77

Table 10. Incoming concentrations and mean removal of pharmaceuticals for the filters.

Substance	Incoming concentration	Mean removal [%]		
	[ng/l]	A1	B1	B2
Amlodipine	<LOD	n.d.	n.d	n.d
Atenolol	365	98	32	37
Bisoprolol	72	97	41	41
Caffeine	<LOD	n.d.	n.d	n.d
Carbamazepine	209	94	11	13
Citalopram	176	98	73	72
Diclofenac	758	89	12	13
Fluoxetine	<LOD	14	14	14
Furosemide	703	97	2	4
Hydrochlorothiazide	1752	99	-34	-35
Ibuprofen	23	84	-31	-21
Ketoprofen	<LOD	n.d.	n.d	n.d
Metoprolol	1309	98	35	36
Naproxen	21	88	-2	0
Oxazepam	201	95	27	30
Paracetamol	<LOQ	14	14	14
Propranolol	61	98	69	69
Ramipril	17	86	7	8
Ranitidine	20	90	84	81
Risperidone	<LOD	n.d.	n.d	n.d
Sertralin	<LOD	n.d.	n.d	n.d
Simvastatin	<LOD	n.d.	n.d	n.d
Terbutaline	10	83	-3	25
Warfarin	<LOD	n.d.	-27	n.d.

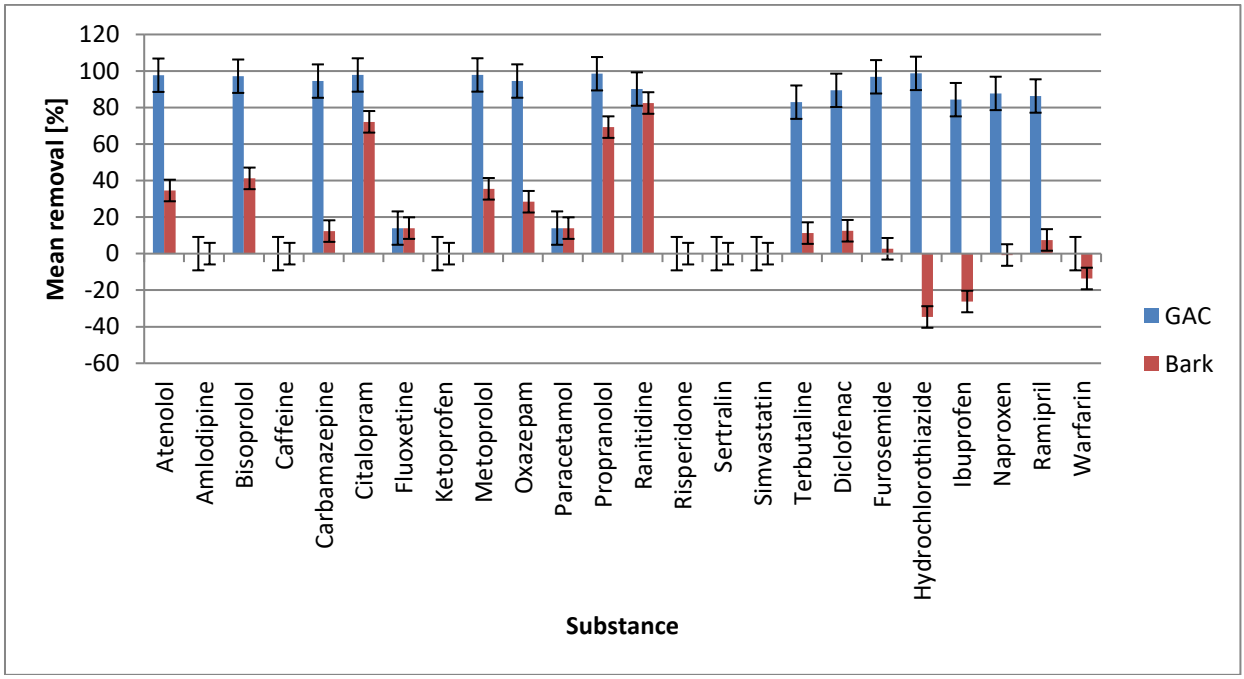

Figure 9. Mean removal of pharmaceuticals for the filters. The error bars show the standard error.

4.2.4 Comparison between different loading rates and bark sizes

Granular active carbon

Some variations in removal rates could be observed for weeks with different loading rates. The responses of the individual target compounds varied as well. For most compounds the removal rates in the GAC filters were high with only small variations. Six compounds: hydrochlorothiazide, propranonlol, furosemide, bisoprolol, citalopram and metoprolol, all had removal rates >90% and standard deviations <3%. Citalopram and oxazepam also had removal rates >90% for most of the experiment, but during week 2 (W2) when loading rates were lowered from 60 to 10 l/day, there was a slight dip to 89% (Table 11).

Table 11. Removal of pharmaceuticals achieved by GAC filter A1 during week 1-6, with different loading rates.

	Removal [%]			
	W1	W2	W3	W5
	Loading rate = 60 l/day	*Loading rate = 10/day*	*Loading rate = 10 l/day*	*Loading rate = 30 l/day*
Amlodipine	n.d.	n.d.	n.d.	n.d.
Atenolol	99	95	98	
Bisoprolol	98	94	98	98
Caffeine	n.d.	n.d.	n.d.	n.d.
Carbamazepine	94	89	96	98
Citalopram	99	95	99	98
Diclofenac	81	94	95	95
Fluoxetine	n.d.	n.d.	n.d.	n.d.
Furosemide	97	96	97	99
Hydrochlorothiazide	99	96	99	100
Ibuprofen	60	92	93	95
Ketoprofen	n.d.	n.d.	n.d.	n.d.
Metoprolol	98	95	99	99
Naproxen	94	86	85	94
Oxazepam	95	89	97	98
Paracetamol	70	n.d.	n.d.	n.d.
Propranolol	99	97	99	99
Ramipril	85	87	94	90
Ranitidine	92	93	95	87
Risperidone	n.d.	n.d.	n.d.	n.d.
Sertralin	n.d.	n.d.	n.d.	n.d.
Simvastatin	n.d.	n.d.	n.d.	n.d.
Terbutaline	97	94	96	63
Warfarin	n.d.	n.d.	n.d.	n.d.

The removal rates of six substances (ranitidine, ibuprofen, naproxen, ramipril, terbutaline and diclofenac) all showed greater variations than the other compounds for weeks with different loading rates. This is illustrated in Figure 10 (compounds with smaller variations in removal rate have been omitted). The removal rate of ranitidine was >90% during W1 and W2-W3 when the loading rates were 60 and 10 l/day respectively, but dropped to 87 and then 83% during W5 (30 l/day) and W6 (45 l/day). The highest removal rates for naproxen were >90%

during W1 (60 l/day) and W5 (30 l/day) and the lowest was 82% during W6. Removal rates for ramipril varied between 75 and 94%, with the highest removal during W3 and the lowest during W6. The lowest removal rates could be found for terbutaline and diclofenac where just over 60% of the compounds were removed during W5 and W6, compared to >90% for W1-W3 (terbutaline) and W2-W3 (diclofenac). Ibuprofen had the largest variations in removal rates, starting at approximately 60% during W1 before rising to >90% during W2-W5 before dropping to just over 80% during W6.

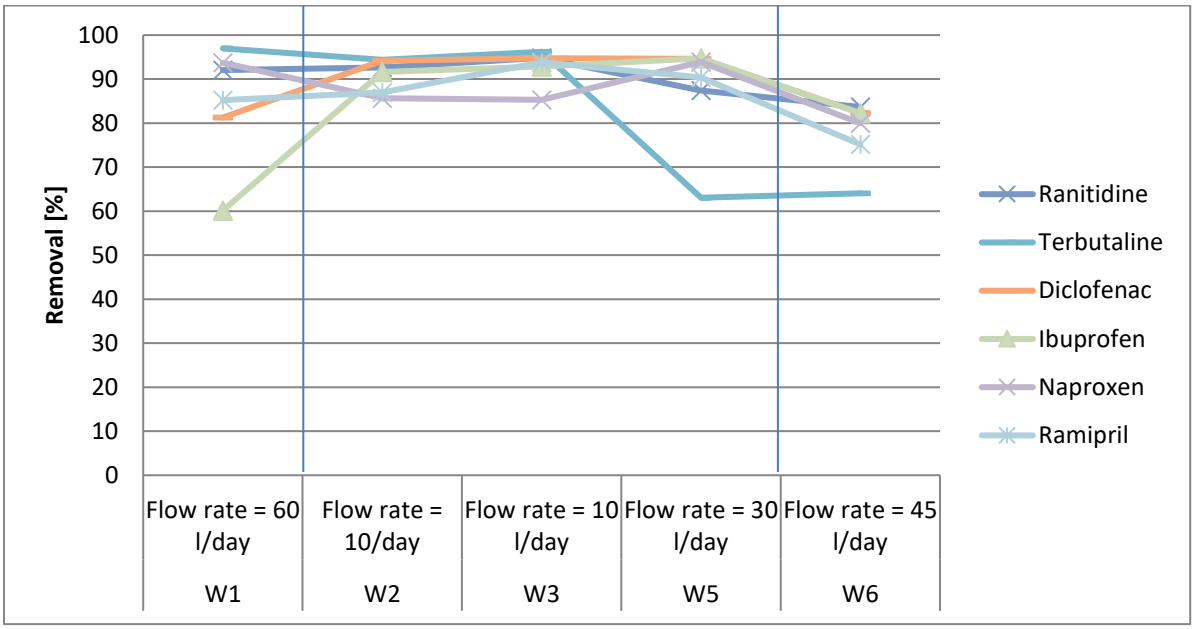

Figure 10. Removal of ranitidine, terbutaline, diclofenac, ibuprofen, naproxen and ramipril achieved by GAC filter A1 during week 1-6, with different loading rates. The substances varied the most during the experiment. The vertical lines (blue) indicate stirring of the upper layers of the filters.

Although the individual compounds responded differently, some trends could be discerned. The removal rates for most compounds were reduced between W1 and W2, when the loading rate was decreased from 60 to 10 l/day. Between W2 and W3, the filters were repacked with fresh filter material, but the loading rate remained at 10 l/day and removal rates increased for all compounds except naproxen, which remained roughly the same. Before W5 the filters were repacked with fresh material again and the loading rate was increased to 30 l/day. During this week, approximately half of the compounds' removal rates increased, while the other half decreased. Between W5 and W6 the loading rate was increased to 45 l/day and the removal rates for most compounds was reduced. For most compounds the differences were small and likely insignificant. Statistical analysis with ANOVA showed that despite the trends observed, there is no statistically significant difference in the between the different weeks and loading rates.

Bark

Variations between different weeks and loading rates could be observed for the bark filters as well. Four substances (atenolol, bisoprolol, metoprolol and oxazepam) had had moderate removal rates of 20-50% with the highest found during W5 (30 l/day, bark >5mm) and the lowest during W1 (60 l/day, bark <5mm) and W6 (45 l/day, bark >5mm) (Table 12). The removal rates of citalopram, propranolol and ranitidine ranged between 60 and 80%. For citalopram and ranitidine the highest rates were found during W2 (10 l/day, bark <5mm) and the lowest during W1 and W6. The removal rates of propranolol were highest during W5 and lowest during W1. Removal rates for diclofenac ranged between 5-29% with the highest during W5 and

the lowest rates during W6. Carbarmazepine removal rates ranged between 5-23% with the highest during W5 and lowest rate during W6 (Table 12).

The removal rates of naproxen varied around zero within a range of -5-9% while ramipril removal rates ranged between -28 and 42% with the highest rates found during W5-W6 and the lowest during W3 (10 l/day, bark <5mm). Furosemide, hydrochlorothiazide and ibuprofen mostly had large negative removal rates and large variations between different weeks and loading rates. However, the two bark filters yielded quite different results on several occasions and this is reflected in the high standard deviations (Table 12). Removal rates for terbutaline were within a range of -6-39%, with lower rates found for weeks with lower loading rates (i.e. W2-W5). The standard deviation for the two filters was large during W1-W3, meaning that the filter's removal rates for terbutaline were quite different from each other during these weeks.

In Table 12 the mean removal rates achieved by the bark filters is shown. Like for the GAC filter some general trends could be discerned despite the varying responses of the individual compounds. For most compounds, removal rates increased between W1 and W2 when loading rates were decreased from 60 to 10 l/day. Between W2 and W3 the loading rate remained at 10 l/day, but the filters were repacked with fresh material. The removal rates of approximately half of the compounds decreased while removal rate of the rest of the compounds increased. When the filters were repacked with fresh bark with a greater particle size and the loading rate was increased to 30 l/day just before W5, the removal rates of all compounds increased. When the loading rate was further increased between W5 and W6, most compounds' removal rates decreased.

Before the start of W5, the filters were repacked with a new kind of bark with larger particle size. The statistical analysis with ANOVA was therefore performed separately on the two periods where different bark types had been used (W1-W4 and W5-W6). A t-test was used on the mean removal during the two periods. The result from the statistical analyses was that there were no significant differences either within or between the two time periods.

Table 12. Mean pharmaceutical removal (and standard deviation) achieved by the bark filters during week 1-6, with different loading rates and bark sizes.

	W1 *Flow rate = 60 l/day, Bark size < 5 mm*		W2 *Flow rate = 10 l/day, Bark size < 5 mm*		W3 *Flow rate = 10 l/day, Bark size = < 5 mm*		W5 *Flow rate = 30 l/day, Bark size > 5 mm*		W6 *Flow rate = 45 l/day, Bark size > 5 mm*	
Substance	Mean re-moval [%]	Standard deviation [%]	Mean re-moval [%]	Standard deviation [%]	Mean re-moval [%]	Standard deviation [%]	Mean re-moval [%]	Standard deviation [%]	Mean re-moval [%]	Standard deviation [%]
Atenolol	23	7	34	7	34	5	50	0	32	0
Amlodipine	n.d.	n.d.	n.d.	n.d.	50	0	0	71	n.d.	n.d.
Bisoprolol	35	2	45	2	43	2	53	0	31	1
Caffeine	-35	50	-21	50	-1	30	10	2	6	15
Carbamazepine	14	7	9	7	10	3	23	0	5	6
Citalopram	66	1	84	1	80	1	74	0	58	5
Fluoxetine	50	71	50	71	85	71	50	21	35	71
Ketoprofen	15	22	37	22	50	52	0	71	0	0
Metoprolol	30	4	33	4	36	2	49	0	28	0
Oxazepam	25	4	33	4	27	0	34	0	22	5
Paracetamol	52	26	10	26	16	15	20	22	19	28
Propranolol	65	1	72	1	73	3	78	0	58	4
Ranitidine	66	8	96	8	87	5	94	6	88	9
Risperidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sertralin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	50	0
Simvastatin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Terbutaline	39	50	-6	50	-2	42	7	0	18	3
Diclofenac	11	6	29	6	5	1	12	0	6	1
Furosemide	-21	14	76	14	-63	5	-8	0	28	6
Hydrochlorothiazide	-12	28	-102	28	-52	21	-11	0	3	5
Ibuprofen	-81	23	-38	23	-2	61	20	0	-30	88
Naproxen	9	1	0	1	-5	10	-4	0	-3	3
Ramipril	-8	8	6	8	-28	1	25	0	42	4
Warfarin	n.d.	n.d.	n.d.	n.d.	-68	0	38	96	1	53

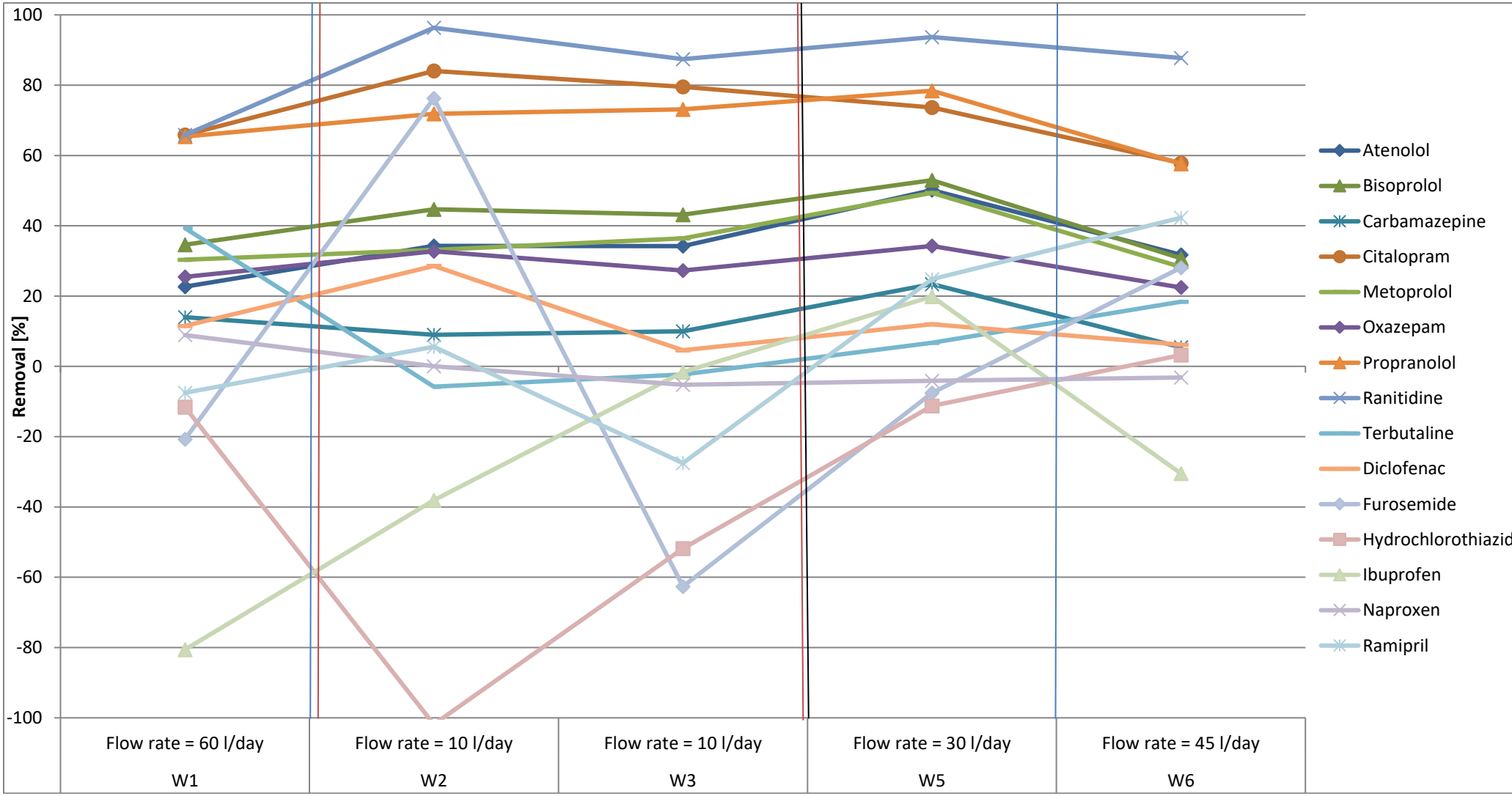

Figure 11. Mean removal of pharmaceuticals with detectable concentrations achieved by bark filters during week 1-6, with different loading rates and bark types. The vertical lines marks the switch from bark <5mm to bark >5 mm(black), floodings (red) and stirring of the filters' upper layers (blue). Note that the last flooding occurred during week four.

5. DISCUSSION

5.1 INCOMING WATER

The mean concentration of COD in the outgoing water at Kungsängsverket in 2015 was 30 mg/l, the mean concentration of Tot-N was 9.8 mg/l and TSS was <5,1 mg/l (Uppsala Vatten och Avfall, 2015). The concentrations measured during the course of the experiment were considerably lower than this for all parameters and weeks with the exception of COD during week 5, where concentration exceeded 90 mg/l. The mean concentrations from 2015 are naturally higher since they encompass a longer time period with larger variations, including overflows which would increase the mean concentrations of all three wastewater quality parameters. However, the measured TSS concentrations are extremely low which is not consistent with the observations of sludge in incoming water. A few of the measurements of Tot-N and COD are also very low. This could possibly indicate unrepresentative samples.

The two betablockers atenolol and metoprolol, the anti-inflammatory drug diclofenac and the diuretics hydrochlorothiazide and furosemide the five most abundant pharmaceuticals present in the treated wastewater to the filter. The high concentrations of these compounds could be a result of their being widely used and therefore present in high concentrations in the WWTP influent. It is also possible that degradation of these compounds during the biological treatment isn't quite as effective as that of other pharmaceuticals. Diclofenac, hydrochlorothiazide and furosemide all contain a chlorine group which can have an inhibiting effect on degradation (Kimura et al., 2007). For atenolol and metoprolol the biological degradation might be stereoselective, meaning that only molecules of a specific three-dimensional orientation are transformed (Nikolai et al., 2006).

Three out of these five most abundant pharmaceuticals have been found to have adverse effects on aquatic life (Table 1). Metoprolol and diclofenac cause damage on gills, liver and kidneys while atenolol reduces the number of red blood cells in rainbow trout Diclofenac also inhibits liver enzyme activity (Triebskorn et al., 2007). Furosemide has been found to inhibit growth in several types of organisms and has a photoproduct that might be mutagenic (Isidori et al., 2006). No studies describing the environmental effects of hydrochlorothiazide have been found. Since these compounds are present in comparatively high concentrations and have a documented negative impact on aquatic life, high removal rates are desirable in complementary treatment methods for Kungsängsverket.

In order to get an idea about how the pharmaceutical concentrations measured at line B of the biological treatment at Kungsängsverket compares to other Swedish WWTPs, a comparison was made with data from Results from the Swedish National Screening Programme, subreport 3 (Fick et al., 2011). In this report, data on pharmaceutical concentrations found (mean values calculated from three samples) in the outflow at four Swedish WWTPs situated at Skövde, Stockholm, Umeå and Uppsala respectively are presented. Mean and maximum (max) concentrations at Kungsängsverket was lower than the concentrations of the same compounds in the 2010 screening. Minimum concentrations (min) were higher for atenolol, metoprolol, ranitidine, diclofenac but otherwise lower than for the screening. It is worth noting that furosemide and hydrochlorothiazide were not measured in the screening programme (

Table 13).

When discussing the pharmaceutical concentrations measured in this experiment, it is important to note that there are some uncertainties concerning the quantification of the pharmaceuticals. Because a few of the internal standards that should have been used for the quantification were missing, an alternative solution had to be used and the accuracy of the quantification could have become somewhat compromised because of this.

Table 13. Removal rates from the project and the 2010 national screening programme. Used with permission from the authors.

	Screening 2010			Kungsängsverket 2016		
Substance	Min	Max	Mean	Min	Max	Mean
Amlodipine	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Atenolol	130	920	461.7	249.3	364.8	284.7
Bisoprolol	59	250	113.6	55.5	72.5	60.3
Caffeine	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Carbamazepine	460	1100	783.3	165.4	208.6	190.5
Citalopram	170	480	295.8	85.6	175.6	135
Diclofenac	280	3900	1080.8	729.8	813.8	777.9
Fluoxetine	5.2	94	34.273	<LOD	<LOD	<LOD
Furosemide	<LOD	<LOD	<LOD	483.4	1149.2	818.2
Hydrochlorothiazide	<LOD	<LOD	<LOD	1357.9	2261.1	1873.8
Ibuprofen	42	990	245.8	23.1	52.4	39.8
Ketoprofen	18	220	113.167	<LOD	<LOD	<LOD
Metoprolol	680	2800	1640	967.3	1309	1094.1
Naproxen	26	490	178.3	6.5	21.1	10.5
Oxazepam	250	730	462.5	111.2	215.3	163.4
Paracetamol	11	580	181.7	<LOD	<LOD	<LOD
Propranolol	<LOD	<LOD	<LOD	35.7	61.4	43.7
Ramipril	<LOD	<LOD	<LOD	10.3	25.5	18.5
Ranitidine	6.8	150	38.6	9.8	31	19.1
Risperidone	1.8	160	47	<LOD	<LOD	<LOD
Sertralin	12	32	21.6	<LOD	<LOD	<LOD
Simvastatin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Terbutaline	<LOD	<LOD	<LOD	5.4	12.9	9.6
Warfarin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

5.2 COMPARISON OF BARK AND GAC

The removal of the wastewater quality parameters (Tables 8 and 9) was not as expected The mean removal rates of Tot- N and COD were negative and indicated increases of around 100% or more. The removal rates also varied greatly between weeks for both filter materials. This was strange, especially for GAC which is known to have good removal rates for most compounds. During the running of the filters some solids were observed in the filter outflow, possibly due to washing out due to overloads and short retention times. COD and Tot-N samples were not filtered and it is possible that this could show as COD in the analysis of WWQP, and would likely contain nitrogen. TSS had extremely low incoming concentrations, practically 0 mg/l. This is not consistent with the observations from the running of the filters; sludge could be seen in the water run-

ning into the filters and on some occasions in filter effluent. It is possible that the sample volumes used for the TSS analysis were not representative despite the careful measures taken (e.g. mixing).

For the compounds with incoming pharmaceutical concentrations below LOD or LOQ, no removal could be determined. Because they were barely present in the wastewater the following nine compounds will be omitted from further discussion with regard to removal rates: amlodipine, caffeine, fluoxetine, ketoprofen, paracetamol, risperidone, sertralin, simvastin and warfarin.

The removal of pharmaceuticals achieved with the GAC filter (A1) were high, >90% for most pharmaceutical compounds which is consistent with results from other studies (Snyder et al., 2007; Ek et al., 2014). The removal rates for terbutaline, ibuprofen, ramipril, naproxen and diclofenac were somewhat lower with a mean ranging between 82 and 89%. For terbutaline the low rates might be due to its comparatively high water solubility and low affinity for organic mattes as indicated by the low log Kow-value (Table 5). Ibuprofen, ramipril, naproxen and diclofenac are all weak organic acids with pKa lower than 5.5. Since the pH of treated wastewater is rather neutral (around 7), the compounds disassociate and thus become negatively charged. This will reduce adsorption to GAC because of the repulsive electrical forces between the compounds and the negatively charged surface area.

For the bark filters removal rates were lower than for GAC and varied greatly between compounds. It was expected that the efficiency of bark would be lower than that of GAC since the material is not quite as porous and therefore the specific surface area is smaller. Decent rates of approximately 70-80% were achieved for some pharmaceuticals, i.e. propranolol, citalopram and ranitidine. For atenolol, bisoprolol, metoprolol and oxazepam removal was lower but not insignificant at 25-40%, while only approximately 10% of the present carbamazepine and diclofenac were removed. For ramipril and furosemide the removal rates were even lower. It is possible that the varying removal rates were influenced by the bark's charge. Relevant information has been difficult to find, and this could be an area of interest for further investigations.

The measured concentrations of hydrochlorothiazide and ibuprofen increased with approximately 30% for both bark filters. For filter B1 some very low increases of the concentrations of terbutaline and naproxen were observed as well. For naproxen the slight increase differs with less than 2% from the extremely low removal rate of B2 (0.3%) and falls within a range that should be considered a normal variation around 0% removal. As mentioned in Section 2 it is possible that biological activity can result in pharmaceutical conjugates and metabolites being transformed back to the parent compound. Although it is a possibility, it is not very likely since the filters were run for such a short time and the microbial communities probably wouldn't have time to get established before the filters were repacked. Another possible explanation is interference during the analysis from other organic compounds. Analyte specificity is a limitation of LC-MS/MS and requires sample clean-up and optimization of chromatography in order to be improved (Grebe and Singh, 2011).

The difference in removal rates between compounds for the bark filters is likely due to variations in degradation due to differences in physiochemical properties like pKa, log

Kow and water solubility (Table 5) Atenolol, bisoprolol, metoprolol, hydrochlorothiazide and terbutaline all have lower log Kow-values and are more water soluable than the compounds with good removal rates while oxazepam has a very low pKa1 and a lower log Kow-value. Just as for the GAC filter, diclofenac is likely to be disassociated due to its low pKa-value. This is also the case for furosemide, ibuprofen, naproxen and ramipril. The water solubility of furosemide and carbamazepine is a bit higher than for the compounds with good removal rates.

The two bark filters had similar removal rates for almost all compounds, the only exception being terbutaline, where the concentration increased with 2% for filter B1 and was reduced by 25% for filter B2. One possible explanation for this difference between the two bark filters is the fact that bark is a more heterogeneous material than GAC.

There was no statistically significant difference between the two bark filters, but as expected, the difference in removal rates between GAC and bark was considerable. It seems that bark is not as efficient as GAC for removal of pharmaceuticals from wastewater under the conditions used in this short time experiment.

Clogging was a problem for the bark filters, but did not occur to the same extent in the GAC filters. This could be related to the shape of the particles, as the bark is “flaky and could be stacked tighter than the GAC. It is also possible for the bark to swell when saturated with water. To avoid the effects of clogging (i.e. flooding), it would perhaps be better to place an “over-flow pipe/channel” before the filters.

5.3 COMPARISON BETWEEN LOADING RATES AND BARK SIZES

For the GAC filter differences in compound removal rates between different weeks and loading rates were usually small. There were, however, six compounds that showed larger variations: ranitidine, terbutaline, diclofenac ibuprofen, naproxen and ramipril. The variations were much greater for the bark filters than for the GAC filter. It is also evident that although the mean removal rates of most compounds were similar for the bark filters, the difference in the removal of a compound during a specific week could be quite different for the two filters, e.g. carbamazepine during week 1 and oxazepam during week 5. These variations could be a result of the heterogeneity of the bark. The differences in removal rates between the weeks were not statistically significant, which would indicate that loading rate and bark size does not have a considerable influence removal rates for either filter type.

Due to the problems with clogging and flooding the experimental plan and project aims were revised as it was discovered that loading rates and bark size had to be changed. But the number of analyses was fixed to five, and at the point where it was clear that a different type of bark had to be used for the three last weeks only two remained. This, coupled with the fact that the weekly sample from week 4 was incomplete due to a clogging-induced flooding, it was decided to use the remaining analyses on the new, larger bark type. This means that there is no pharmaceutical data for the same loading rates for the two bark sizes.

It is possible that the removal rates were affected by human interaction with the filters, e.g. stirring to break up sludge mats to prevent clogging and repacking filters with fresh material. It is unfortunate but had to be done in order to be able to continue the experiment. This, together with other insecurities like the short amount of time that each filter

was run, means that the results are mere indications on the possible performance of bark filters when it comes to pharmaceutical removal.

5.4 IMPLEMENTATION ASPECTS AND FURTHER RESEARCH

The main problem concerning the practical implementation of bark filters for the removal of pharmaceuticals from wastewater encountered during this experiment was that not all pharmaceuticals were removed. For some compounds the concentrations even seemed to increase. This was a serious flaw and indicated that bark was not only less effective; it might not be a suitable filter material for pharmaceutical removal at all. In order to remove the remaining pharmaceuticals further treatment, either another complementary treatment method or a biological polishing step would be needed. This might not be an attractive solution for most wastewater treatment plants when considering the economic costs and practical requirements (i.e. space). There also seemed to be some leaching of organic compounds from the bark filters, as evidenced by the color and smell of the outgoing water, which could be an obstacle for subsequent treatment.

Another factor that contributed to making bark unsuitable was the fact that the bark filters used in this experiment were considerably more sensitive to clogging than the GAC filters. This could be related to the different shape of the particles; the GAC particles were shaped like cylinders while the bark particles were quite flat. The flat bark particles were likely more tightly stacked and as a result of this, more exposed to clogging. If bark filters were ever to be implemented as a treatment method, frequent backwashing would be required in order to prevent clogging of the filters. This would be a disadvantage for both economical and practical reasons since the filters cannot be in operation during the procedure.

In order to avoid clogging-induced floods, the set-up of the filters could be altered. If surplus water was lead to the waste stream before the filters instead of after, the overflowing water would merely join the waste stream. This would not remove clogging, but merely alleviate the symptoms of the actual problem. Installing proper pre-filters with a pore size <10µm could be one way to reduce the risk of clogging. However, the operating experiences from this experiment indicate that sludge flocks might form again after passing the pre-filters used.

When it comes to further research needs, it is important to determine the reason for the extremely low and negative removal rates of certain pharmaceuticals. As mentioned previously the increase of the concentrations of certain pharmaceuticals could be due to interference from other organic compounds during the analysis, which could signify a need to determine the origin of the compounds and/or for improved analytical methods. If there is an actual increase in pharmaceutical concentrations, determining the reason might provide insight in ways of neutralizing this effect. In future experiments, it would be interesting to take more wastewater quality parameters into consideration, e.g. pH, oxygen and total phosphorous because of their impact on microbial communities.

This project did not manage to give much insight into how the performance of bark filters varies depending on loading rates and bark particle size. More research where the filters are run at the same loading rate/bark size for a longer time and without human interference would be needed in order to get an idea about the influence of these factors on the pharmaceutical removal rates of bark filters. It could also be interesting to research alternative treatment designs, e.g. biofilters.

6. CONCLUSIONS

The pharmaceutical concentrations measured at Kungsängsverket were generally low, with the exception of atenolol, metoprolol, diclofenac furosemide and hydrochlorothiazide. All mean compound concentrations were lower than the corresponding mean concentration from the 2010 Swedish Screening Programme, where effluent concentrations of pharmaceuticals from four different WWTPs were examined. Four of the five most abundant substances in the effluent have been shown to have a potential to give a negative impact on aquatic life, and it would be preferred if they were not released into the recipient.

Bark was not as good at removing pharmaceuticals from wastewater as granulated activated carbon (GAC) in this experiment, but decent removal rates were achieved for several compounds. One problem was that not all pharmaceuticals were removed, and for some compounds the analysed concentrations even increased for unclear reasons, possibly through interference with other organic substances during the analysis. Determining the reason for this increase should be prioritized if more research is conducted on the subject.

The removal rates of GAC and bark filters were not significantly impacted by variations in either loading rate or bark size. But the uncertainties during this project have been large, mainly because of human interference to keep the filters running (i.e. stirring the upper layers of the filters to break-up clogging layers), and short operation for each loading rate. The results of this project should therefore be viewed as indications. More clarity regarding the influence of bark size and loading rates on pharmaceutical removal could be achieved if filters were operated at different loading rates for longer time periods.

Before an implementation of bark filters for removal of pharmaceuticals from wastewater can be discussed in earnest, it is important to investigate the origins of the observed increases of certain compounds. It is also of import to find a solution for the clogging problem.

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