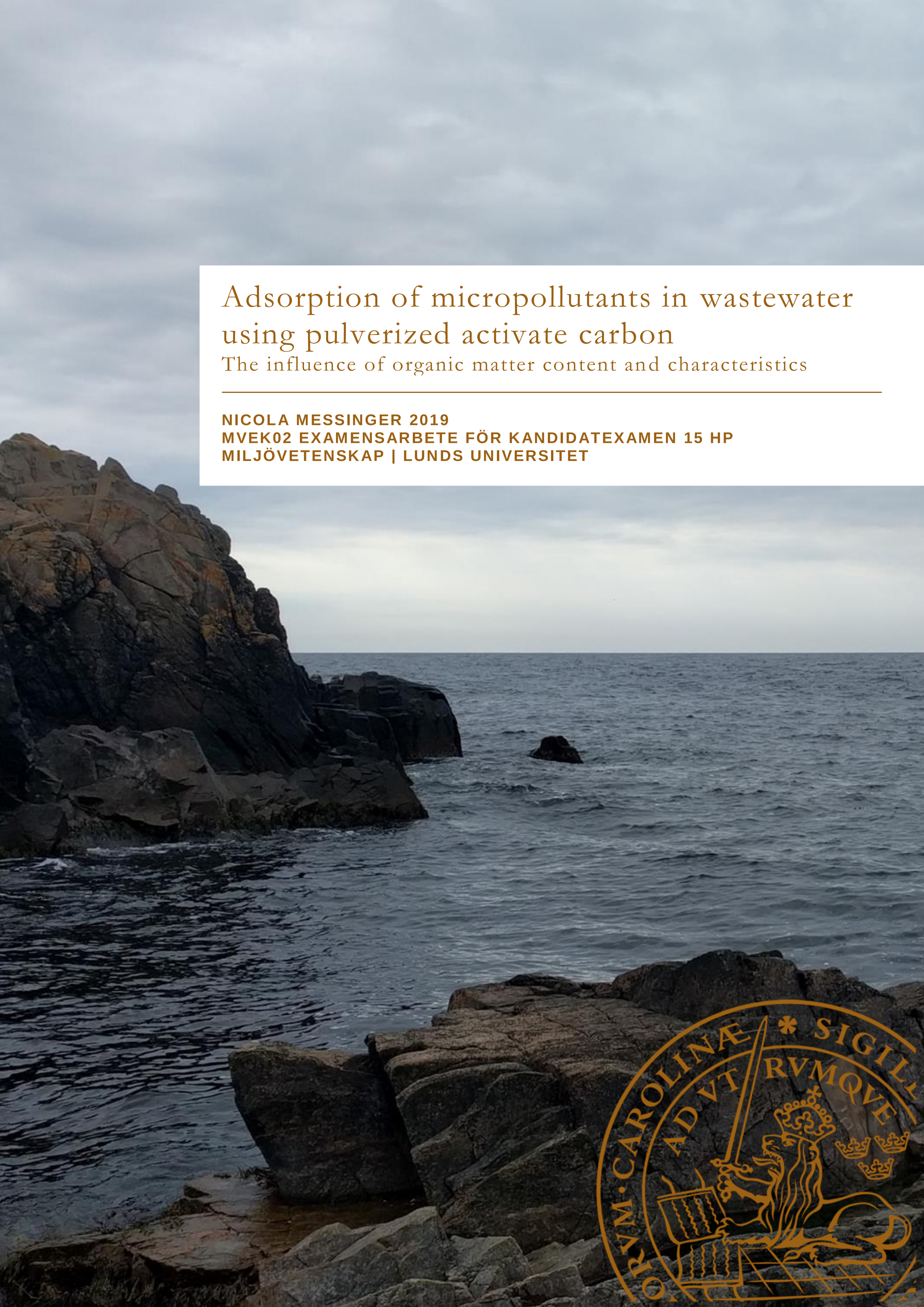

Adsorption of micropollutants in wastewater using pulverized activate carbon

The influence of organic matter content and characteristics

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The influence of organic matter content and character

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Abstract

Wastewater is one of the biggest emission sources of organic micropollutants to the aquatic environment. Due to the negative effects of micropollutants on the receiving waters, advanced treatment steps are needed to reduce these emissions. Activated carbon is one promising approach. However, the adsorption of micropollutants to activated carbon is affected by the content of organic matter in the wastewater. This study aims to investigate how the adsorption capacity of activated carbon varies between different organic micropollutants, and how the adsorption is affected by the presence of organic compounds in different wastewaters. The adsorption of the micropollutants carbamazepine, mecoprop, sulfamethoxazole and diclofenac onto pulverized organic carbon (PAC) was tested in three wastewaters with different amounts of organic matter. Eight PAC doses were added ranging from 0 to 100 mg PAC/L and the remaining micropollutants in the water were measured after equilibrium was reached. The results were then normalized with three different measurements of organic content, DOC (dissolved organic carbon) and UVA_{254} (Adsorption of UV light at 254 nm) for filtered and raw water. Carbamazepine was adsorbed to the highest extent followed by diclofenac, mecoprop and sulfamethoxazole. A difference in adsorption between the three wastewaters was observed and DOC was observed to be a too broad measurement of organic matter to be used for normalization. The normalization with UVA_{254} of raw and filtered water superimposed the adsorption data from the different wastewaters equally well and they could potentially both be used as a parameter for PAC dosing in wastewater treatment plants.

Abbreviations

BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DOC	Dissolved Organic Carbon
GAC	Granular Activated Carbon
logP	Partitioning coefficient (water/octanol)
MBBR	Moving Bed Biofilm Reactor
PAC	Pulverized Activated Carbon
pKa	Acid dissociation constant
TOC	Total Organic Carbon
UVA_{254}	Adsorption of UV light with the wavelength 254 nm

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1. Introduction

Organic micropollutants such as pharmaceuticals, herbicides or insecticides are continuously discharged into the aquatic environment by wastewater. At least 70 different non-antibiotic pharmaceuticals have been detected in Sweden's influent wastewater in concentrations ranging from a few ng/L to several µg/L (Falås et al., 2012). More than 60 of these substances were detected in the treated wastewater in concentrations ranging mostly between 1 to 500ng/L and a few were close to 1µg/L (Falås et al., 2012). These results indicate that the reduction of compounds in wastewater treatment plants differ greatly between different compounds.

Even though these concentrations are low they can affect the ecosystem. One well known example of the effects of micropollutants on the environment is the sexual disruption in fish, which was observed throughout the United Kingdom (Jobling et al., 1998). This sexual disruption was caused by estrogenic substances being discharged from wastewater treatment plants (Jobling et al., 1998). Another example is the harmful effects of diclofenac, a commonly used non-steroidal anti-inflammatory drug, on brown trout tissues (Hoeger et al., 2005). In addition to the damage of individual substances, a study by Vasquez et al. (2014) warns about the effect from chronic exposure as well as from the cocktail effect of different pharmaceuticals.

Due to the fact that effluent water from conventional wastewater treatment plants is a major source of micropollutants to the environment (Eggen et al., 2014), it is important to consider implementing additional advanced treatment steps to remove micropollutants from the wastewater. Even though current wastewater treatment requirements in Sweden are restricted to the biological oxygen demand (BOD), the chemical oxygen demand (COD), the concentration of phosphorous and, depending on the treatment plants location, the concentration of nitrogen (NFS 2016:6), new requirements on the wastewater treatment including micropollutants could be expected (Cimbritz et al., 2016). Therefore, a lot of research regarding different advanced treatment steps as well as the implementations of new treatment technologies in wastewater treatment plants has been conducted in Germany, Switzerland and Sweden (Cimbritz et al., 2016).

There are several different approaches for advanced wastewater treatments, out of which oxidation and adsorption are the most common (Bansal and Goyal, 2005). This study will focus on adsorption of micropollutants with activated carbon, which is the most common adsorbent presently used for wastewater treatment (Cecen and Aktas, 2011).

Activated carbon is a processed, amorphous material that is carbon based. It is called activated carbon due to its adsorption properties, which can be achieved thermally with oxidative gases or chemically with impregnation (Cecen and Aktas, 2011). The activated carbons porosity gives it a large surface area of about 500-1500 m^2g^{-1}, also referred to as specific surface area, onto which organic micropollutants can be adsorbed (Bansal and Goyal, 2005; Cecen and Aktas, 2011). Activated carbon exists in various forms, but the most usual forms are powder or granulates (Cecen and Aktas, 2011). Activated carbon in powder form is generally referred to as powdered activated carbon and has the abbreviation PAC. PAC consists of small particles that are about 44 μm big, while granular activated carbon (referred to as GAC), has a particle size of 0.6-4.0 mm (Bansal and Goyal, 2005).

The adsorption capacity of activated carbon is influenced by many factors, such as the different characteristics of the compound that is adsorbed and the properties of the solution from which the compound is being adsorbed from. Characteristics of the compound that can influence adsorption include e.g. molecular weight, number of functional groups, spatial arrangements and the adsorbates polarity (Cecen and Aktas, 2011). In general, higher molecular weight and the number of functional groups increase the adsorption capacity of the compound (Cecen and Aktas, 2011). However, other studies have proven that if the molecules are too big to fit into the pores the adsorption of these substances are lower (Zietzschmann et al., 2014b). Furthermore, the spatial arrangement has a large impact as well (Cecen and Aktas, 2011). For instance, aromatic compounds are more easily adsorbed than aliphatic compounds (Cecen and Aktas, 2011). The adsorbates polarity is important since activated carbon adsorb nonpolar compounds better than polar ones(Cecen and Aktas, 2011).

Characteristics of the solution that are important are e.g. the concentration of the compound in the solution, temperature, the solubility of the compound in the solution, pH and the presence of competing substances (Bansal and Goyal, 2005). A higher concentration of the compound in the solution allows the compound to reach the adsorption site faster. Temperature influences the adsorption since the adsorption reactions are exothermic. Therefore, increasing temperature should decrease the adsorption. However, higher temperature increases the diffusion rate of the compound in the solution allowing the compound to reach the adsorption site more easily (Cecen and Aktas, 2011). Furthermore, if the solubility of the compound in the solution is high, the bonds between the compound and the solution are strong, which leads to a lower adsorption (Cecen and Aktas, 2011). If instead the solubility is low the attractive forces between the compound and the activated carbon are stronger and the adsorption will increase (Cecen and Aktas, 2011). The solubility is strongly connected with the polarity of the compound, which can depend on pH. The pH of a solution can alter the charge of some components, since many water-soluble organic molecules have functional groups that can be protonated or deprotonated depending on pH (Cecen and Aktas, 2011). If the solution contains other substances that are able to adsorb to activated carbon, the adsorption of the target compound might be decreased depending on the target compound and the other substances adsorption capacities (Bansal and Goyal, 2005).

Wastewater often contain high amounts of organic compounds that are not harmful to the environment, but may have similar adsorption characteristics as organic micropollutants. This presents a problem when trying to adsorb organic micropollutants to activated carbon from wastewater, due to the competition for adsorption between the organic compounds and the organic micropollutants. The amount and the characteristics of the organic compounds in effluent water varies between different wastewater treatment plants. This variation depends on the influent water characteristics and the different treatment processes that are implemented in the wastewater treatment plant. Due to the fact that organic compounds can compete for adsorption with organic micropollutants, it is important to study the effect of these compounds on the adsorption capacity of activated carbon. However, there are several different measurements of the content of organic compounds in water.

This study will only investigate the concentration of dissolved organic carbon (DOC) and the organic carbons that adsorb UV light at the wavelength 254nm (UVA_{254}). UVA_{254} indicates the amount of unsaturated carbon bonds such as double bonds and aromatic structures in the water (Cecen and Aktas, 2011). Since aromatic structures are more likely to bind to activated carbon, the amount of aromatic structures present in the water are of great interest when using PAC (Cecen and Aktas, 2011). UVA_{254} has been tested in connection with PAC adsorption in previous studies. In these studies, this method showed promising results (Zietzschmann et al., 2014a; Altmann et al., 2016).

1.1 Aim

In order to estimate micropollutant removal by PAC, the adsorption of micropollutants as well as how organic matter in wastewater affects the adsorption is important to study. Therefore, the aim of this study is to investigate how the adsorption capacity of the activated carbon varies between different organic micropollutants, and how this adsorption is affected by the presence of organic compounds in different wastewaters. This will be studied by investigating the following questions:

1. Does the adsorption of mecoprop, sulfamethoxazole, diclofenac and carbamazepine onto PAC differ?
2. Does the adsorption of micropollutants to PAC differ between wastewaters with different amounts of organic compounds?
3. Can any differences in adsorption between wastewaters be explained by differences in organic content measured as dissolved organic carbon (DOC) or UVA_{254}?

2. Method

Wastewater from three different wastewater treatment processes were collected. Each of the three wastewaters were divided into four different containers, into which the four micropollutants mecoprop, sulfamethoxazole, diclofenac and carbamazepine were added. These solutions were then separated into eight falcon tubes (20 ml in each) per substance, into which 8 PAC concentrations were added (0 mg PAC/L, 5 mg PAC/L, 15 mg PAC/L, 25 mg PAC/L, 35 mg PAC/L, 50 mg PAC/L, 75 mg PAC/L and 100 mg PAC/L). The falcon tubes were placed on a shaker board, allowing enough time for adsorption to be reached. As a reference, 240 min was enough to reach adsorption equilibrium for PAC in a study by Açıkyıldız et al. (2015). In this study the falcon tubes were placed on the shaker board for about 24 hours. The water was finally separated from the PAC particles by centrifugation at 13000 rpm for 10 minutes from which the concentrations of micropollutants left in the water were measured.

The water parameters pH, ammonium and nitrate concentration, chemical oxygen demand (COD), total organic carbon (TOC), UVA_{254} in filtered and raw water and dissolved organic carbon (DOC) were measured before the micropollutants were added. DOC and UVA_{254} for filtered and raw water will be presented in the results, while the other parameters will be added as complementary information in the Appendix. The pH was measured using the pH electrode WTW pH320. UVA_{254} was measured in a spectrophotometer, HachLange DR6000, on raw water and on water that was filtered through a 0.45 μm filter. Concentrations of TOC, COD, ammonium and nitrate were measured using commercial measuring kits called Hach Lange test cuvettes; LCK 386, LCK 514, LCK 303 and LCK 339 respectively. For the DOC measurements the water was first filtered through a 0.45μm filter and then analyzed with the Hach Lange test cuvette LCK386.

The different PAC doses were also added to the three wastewaters samples without addition of micropollutants. These experiments were performed to study the adsorption of organic carbon, as detected by DOC or UVA_{254}, to PAC.

2.1. Water samples

Three different wastewaters with different wastewater treatments were collected. These wastewaters were chosen to differ in organic content. Two of these wastewaters were sampled at Sjölunda wastewater treatment plant and one at Lundåkra wastewater treatment plant.

2.1.1. Sjölunda wastewater treatment plant

Sjölunda wastewater treatment plant receives domestic wastewater from about 330 000 persons as well as from some industries (VA SYD, 2017). First the water passes through a sieve and an aerated grit chamber, into which an iron-based coagulant is added (Figure 1.) (VA SYD, 2017). The coagulant precipitates phosphorous and smaller particles. The grit chamber is followed by a clarifier and then continues into an activated sludge system for biological oxygen demand removal (BOD removal) (VA SYD, 2017). A sedimentation basin separates the activated sludge before the water continues into a nitrifying trickling filter (VA SYD, 2017). After the trickling filter the water is lead into an anoxic Moving Bed Biofilm Reactor (MBBR) for denitrification (VA SYD, 2017). The MBBR is followed by a clarifier before the water is discharged into Öresund (VA SYD, 2017).

The water was sampled at two different locations at Sjölunda wastewater treatment plant. One sample was collected after the BOD-removal and the sedimentation basin but before the trickling filter and the other sample was collected from the effluent water. The samples will be denoted Sjölunda after BOD removal and Sjölunda effluent water in the report.

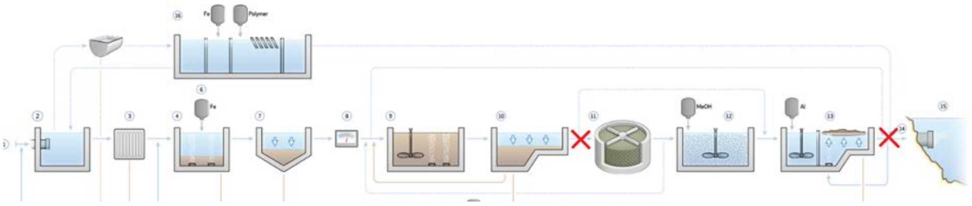


Figure 1. Sjölunda wastewater treatment plant.
Sjölunda wastewater treatment plants treatment process. Two red crosses were added to mark the sampling points. Picture source: VA SYD, 2014.

2.1.2. Lundåkra wastewater treatment plant

Lundåkra wastewater treatment plant treats domestic wastewater from about 40 000 persons. The treatment starts with the mechanical treatment including sieves and a grit chamber followed by two sedimentation basins (Figure 2.). The subsequent biological treatment is achieved in an activated sludge process with a BioDenipho configuration for biological nitrogen and phosphorous removal (NSVA, 2017). The process ends with a chemical treatment, in which a coagulant is added to the water. The coagulant is added to sediment phosphorous before the water is released into Öresund (NSVA, 2017). The water sample from Lundåkra was collected from the effluent and will be denoted Lundåkra effluent water in the report.

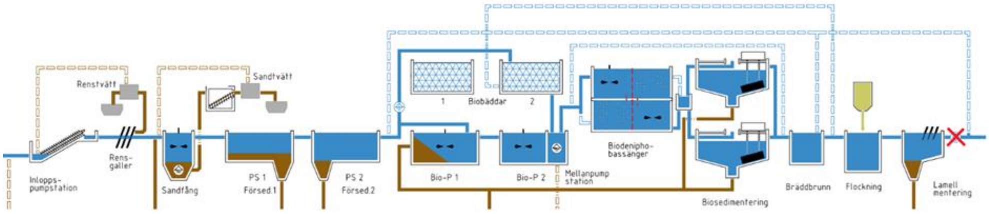


Figure 2. Lundåkra wastewater treatment plant
The treatment process of wastewater in Lundåkra wastewater treatment plant. Picture source: NSVA, 2019-04.04. A red cross was added to mark the sampling point.

2.2. PAC

One PAC product was used throughout the study in order to eliminate adsorption differences depending on different PAC products. The PAC used is called Norit Sae Super (Cabot) and has been characterized in a previous study (Betsholtz et al., 2018). It has a surface area of 975 m^2/g and a mean pore size of 38 Å. Furthermore, Norit Sae Super has a micropore volume of 0.22 cm^3/g and a combined meso- and macropore volume of 0.33 cm^3/g. Before adding PAC to the samples, a stock solution of PAC in deionized water was prepared that had a concentration of 10 g/L was. The solution was prepared more than a month before the experiments to minimize the risk of air blocking the pores of PAC.

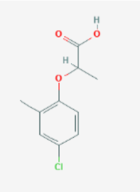
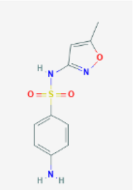
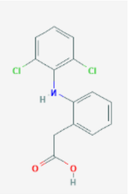
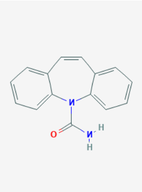
2.3. Organic micropollutants

In this study four organic micropollutants were examined: mecoprop, sulfamethoxazole, diclofenac and carbamazepine. Mecoprop is a chlorinated phenoxy acid herbicide commonly used for plant control in lawns (Nationalencyklopedin, 2019-04-19). Sulfamethoxazole is a germicidal antibiotic, that is commonly used combined with trimethoprim to cure urinary infection or respiratory infections (Schelin, 2017). Diclofenac is one of the most commonly used non-steroidal anti-inflammatory drug and carbamazepine is an anticonvulsant medication that is mainly used in the treatment against epilepsy (FASS, 2017, 2019).

Mecoprop, sulfamethoxazole, diclofenac and carbamazepine have different structures and different chemical characteristics that could affect the adsorption. Mecoprop has the lowest molecular mass out of the four compounds, while diclofenac has the highest mass. Diclofenac has the highest log P value, which is above 1. This means that the compound is more soluble in octanol than in water. Sulfamethoxazole has the lowest log P which is below 1. Therefore, the compound is the most soluble in water. Furthermore, sulfamethoxazole, diclofenac and mecoprop have the physiological charge -1, while carbamazepine has no charge. Physiological charge is the compounds charge at physiological pH, which is around 7.4.

Tabel 1. Mecoprop, sulfamethoxazole, diclofenac and carbamazepine

The structure, molecular weight, log P (partitioning koefficient between water and octanol), the acid dissociation constant, pKa, of the strongest acidic and strongest basic and the physiological charge for the substances mecoprop, sulfamethoxazole and diclofenac are listed in the table. References of the table: (1)PubChem, 2019c; (2) DrugBank, 2019c; (3)DrugBank, 2019b (4) DrugBank, 2019a; (5)PubChem, 2019d; (6)PubChem, 2019b; (7) PubChem, 2019a.

	Mecoprop	Sulfamethoxazole	Diclofenac	Carbamazepine
Structure	 (1)	 (5)	 (6)	 (7)
Molecular weight (g/mol)	214.645(1)	253.278(2)	296.147(3)	236.269(4)
Log P	3.13(1)	0.79(2)	4.26(3)	2.77(4)
pKa (strongest acidic)	3.78(1)	6.16(2)	4(3)	15.96(4)
pKa (strongest basic)	-	1.97(2)	-2.1(3)	-3.8(4)
Physiological charge	-1(1)	-1(2)	-1(3)	0(4)

2.4. Analytic method

The micropollutants used in the experiment were radiometric labelled with C-14, making it possible to detect and quantify them by counting decays in a Liquid Scintillator counter. An amount of 0.1 µCi of the different micropollutant were added to the different wastewaters, which corresponded to concentrations between roughly 4-10 µg/L. These concentrations were chosen to greatly exceed the amount of micropollutants that might already have been in the sample. When detecting the amount of micropollutants left in the water the scintillation cocktail Hionic-Fluor from PerkingEluer was added to convert the radiation into flashes of light, which then can be detected by a Liquid Scintillation counter ('Scintillation counter', 2011). In this case the Liquid Scintillation counter Tri-Carb 49010TR was used.

2.5. Freundlich isotherm

Freundlich isotherm were fitted to the data collected. The Freundlich isotherm is an equation that explains the adsorption equilibrium in a specific system at a fixed temperature in a mathematical form (Cecen and Aktas, 2011). This equation is commonly used for activated carbon measurements to determine the adsorption capacity of activated carbon (Cecen and Aktas, 2011). The Freundlich exponent (K_F) is an indicator of the adsorption capacity, while the Freundlich slope indicates the adsorption intensity. In this study the adsorption capacity will instead be expressed as the fraction of radioactivity adsorbed per concentration of PAC, as the method used cannot determine concentrations, just relative changes in radioactivity. The Freundlich isotherm equation is shown below (Cecen and Aktas, 2011).

$$q = K_F S_e^{1/n}$$

q: adsorption capacity (mass pollutant adsorbed per mass adsorbent)
S_e: the concentration of the pollutant in the liquid at equilibrium (mg/L)

K_F: Freundlich exponent

1/n: Freundlich slope

2.6. Normalization with DOC and UVA_{254}

The adsorption of each organic micropollutant in the different wastewaters as well as the calculated Freundlich isotherm were normalized with DOC and UVA_{254} of the filtered and raw wastewater, by dividing the PAC concentration with the specific DOC or UVA_{254} absorbance of filtered or raw water. This procedure shall compensate for the binding of natural organic compounds to PAC, which competes with the binding of the micropollutants. If the adsorption of the organic micropollutant in the different water samples align, the parameter may be used to estimate the adsorption differences in waters with different concentrations of DOC or UVA_{254}.

2.7. Ethical reflection

No experiments are performed in this study that directly involve humans or animals as object of study. Thus, ethical concerns shall be minimal. Nevertheless, radiometric labelled chemicals will be used. Radioactivity can be harmful to humans or other lifeforms, if they are exposed to a high dose of radioactivity. In addition, the chemicals used can be harmful to the environment. Thus, from an ethical perspective, one need to balance the potential risks of the experiments to human and animal health with the potential benefits of the outcomes, which intend to benefit the development of improved wastewater treatment plants. Since the risks were minimalized by attending a radiation safety course that enabled me to handle the radiometric labelled chemicals safely, and since only small amounts were used in a safe environment, which lowers the risks of harmful effects, the potential benefits should clearly out way any potential risk. I thus see no ethical concerns related to the experiments in this study.

3. Results and Discussion

Results and discussion will be combined to avoid repetition and to make the discussion easier to follow.

3.1. Comparison of the adsorption of micropollutants

The adsorption of carbamazepine, diclofenac, mecoprop and sulfamethoxazole was measured in the three different wastewater samples; Sjölunda after BOD removal, Sjölunda effluent water and Lundåkra effluent water. A clear difference in adsorption patterns was detected between the different organic micropollutants (Figure 3.). Carbamazepine showed the highest adsorption in all wastewaters, followed by diclofenac and mecoprop. Sulfamethoxazole has the lowest adsorption in all the three wastewaters. A PAC dosage of 25 mg/L lead to a reduction of about 84-88 % carbamazepine, 52-70 % diclofenac, 37-49 % mecoprop and 19-27 % sulfamethoxazole, depending on the wastewater the micropollutant was adsorbed from. The extent of the removal of the organic micropollutants diclofenac and carbamazepine was with 20 mgPAC/L from Sjölunda effluent water similar to the results of Cimbritz et al. (2019). However, the results for the removal of sulfamethoxazole is higher in Cimbritz et al. (2019) study. The study of Cimbritz et al. (2019) tested the removal with PAC in a moving bed biofilm reactor (MBBR) with effluent water from Sjölunda wastewater treatment plant. The MBBR should according to Cimbritz et al. (2019) not affect the adsorption of the micropollutants. Even though the extent of the removal of sulfamethoxazole was higher in Cimbritz et al. (2019) study, sulfamethoxazole is adsorbed the least of the three compounds both in their study and in the present study.

Furthermore, carbamazepine has the highest adsorption intensities, 1/n, in all the different waters (Table 2.), followed by mecoprop and diclofenac, which have the same mean adsorption intensities. Sulfamethoxazole has the lowest adsorption intensities of all the wastewater samples. One factor for the differences between the adsorption intensities of the micropollutants might be the difference in their charge. Khan et al. (2013) observed in their study that PAC has a higher adsorption capacity and selectivity towards hydrophobic DOC. The pH of the different wastewaters tested in this study were between 7.4-7.9 (Appendix Table A1.), which implicates that carbamazepine is charged neutral, while sulfamethoxazole, diclofenac and sulfamethoxazole are negatively charged (Table 1.). Due to that carbamazepine is uncharged it should be the most hydrophobic compound within the present set of micropollutants, which might be the reason for the relatively high adsorption intensity. However, the logP value, which is a common measure for hydrophobicity, is lower for carbamazepine than both diclofenac and mecoprop. Another explanation might be the structure of carbamazepine. Carbamazepine is a flat molecule with 3 aromatic rings, which might be beneficial for the adsorption to PAC (Cecen and Aktas, 2011).

In contrast, the difference in adsorption intensity between diclofenac, mecoprop and sulfamethoxazole follow the partitioning coefficient, logP, well (Table 1.). However, as seen for example of carbamazepine, other factors such as size, structure and functional groups could influence the adsorption as well (Cecen and Aktas, 2011). Therefore, no simple specific characteristic can be used to determined adsorption of all different micropollutants.

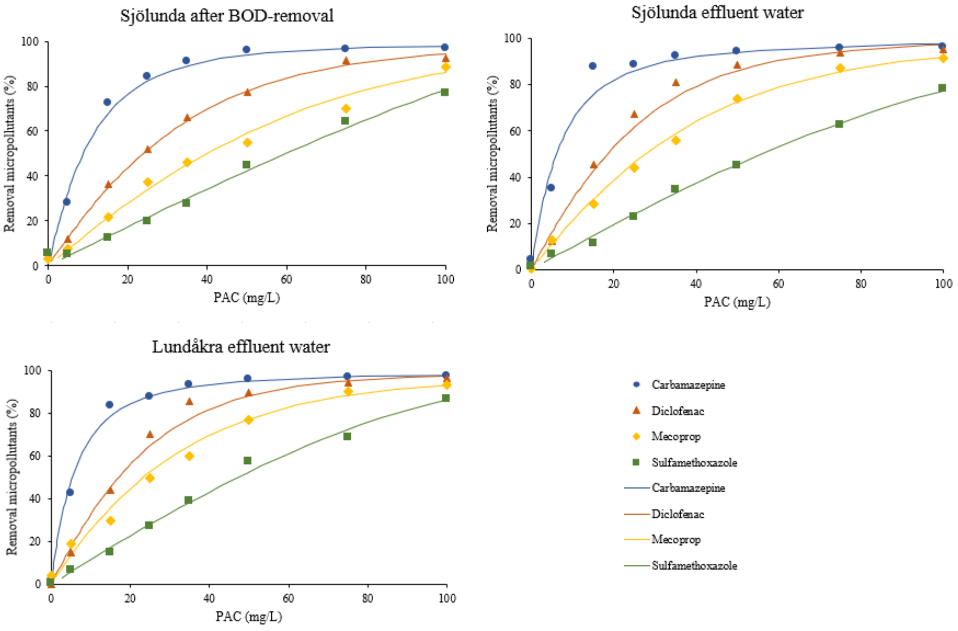


Figure 3. Adsorption of different micropollutants

The adsorption of carbamazepine (blue), diclofenac (red), mecoprop (yellow) and sulfamethoxazole (green) as a function of activated carbon concentrations in the three wastewaters: Sjölunda after BOD-removal, Sjölunda effluent water and Lundåkra effluent water. Freundlich isotherms were fitted to the adsorption and they are represented as lines.

The coefficient of determination (R^2) of the fitted isotherms were high for carbamazepine, diclofenac and mecoprop, while the coefficient of determination of sulfamethoxazole was low (Table 2.). No clear explanation could be found. However, the European Centre for Ecotoxicology and Toxicology of Chemicals (2019-06-14) state that if the K_F value is above 50 or below 0.5 the R^2 value can be expected to be lower. The K_F values in this study are however hard to compare to these numbers due to that different units were used than normal. Furthermore, European Centre for Ecotoxicology and Toxicology of Chemicals (2019-06-14) advise to visually judge the data reliability of the linear adsorption Freundlich isotherm. The Freundlich isotherm of Sulfamethoxazole is rather linear and visually the fit of the data to the isotherm is satisfying.

Table 2. Freundlich isotherm

The Freundlich exponent (K_F), the Freundlich slope (1/n) and the R^2-value of the Freundlich isotherms fitted to the adsorption of carbamazepine, diclofenac, mecoprop and sulfamethoxazole to PAC in the three different wastewaters Lundåkra effluent water, Sjölunda after BOD removal and Sjölunda effluent water.

	Carbamazepine			Diclofenac			Mecoprop			Sulfamethoxazole		
	K_F	1/n	R^2	K_F	1/n	R^2	K_F	1/n	R^2	K_F	1/n	R^2
Lundåkra effluent water	1.24	0.68	0.95	3.06	0.35	0.87	1.17	0.41	0.82	2.70	0.15	0.54
Sjölunda after BOD removal	1.90	0.53	0.92	2.05	0.37	0.95	1.32	0.29	0.83	3.37	0.08	0.15
Sjölunda effluent water	1.09	0.68	0.78	2.77	0.36	0.82	1.28	0.37	0.93	1.94	0.18	0.25
Mean value	1.41	0.63		2.63	0.36		1.26	0.36		2.67	0.14	

3.2. Adsorption in different wastewaters

The water from Sjölunda after BOD removal contained the highest amount of dissolved organic matter (DOC) and the highest UVA_{254} in filtered and raw water, followed by Sjölunda effluent water. Lundåkra effluent water had the lowest amount of DOC and UVA_{254} in filtered and raw water (Table 3.).

Table 3. Organic carbon in the wastewaters

The dissolved organic carbon (DOC) content and the UV adsorption at the wavelength 254 nm (UVA_{254}) in filtered water and unfiltered water of the three wastewaters Lundåkra effluent water, Sjölunda after BOD removal and Sjölunda effluent water.

	Lundåkra effluent water	Sjölunda after BOD removal	Sjölunda effluent water
DOC (mg/L)	10.9	19.0	16.4
UVA_{254} (filtered water) (m^{-1})	24.1	29.4	24.8
UVA_{254} (raw water) (m^{-1})	24.6	38.1	30.0

Figure 4. compares the adsorption capacity of the different micropollutants to activated carbon in the three different wastewaters tested. Even though the differences between the tested wastewaters are not as pronounced as the difference between the adsorption patterns of the tested micropollutants, a general pattern can be established. The adsorption in the effluent water of Lundåkra has the most efficient adsorption for all tested micropollutants, closely followed by the effluent water from Sjölunda. The adsorption was the least efficient in the water from Sjölunda after the BOD removal (Figure 4.). This reflects to the amount of DOC and UVA_{254} for filtered and unfiltered in the three different wastewaters, where Lundåkra effluent water has the lowest amounts for DOC and UVA_{254} and Sjölunda after BOD removal has the highest (Table 3.). Furthermore, the differences between the different waters seem to be larger for mecoprop and sulfamethoxazole than for diclofenac and carbamazepine. This might be due to a lower affinity of mecoprop and sulfamethoxazole to PAC compared to carbamazepine, which might increase the number of compounds that are able to compete for adsorption spots. A similar hypothesis is stated in the study by Zietzschmann et al. (2014b), although they studied adsorption differences of organic micropollutants depending on the molecule size of the natural organic compounds.

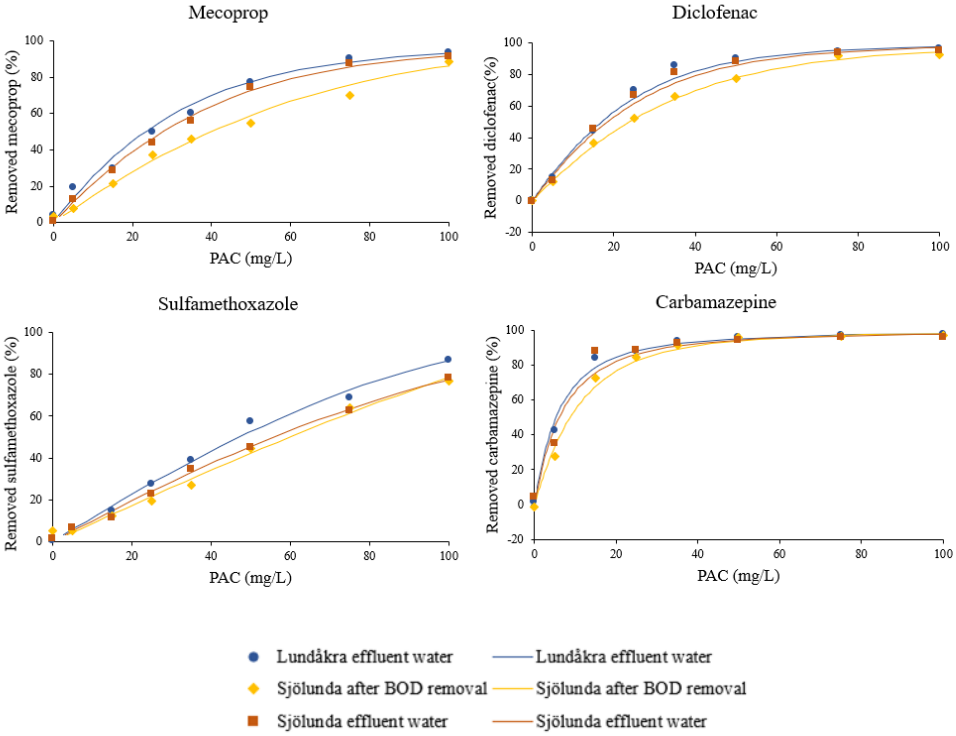


Figure 4. Comparison between the three wastewaters
The adsorption of the four micropollutants mecoprop, diclofenac, sulfamethoxazole and carbamazepine from the three different wastewaters Lundåkra effluent water (blue), Sjölunda after BOD removal (yellow) and Sjölunda effluent water (red) onto PAC. Freundlich isotherms were fitted to the adsorption of the different micropollutants in the different waters, represented as lines.

3.3. Normalization with DOC and UVA254 of filtered and raw water

When adding the eight different amounts of PAC into the three different wastewaters without adding any micropollutants, a decrease in both DOC and UVA_{254} in the filtered water was observed (Figure 5.). This suggests that the organic compounds in the water are adsorbed by activated carbon and they could therefore compete with the micropollutants for adsorption to the activated carbon. Sjölunda after BOD removal has the highest amount of substances detected by DOC and UVA_{254} and Lundåkra effluent has the lowest. The removal of organic substances as a function of PAC as measured by DOC and UVA_{254} is overall similar in the different wastewaters. However, the decline of UVA_{254} is higher than the decline of DOC in all the wastewater samples. Additionally, the adsorption of UVA_{254} in Sjölunda effluent water and Lundåkra effluent water are closer to each other than in the adsorption of DOC, which is similar to the adsorption of the micropollutants (Figure 5.).

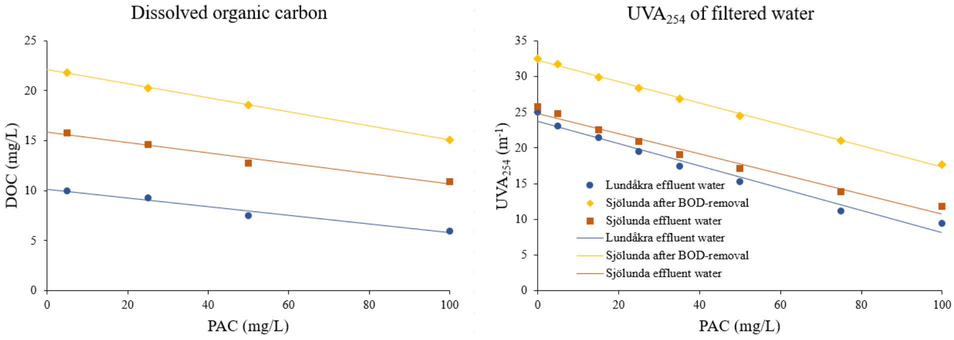


Figure 5. Adsorption of DOC and UVA_{254} of filtered water
The effect of activated carbon on the DOC concentration and UVA_{254} absorbance in the three wastewaters Lundåkra effluent water (blue), Sjölunda BOD removal (yellow) and Sjölunda effluent water (red), including trend lines of the adsorption in the different waters.

In Figure 6. the adsorption of the four micropollutants tested are shown on the left side, while the DOC normalized graphs are on the right side for comparison. The normalization with the DOC concentrations in the different wastewaters does not superimpose the adsorption values for the different wastewater samples, nor the fitted Freundlich isotherm. The Freundlich constants are presented in Appendix Table A2. In the not normalized graphs on the left side of Figure 6. the adsorption in the effluent waters from Lundåkra and Sjölunda are more similar to each other than to the water from Sjölunda after the BOD removal, but the DOC concentrations of Lundåkra effluent and Sjölunda effluent water differ more than the DOC concentrations of Sjölunda effluent and Sjölunda after BOD removal (Table 3.). Therefore, DOC most likely includes organic compounds that do not seem to compete significantly for adsorption sites. Zietzschmann et al. (2016) compared organic micropollutant breakthrough behaviors in different waters, in which they normalize their results with DOC. As in this study their conclusion was that DOC concentrations cannot explain the breakthrough behaviors of the different organic micropollutants in the different waters. DOC seems to be a too broad measurement of organic compounds that might compete with the organic micropollutants.

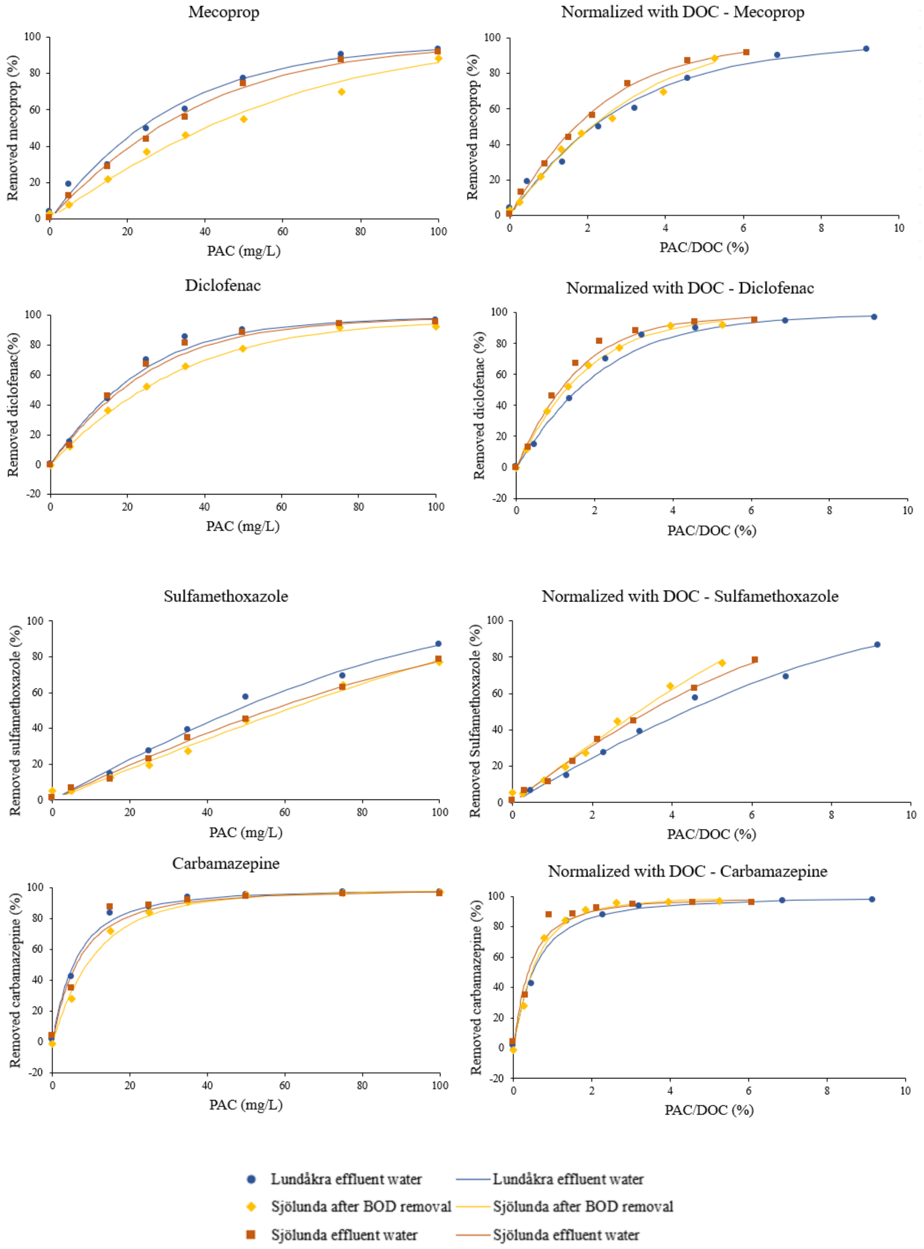


Figure 6. Normalization with DOC
The adsorption of mecoprop, diclofenac, sulfamethoxazole and carbamazepine in the wastewaters Lundåkra effluent water (blue), Sjölunda after BOD removal (yellow) and Sjölunda effluent water (red). On the left side the adsorption was not normalized and on the right side the adsorption was normalized with the wastewaters DOC concentrations. Freundlich isotherms were fitted to the graphs and are represented as lines.

The normalization with UVA_{254} of the filtered and the raw water aligned the measured adsorption and the fitted Freundlich isotherm lines of the different wastewaters tested more closely than the normalization with DOC (Figure 7.). UVA_{254} therefore seems to function better as a parameter for evaluating adsorption in wastewater than DOC. These results match results from other studies. For instance, Zietzschmann et al. (2014a) found that PAC induced UVA_{254} adsorption correlated well with the adsorption of organic micropollutants. The two parameters correlated, and they therefore suggest UVA_{254} as an indicator for organic micropollutant removal as well as an indicator for PAC dosing for an efficient and reliable removal of the organic micropollutant. Furthermore, (Altmann et al., 2016) used UVA_{254} as real time measurement to evaluate adapted PAC dosing strategies, which they also concluded to be effective.

The normalization with UVA_{254} of the raw water in this study had a slightly closer alignment of the different wastewaters when normalizing the adsorption of mecoprop, diclofenac and carbamazepine than the normalization with UVA_{254} of filtered water. This might indicate that some bigger molecules that are removed when filtrating the water are able to compete for adsorption with the micropollutants. However, Velten et al. (2011) concluded that low molecular weight organic compounds are adsorbed the most. Furthermore, Zietzschmann et al. (2016) normalized the adsorption in two different waters with the amount of low molecular weight organic compounds and the UVA_{254} of low molecular weight organic compounds. From their study they conclude that the normalization with the UVA_{254} of low molecular weight organics aligns the breakthrough concentrations of the organic micropollutants better than the normalization with the amount of low molecular weight. Due to the fact that the differences in the normalization with UVA_{254} of raw and filtered water are very small and other studies have proven that the size of the organic compounds matter, no conclusion on which factor works better can be drawn from the results of this study.

Furthermore, the carbamazepine data are best aligned, followed by the diclofenac and mecoprop data, while the sulfamethoxazole data aligned the least well. This is the same order as the adsorption intensities (Table 2.). UVA_{254} measures all organic substances that are unsaturated (Cecen and Aktas, 2011). All unsaturated carbons will however not adsorb the same. As earlier mentioned, factors such as hydrophobicity, hydrophilicity, the size or structure of the organic compounds and of the micropollutants affect their relative adsorption to PAC (Khan et. al. 2013; Zietzschmann et al., 2014b; Cecen and Aktas, 2011). A lower adsorption intensity might allow more of the unsaturated fraction of organic carbons, or even organic carbons not measured by UVA_{254} to effectively compete with the substance. This may lead to a less accurate normalization. However, more micropollutants should be studied to confirm this hypothesis.

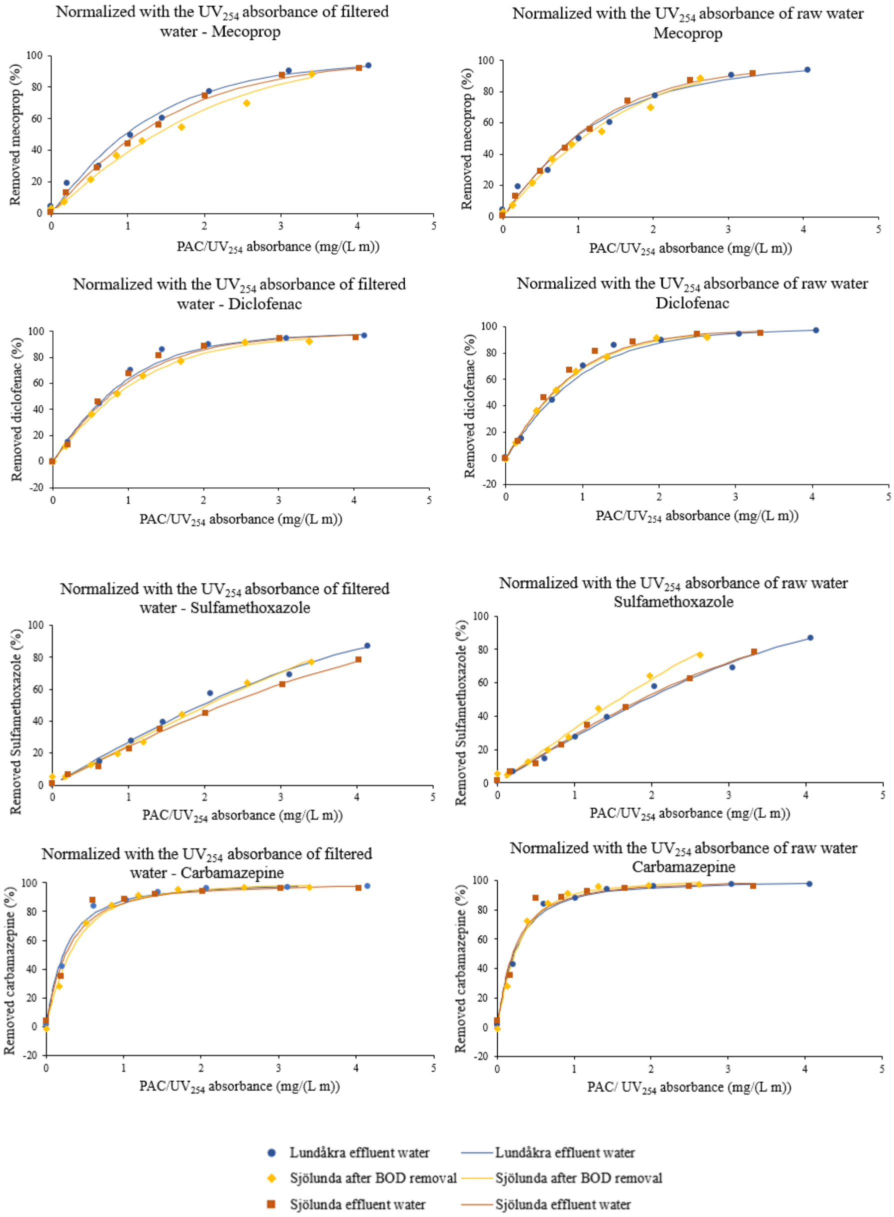


Figure 7. Normalization with UVA254 of filtered and raw water
The adsorption of mecoprop, diclofenac, sulfamethoxazole and carbamazepine in the wastewaters Lundåkra effluent water (blue), Sjölunda after BOD removal (yellow) and Sjölunda effluent water (red) normalized with UVA_{254} of filtered water (left) and normalized with UVA_{254} of raw water (right). Freundlich isotherms were fitted to the normalized and not normalized adsorption and are represented as lines. The Freundlich exponent and Freundlich slope are presented in the appendix (Table A3. and A4.)

3.4. PAC as an advanced treatment step in wastewater treatment plants

Financially, a dose of about 25-30 mg PAC/L are reasonable for usage in wastewater treatment plants. At 25 mg PAC/L the percentage of the tested micropollutants removed vary from about 20-85 % in the water Sjölunda after BOD removal (Figure 3.). Therefore, it is important to know which micropollutant are present in the effluent water and if the PAC dose is enough to be able to clean the water to the wanted extent.

Furthermore, the amount of organic matter seems to influence the adsorption (Figure 4.) and the PAC treatment could therefore be enhanced if a larger reduction of organic matter can be achieved prior to the PAC treatment.

UVA_{254}, which in general seems to be a good parameter for PAC dosage in different wastewaters, is an easy parameter to measure in wastewater treatment plants. UVA_{254} of raw water would be the simplest to use due to that it could be measured continuously without the need of filtration. Therefore, further studies of the differences of UVA_{254} of filtered and raw water should be conducted.

Lastly, other factors such if PAC is reusable, how to implement PAC in the wastewater treatment as well as how to clean the water from PAC are needed to be studied to be able to implement the PAC treatment in a wastewater treatment plant.

4. Conclusion

The adsorption of different organic micropollutants vary a lot depending on the micropollutants characteristics. Therefore, when using activated carbon as an advanced treatment step, it is necessary to know which micropollutant are present in the water and what their specific adsorption looks like to be able to draw a conclusion on how much of the pollutant that will be removed when adding a specific amount of PAC.

A pattern between the adsorption of the organic micropollutants in the different wastewater samples could be established. It is shown that DOC is a too broad measurement to be able to align the adsorption data obtained for the same micropollutant in different wastewaters. Normalization with UVA_{254} of raw and filtered water on the other hand aligned the adsorption of micropollutants in the different wastewaters well. This indicates that UVA_{254} might be a good parameter to use as an indicator for the adsorption of micropollutants in different wastewater. However, the UVA_{254} measurements of the tested wastewaters were quite similar and wastewater with greater differences should be tested.

The normalization with UVA_{254} of raw and filtered water did not differ much, therefore no conclusion on which measurement might be better for normalization could be made. If both parameters work similarly well UVA_{254} of raw water would probably be preferred in wastewater treatment plants due to that it could be measured continuously in the water without having to filter it.

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Appendix

Table A1. Wastewater characteristics

The concentrations of ammonium, nitrate, phosphate, Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) aswell as the pH and UVA_{254} of filtered and raw water in the wastewaters Lundåkra effluent water, Sjölunda after BOD removal and Sjölunda effluent water.

	Lundåkra effluent water	Sjölunda after BOD-removal	Sjölunda effluent water
Ammonium (mg/L)	1.86	31.1	4.76
Nitrate (mg/L)	3.88	0.69	2.27
Phosphate (mg/L)	0.170	0.524	0.549
UVA_{254} (filtered water)	24.1	29.4	24.8
UVA_{254} (raw water)	24.6	38.1	30.0
TOC (mg/L)	10.9	24.5	18.5
DOC (mg/L)	10.9	19.0	16.4
COD (mg/L)	28.5	47.1	42.8
pH	7.5	7.4	7.9

Table A2. The Freundlich Isotherm constants for the DOC normalized graphs

The Freundlich exponent (K_F), the Freundlich slope (1/n) and the R^2-value of the Freundlich isotherms fitted to the normalized adsorption of carbamazepine, diclofenac, mecoprop and sulfamethoxazole with DOC to PAC in the three different wastewaters Lundåkra effluent water, Sjölunda after BOD removal and Sjölunda effluent water.

DOC	Carbamazepine			Diclofenac			Mecoprop			Sulfamethoxazole		
	K_F	1/n	R^2	K_F	1/n	R^2	K_F	1/n	R^2	K_F	1/n	R^2
Lundåkra effluent water	13.5	0.68	0.95	33.4	0.35	0.87	12.8	0.41	0.82	29.4	0.15	0.54
Sjölunda after BOD removal	36.0	0.53	0.92	38.9	0.37	0.95	25.1	0.29	0.83	64.0	0.08	0.15
Sjölunda effluent water	18.0	0.68	0.78	45.5	0.36	0.83	21.0	0.37	0.93	31.8	0.18	0.25

Table A3. The Freundlich Isotherm constants for the normalized graphs with UVA_{254} of filtered water.

The Freundlich exponent (K_F), the Freundlich slope (1/n) and the R^2-value of the Freundlich isotherms fitted to the normalized adsorption of carbamazepine, diclofenac, mecoprop and sulfamethoxazole with UVA_{254} of filtered water to PAC in the three different wastewaters Lundåkra effluent water, Sjölunda after BOD removal and Sjölunda effluent water.

UV filtrerad	Carbamazepine			Diclofenac			Mecoprop			Sulfamethoxazole		
	K_F	1/n	R^2	K_F	1/n	R^2	K_F	1/n	R^2	K_F	1/n	R^2
Lundåkra effluent water	29.8	0.68	0.95	73.9	0.35	0.87	28.3	0.41	0.82	65.1	0.15	0.54
Sjölunda after BOD removal	55.8	0.53	0.92	60.2	0.37	0.95	38.8	0.29	0.83	99.0	0.08	0.15
Sjölunda effluent water	27.2	0.68	0.78	68.8	0.36	0.82	31.8	0.37	0.93	48.1	0.18	0.25

Table A4. The Freundlich Isotherm constants for the normalized graphs with UVA_{254} of raw water.

The Freundlich exponent (K_F), the Freundlich slope (1/n) and the R^2-value of the Freundlich isotherms fitted to the normalized adsorption of carbamazepine, diclofenac, mecoprop and sulfamethoxazole with UVA_{254} of raw water to PAC in the three different wastewaters Lundåkra effluent water, Sjölunda after BOD removal and Sjölunda effluent water.

UVA_{254} raw water	Carbamazepine			Diclofenac			Mecoprop			Sulfamethoxazole		
	K_F	1/n	R^2	K_F	1/n	R^2	K_F	1/n	R^2	K_F	1/n	R^2
Lundåkra effluent water	30.4	0.68	0.95	75.4	0.35	0.87	28.9	0.41	0.82	66.4	0.15	0.54
Sjölunda after BOD removal	72.3	0.53	0.92	78	0.37	0.95	50.3	0.29	0.83	128.4	0.08	0.15
Sjölunda effluent water	32.9	0.68	0.78	83.2	0.36	0.82	38.5	0.37	0.93	58.2	0.18	0.25

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