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Evaluation of sludge biochar for removal of PPCPs in treated greywater

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Abstract

Contaminants of emerging concern, including pharmaceuticals and personal care products (PPCPs), are detected in already vulnerable freshwater sources all over the world and lack of sufficient wastewater treatment and sludge management are the main pathways for PPCPs to enter the environment. Reuse of water could be necessary to cover the water demand in the future. The aim with this study is to evaluate a sludge biochar, pyrolyzed at 600°C, as a polishing step for PPCPs removal in treated greywater. Sludge is an on-site available feedstock for production of biochar for water treatment purposes and can contribute to a safe sewage sludge management. Activated carbon was used to compare the performance of the sludge biochar in a 16-day sorption column experiment. Greywater from a student housing at NMBU was treated with BAF reactor before spiked with the five selected PPCPs; Acetaminophen, Carbamazepine, N,N-Diethyl-meta-toluamide (DEET), Diclofenac and Octocrylene, to a concentration of 1 mg/L. Greywater quality after BAF treatment was exciding the limits for reuse of greywater suggested by IWA and EU, but was within the limits after polishing-step with biochar or activated carbon. The removal rates from the biochar and activated carbon effluents were > 90% for TSS, turbidity, BOD_5 and $COD_{T,}$ and ≥80% for total phosphorus and total nitrogen. pH was unchanged in the biochar column effluents, while pH was increased in the activated carbon column effluents from day 1 to 10.

LC-MS/MS was used to measure PPCPs concentrations. Acetaminophen, carbamazepine, and diclofenac were removed with more than 99% by the biochar and activated carbon. Octocrylene was removed with more than 93% on day 1 to 10 and 80% on day 16. The sorption materials were not saturated at the end of the experiment, and sorption capacity of the biochar and activated carbon material could therefore not be calculated. The PPCPs loadings on the activated carbon and biochar in each column, were in average 0.26 mg PPCP/g activated carbon and 0.17 mg PPCP/g biochar. The evaluation of the sorption mechanisms of PPCPs onto biochar and activated carbon were based on the properties of the sorption materials and the PPCPs. ICP-MS/MS was used to decide heavy metal (As, Cd, Cr, Cu, Ni, Pb and Zn) concentrations in the column effluents. The results showed little or no leach from the biochar and the activated carbon material and some sorption of Ni and Zn were observed.

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Acronyms

AC Activated carbon

ACET Acetaminophen

ASP Activated sludge plant

BAF Biological aerated filter

BC Biochar

BOD Biochemical oxygen demand

CBZ Carbamazepine

CECs Contaminants of emerging concern

CM Carbonaceous material

COD Chemical oxygen demand

DEET N,N-Diethyl-meta-toluamide

DFC Diclofenac

ECs Emerging contaminants

GW Greywater

ICP-MS/MS Inductively coupled plasma mass spectrometry

LC-MS/MS Liquid chromatography – mass spectrometry

OCT Octocrylene

LOD Limit of detection

LOQ Limit of quantification

PAC Powdered Activated carbon

PPCP Pharmaceuticals and personal care products

Q_m Sorption capacity

SSA Specific surface area

STP Sewage treatment plant

TN Total nitrogen

TP Total Phosphorus

TSS Total suspended solid

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1. Introduction

There is an increasing concern of emerging organic contaminants released into the environment, including pharmaceuticals and personal care products (PPCPs). PPCPs are a broad group of organic contaminants used for medical and personal care purposes for both humans and animals (Yang et al., 2017). PPCPs are released into the environment through several pathways, with sewage treatment plant (STP) effluents as the main point source (Quintana et al., 2005). Low-income countries were estimated to treat only 8% of wastewaters in 2018 (WWAP, 2018). Pharmaceuticals and pharmaceutical metabolites are excreted in faeces and urine after use and enter the environment indirectly from STP effluents or sludge disposal. Some unused or expired PPCPs are directly disposed and are realised from direct waste disposal which enter the environment through landfill leachate. Pharmaceuticals are also extensively used in veterinary medicine and can be found in manure. Personal care products are mainly released through the effluent of STPs and sludge but are also washed off directly into marine waters. PPCPs have been detected in STP effluents, surface waters, groundwater and treated drinking water in concentrations in the ng/L to µg/L range (Samal et al., 2022; Yang et al., 2017). These findings show that today's STPs are insufficient and not designed to remove these emerging contaminants. Lack of systems handling sludge and solid wastes with respect to emerging contaminants are serious problems resulting in significant pollution of freshwater sources with community chemicals, pharmaceuticals, heavy metals and pathogenic organisms (WWDR, 2022). Several studies have confirmed that effluent from STPs is the main pathway for PPCPs to enter the environment.

Freshwater ecosystems are essential for health, economics, and development. Similarly, wetlands, rivers, and lakes are the foundation for life. Good drinking water sources and freshwater for agricultural use are under pressure and degradation with the growing demand of these resources from the growing population. United Nations (UN) World Water Development Report (WWDR) stated that in 2022 freshwater withdrawal is increasing with 1% each year and is estimated to do so over the next 30 years (WWDR, 2022). At the same time, in the developing world, poor urban sanitation has been found to show a major impact on the groundwater quality and freshwater environment. Restoring and protecting freshwater sources is also important to face the climate changes and prevent conflicts (UN, 2017). The freshwater challenge is closely linked to UN's Sustainability Development Goal 6; "Ensure availability and sustainable management of water and sanitation for all". In addition, water-related challenges are also related to UN’s goals on preventing disasters, conflicts and climate change, food and energy security and terrestrial and marine ecosystems, and peaceful and inclusive societies. It is a need of change of focus to reach these goals. Focus on wastewater treatment technology development, safe sludge and waste management, resource recovery and reuse of water is important factors.

Reuse of water is a possible solution to cover the freshwater demand and resource recovery, but it comes with a great health risk if done incorrectly. Reuse of water is happening intentionally and unintentionally. Wastewater is intentionally reused in many developing countries with insufficient water quality and causing high health risks, in some cases for drinking water purposes, but mostly for agricultural use, up to 7% of irrigated land in developed countries reuse wastewater untreated (WWDR, 2022). Untreated wastewater is also used to refill groundwater sources. Wastewater is reused unintentionally and can reach surface water and groundwater by infiltration and direct disposal in places where there is a lack of proper sewage infrastructure and treatment possibilities. The reuse of wastewater causes spreading of pollutants such as PPCPs residuals and have been detected in surface waters, groundwater and treated drinking water (Samal et al., 2022; Yang et al., 2017).

Greywater (GW) is considered suitable for reuse, but studies of GW characteristics have confirmed the presence of several organic pollutants such as personal care products, household chemicals and pharmaceuticals (Eriksson et al., 2009). Therefore, treatment and removal of such compounds needs to be considered in GW treatment as well. The magnitude of the health risks and the effects on the environment from the pollutants are not known. Therefore, reuse of water will require good water quality after treatment and effluent from STPs should be free from contaminants.

The performance of the STPs is essential in this principle. Today’s treatment methods are insufficient in removal of some contaminants and need to be upgraded (Zhang et al., 2022). To do so, research and new technologies must be explored. Carbonaceous materials (CMs) such as activated carbon (AC) and biochar (BC) have performed good sorption capacities for PPCPs in earlier studies but needs to be further tested. CMs can be made from a wide range of raw materials. BC from sludge or other waste materials can be a contribution in an environmental circular model due to the recycling of waste materials.

2. Background

2.1 Contaminants of emerging concern and pathways to water sources

Contaminants of emerging concern (CECs) and organic pollutants are increasingly detected in the environment, and freshwater sources are especially vulnerable. Emerging contaminants (ECs) include pharmaceuticals and drugs, industrial pollutants, fire-retardants and personal care and household products. Pharmaceuticals and personal care products (PPCPs) have been recognized as contaminants of emerging concern based on the risk factors of being persistence, bioaccumulate, and toxic (PBT) in the aquatic environment (WHO, 2017). Some PPCPs can be degraded in the environment by biodegradation processes, but some PPCPs act as persistent compounds because of their continuous infusion into the environment through STP effluents (Ferrari et al., 2003).

The consequences of PPCPs contaminations are not completely identified for all compounds, but PPCPs are found in human and animal tissues, food, soil, and waters. Pharmaceuticals perform with a biological effect and can possibly affect nontarget organisms in the environment (Boxall, 2004). Studies have shown health effects on organisms after long-term exposure of organic pollutants at concentrations in the ng/L range (Murray et al., 2010; Zhu et al., 2022). PPCPs have been detected in concentrations, normally in ng/L to µg/L range, in STP influent, effluent, surface water, groundwater and treated drinking water (Langford et al., 2015; Liu et al., 2012; Murray et al., 2010; Quintana et al., 2005; Ternes, 1998; Yang et al., 2017).

PPCPs are released into the environment through several pathways, including through STP effluents (Figure 1). Some pharmaceuticals are not completely degraded after intake, as a result pharmaceuticals and their metabolites are excreted and enter the sewage system. Personal care products applied on skin and hair will wash off and discharge through sinks and showers. PPCPs enter the STPs as a part of the influent and will reach receiving waters from the effluent, due to insufficient removal in the treatment processes (Heberer, 2002a; Heberer, 2002b; Murray et al., 2010; Yang et al., 2017).

PPCPs can also enter the environment through solid waste disposal. A survey in 2004 from UK discovered that 63.2% disposed their unused drugs in household waste and 11.5% discharged them into the sink or toilet (Clara et al., 2004). In Germany, it was estimated that up to 16 000 tons of pharmaceuticals were disposed each year, and 60-80% of the these were flushed down toilets or disposed in normal household waste (Scheytt et al., 2006).

Agricultural runoff is the main source of nutrient loading into surface water, but other pollutants are also released into water sources (WWAP, 2018). Organic compounds in manure or fertilizers can also infiltrate and reach groundwater (Figure 1). Compounds from agricultural runoff or infiltration can be traced back to irrigation with wastewater and fertilization with sewage sludge or manure from animals. Other pathways observed to groundwater is through sludge landfill and waste disposal leachates. Especially polar PPCPs is found in sludge disposal and can leach through the subsoil and enter the groundwater (Heberer, 2002a).

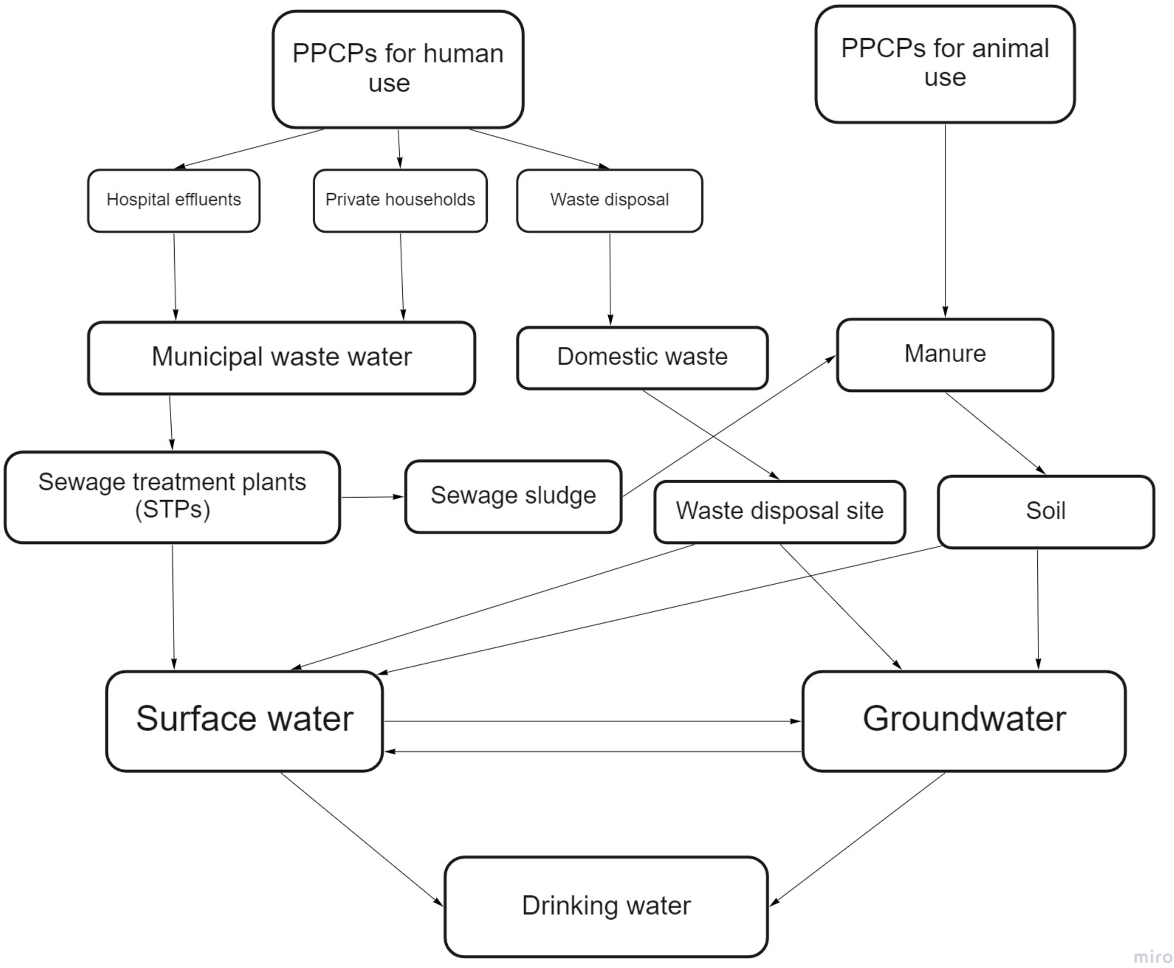


FIGURE 1 PATHWAYS FOR PHARMACEUTICALS AND PERSONAL CARE PRODUCTS TO ENTER SURFACE WATER, GROUNDWATER, AND DRINKING WATER SOURCES, THROUGH INFILTRATION, LEACHATE, RECHARGE AND RUNOFF (HEBERER, 2002A).

2.2 PPCPs

Pharmaceuticals and personal care products (PPCPs) are a broad group of organic contaminants used in medical and personal care of humans and animals (Yang et al., 2017). Pharmaceuticals can be classified according to their purposes and use. Generally, they can be classified into antibiotics, hormones, analgesics, anti-inflammatory drugs, blood lipid regulators, β-blockers, and cytostatic drugs (Samal et al., 2022). Personal care products include preservatives, bactericides, disinfectants, insect repellents, fragrances, and sunscreen ultraviolet (UV) filters. More than 3000 PPCPs have been used for the medical treatment of humans and animals and several of them have been detected in wastewaters and water environment (Yang et al., 2017). Table 1 presents examples of some of the important PPCPs contaminants detected in the environment and their classes (Samal et al., 2022; Zhang et al., 2022)

TABLE 1: PPCPS CLASSIFIED ACCORDING TO THEIR USE (SAMAL ET AL., 2022; ZHANG ET AL., 2022).

PPCP Groups	**Subgroups**	**Examples of representative compounds**
Pharmaceuticals	Antibiotics	Clarithromycin Ciprofloxacin
	Hormones	Estrone Estradiol Ethinylestradiol
	Analgesics and anti-inflammatory drugs	Diclofenac Ibuprofen Acetaminophen Naproxen
	Antiepileptic drugs	Carbamazepine
	Blood lipid regulators	Clofibrate Gemfibrozil
	Beta-blockers	Metoprolol Propranolol

	Cytostatic drugs	Ifosfamide Cyclophosphamide
Personal Care Products	Antimicrobial agents/disinfectants	Triclosan
	Synthetic musk/fragrances	Galaxolide
	Insect repellents	N,N-diethyl-m-toluamide (DEET)
	Preservatives	Parabens(alkyl-p-hydroxybenzoates)
	UV-filters	Octocrylene

The consumption volume of a pharmaceutical can be estimated by dose per capita, with differences between developed and developing countries (Zhang et al., 2008). For example, it is estimated that 1014 tons of carbamazepine (CBZ) and 940 tons of diclofenac (DFC) are consumed yearly worldwide (Clara et al., 2004; Zhang et al., 2008).

Analgesics and anti-inflammatory drugs used as painkillers are sold in large amounts, often in higher quantities because they can be bought without a prescription. Acetaminophen (ACET) is one of the most popular painkillers and is mainly sold without a prescription. Herberer (2002a) estimated in 2002 that more than 500 tons of ACET was sold each year in Germany only. Other analgesics such as diclofenac (DFC) and Ibuprofen was sold in quantities of 75 and 180 tons per year and have been recognized as important pollutants in the water-cycle (Heberer, 2002a).

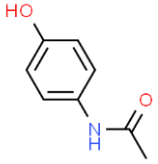
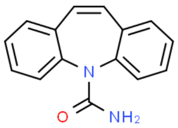
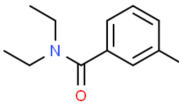
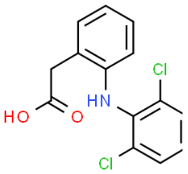
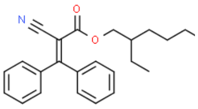
Knowledge about consumption of a PPCP can, together with the molecular properties of the PPCP, be used to estimate their presence in the environment, efficiency of treatments and the long-term risks. For example the pharmaceutical Acetaminophen (ACET), one of the most commonly used pharmaceuticals all over the world, is constantly present in the sewage system inlets, but it is only detected in 10% of the effluents from STPs and was not detected in river downstream in Germany (Heberer, 2002a). Despite the high consumption, ACET was only detected in 17% of all samples from 142 streams in the US in 2002 (Kolpin et al., 2002). The explanation can be found in ACET's properties. It is easily degradable in some treatment processes and therefore removed more effectively in STPs (Yang et al., 2020). On the other hand, CBZ and DFC are the two pharmaceuticals most often found in the environment, due to ineffectively removal in STPs (Clara et al., 2004). CBZ is removed with less than 10% in most cases and DFC removal varies from 0-80% (Rossi et al., 2013). Their properties make them less degradable and sludge retention time does not influence the removal. Therefor they are often detected in the STP effluent, surface water and groundwater. They have been detected in µg/L range in surface waters in Austria, Brazil, Germany, Greece, Spain, Switzerland, and the US (Heberer, 2002a).

It is a risk of PPCPs exposure through food from agricultural transfer from sludge disposal directly to agricultural lands, wastewater irrigation and manure. PPCPs have been detected in human breast milk, blood, and urine from children (Chopra & Kumar, 2018). And studies have shown accumulation of benzyl paraben and benxopheone-4 in placenta, suggesting that mother-foetal transfer is possible (Zhang et al., 2022). Most PPCPs are detected in low concentrations in the environment and will not cause acute toxic effects, but their chronic effects cannot be excluded (Zhang et al., 2008). The risk of adverse health effects from PPCPs in the environment can be calculated and is called PNEC-value (predicted no-effect concentrations).

2.3 PPCPs in this experiment

The five different PPCPs, Acetaminophen (ACET), Carbamazepine (CBZ), N,N-diethyl-m-toluamide (DEET), Diclofenac (DFC) and Octocrylene (OCT) were selected for this experiment because of their varieties in properties, the extent of worldwide use, challenging removal, and removal efficiency in STPs and frequent and high detection in the aquatic environment. The properties of the selected PPCPs can be found in Table 2. An important property for PPCPs long-time pollution in the environment are octanol-water partition (log K_{ow}) the ability to adsorb to soil and organisms, inversely related to water solubility, hydrophilicity and proportional to molecular weight.

Table 2: Selected PPCPs for this thesis with their properties.

	Acetaminophen (ACET)	**Carbamazepine (CBZ)**	**N,N-diethyl-m-toluamide (DEET)**	**Diclofenac (DFC)**	**Octocrylene (OCT)**
CAS No.	103-90-2	298-46-4	134-62-3	15307-79-6	6197-30-4
Therapeutic class	Nonsteroidal anti-inflammatory	Antiepileptic	Insect repellent	Nonsteroidal anti-inflammatory	UV-filter in PCPs
Molecular structure					
Molecular Formula	$C_8H_9NO_2$	$C_{15}H_{12}N_2O$	$C_{12}H_{17}NO$	$C_{14}H_{11}Cl_2NO_2$	$C_{24}H_{27}NO_2$
Molecular weight [g/mol]	151.2	236.3	191.27	296.16	361.48
logK$_{ow}$	0.46	2.45	2.02	1.9	7.3
Reference	(Garcia-Ivars et al., 2017; Kim et al., 2007; Yanyan et al., 2017) (ChemSpider, 2022a)	(Kim et al., 2007) (ChemSpider, 2022b)	(ChemSpider, 2022c; Information, 2022)	(Garcia-Ivars et al., 2017) (ChemSpider, 2022d)	(ChemSpider, 2022e; Langford et al., 2015)

2.3.1 Acetaminophen (ACET)

Acetaminophen (ACET) is one of the most commonly used drugs for pain and fever treatment, also marketed as Paracetamol. It has relatively few side effects in human body, and is a low cost drug (Montaseri & Forbes, 2018). It is constantly introduced to the environment because of its extensive use.

Studies have shown ACET to be non-persistent in the nature and it is therefore expected to biodegrade in the environment. The potential of bioaccumulation is low due to its low octanol-water partition coefficient (log $K_{OW} < 1$) (Table 2), but it has been detected in concentrations from ng/L to µg/L in aquatic environments and can be explained by the constant discharge. Acute and chronic damage to aquatic organisms have been recorded at low levels (Phillips et al., 2010).

2.3.2 Carbamazepine (CBZ)

Carbamazepine is an anti-epileptic drug and is a well-established drug used to control psychomotor epilepsy. Estimated consumption in 2002 was 1040 tons worldwide (Zhang et al., 2008). The extent of the use and the properties of the PPCP makes it one of the most frequently detected persistent organic pollutant in European rivers (Murray et al., 2010). It has a low removal rate from STPs, and a study from Berlin in 2001 showed only 8% removal after treatment with maximum effluent value of 5 µg/L, with average concentration of 1.78 and 1.86 µg/L (Heberer, 2002b). It is not expected to bioaccumulate, but it has shown little biodegradation in STPs with activated sludge (Zhang et al., 2008).

CBZ is one of the most detected PPCP in the aquatic environment. Several studies have measured CBZ in surface waters, groundwater and drinking water. 1075 ng/L was detected in the Berlin River, while in the US; 610 ng/L in groundwater, 2 ng/L in marine waters, 60 ng/L and 41.6 ng/mg in sediments of 44 rivers (Clara et al., 2004; Heberer, 2002a; Heberer, 2002b; Yang et al., 2017). A study carried out in the Mediterranean in 2006 also detected concentrations of 43.2 and 13.9 ng/L of CBZ in drinking water wells (Zhang et al., 2008). The properties of CBZ increase the chance of presence in groundwater in regions where STP effluents are used for groundwater recharge (Rabiet et al., 2006).

2.3.3 N,N-diethyl-m-toluamide (DEET)

DEET is the most common active ingredient in insect repellents and provide protection against mosquitoes, ticks, fleas, and many biting insects. It can be found in many different products such as spray, liquid and lotions in concentrations up to 100%, or it can be incorporated into clothes (Pennetier et al., 2010). The estimated usage of DEET was calculated to be 1810 tons in the US in 1998 (Fediuk et al., 2012).

DEET is not expected to bioaccumulate due to its low $\log K_{ow}$ properties but is still detected in low concentrations in water bodies. DEET is biodegradable, but DEET was still one of the most frequently detected polar organic contaminants in a groundwater study from 23 European countries in 2010 (Loos et al., 2010). It was detected in 84% of the samples and the maximum concentration detected was 454 ng/L (Loos et al., 2010). It was also the most frequently detected compound in a study of groundwater in the US in 2000 (Barnes et al., 2008). DEET retain in the liquid phase in wastewater due to little sorption to sludge. The release to the environment will therefore largely depend on the treatment processes (Santos et al., 2019). DEET is found moderately toxic to aquatic organisms, with algae at most risk (ECHA, 2010).

2.3.4 Diclofenac (DFC)

Diclofenac (DFC) is a non-steroidal anti-inflammatory drug (NSAIDs) and used to relieve pain. The PPCPs is sold in large quantities every year, estimated to 940 tons every year worldwide in 2001 (Zhang et al., 2008). It is an often-studied PPCPs in the environment, due to its frequently detection in the environment.

A study from Berlin in 2001 reported STP influents and effluents average concentrations to be 3.02 µg/L and 2.51 µg/L with an removal rate on 17% (Heberer, 2002b). In the same study DFC was detected at concentrations up to 1000 µg/L in surface water downstream from a STP. The removal rate of DFC is reported to varies from 0-80% in STPs and is highly dependent on treatment processes due to its properties (Yang et al., 2017). According to European chemical agency, DFC is toxic to aquatic life with long lasting effects (Cleuvers, 2003).

2.3.5 Octocrylene (OCT)

Octocrylene (OCT) is an organic compound used in sunscreens, personal care products and cosmetics. It absorbs UVB and short-wave UVA with wavelengths from 280 to 320 nm (Carve et al., 2021). It enters the environment directly by being washed of the skin during swimming or indirectly by landfill leaching from sludge or as effluent from STPs (Carve et al., 2021). It is predicted an increase in use of products containing OCT because of the increased awareness of the dangers of UV radiation exposure.

OCT has been detected in dolphins, fish, molluscs and corals in concentrations from ng/L to µg/L (Carve et al., 2021) and has potential of bioaccumulation with $\log K_{ow} > 7$. In a study from the Oslofjord in Norway OCT was detected in 12 out of 15 cod livers tested, with a maximum detection of 12 µg/g liver (Langford et al., 2015). In the same study OCT was detected in sewage sludge from 5 to 51 µg/g. OCT is according to European Chemical Agency registered under substances very toxic to aquatic life with long lasting effects(ECHA, 2022). It was added to bioaccumulation and toxicity list (PBT) in 2022.

2.4 PPCP removal in wastewater treatment

The detection of PPCPs in STPs effluent and the environment is evidence of insufficient removal of organic compounds during treatment. STPs are designed to remove solids, suspended particles, nutrients, and dissolved biodegradable organic matter, but not specifically designed to eliminate emerging contaminants such as PPCPs. The properties of PPCPs vary and the removal therefore require different technologies to target and prevent pollution. Sewage treatment includes physical, chemical, or biological treatment processes, often applied as a combination of multiple technologies. Some of today’s technologies are sufficient for removal of some PPCPs, but other PPCPs have no reduction after treatment. Several studies have observed the behaviour of PPCPs in STPs and different treatment techniques.

2.4.1 Physical/Physicochemical processes

Physical processes including sedimentation, sorption and membrane filtration have been tested for PPCP removal. In sedimentation suspended solids are removed by gravity. For most PPCPs sedimentation results in low removal, because many PPCPs are hydrophilic (Luo et al., 2014; Yang et al., 2017). A few PPCPs can be reduced by sedimentation through sorption to solids. In STPs PPCPs also can be removed by sorption during the activated sludge process (Ebele et al., 2017). The removal efficiency by sedimented sludge varies due to the physical-chemical properties of the PPCPs. Especially highly water soluble PPCPs will not have any removal effect. Removal of PPCPs by sludge can also be a challenge because of insufficient sludge management and therefore be a pathway for PPCPs pollutants to the environment.

Membrane filtration is another physical treatment process. PPCPs removal with membrane filtration relies on size exclusion, sorption onto membrane and charge repulsion (Zhang et al., 2022). The filtration removal efficiency is dependent on molecular weight and hydrophobicity. Molecules smaller than the membrane cannot be removed efficiently. A nanofiltration experiment showed that triclosan was removed with 80%, while acetaminophen (ACET) was only reduced with 30-40% (Garcia-Ivars et al., 2017). The results can be explained by comparing their molecule size and hydrophobicity. ACET is hydrophilic with log $K_{OW} < 1$ and has a lower molecular size than some membrane pores. Triclosan is highly hydrophobic with log $K_{OW} > 4$ and nearly doble molecular weight (Garcia-Ivars et al., 2017). Other studies have shown promising results for removal of PPCPs in reverse osmosis (RO), and less removal with ultrafiltration (UF) (Urtiaga et al., 2013).

2.4.2 Chemical processes

Several chemical processes have been tested for PPCPs removal from water such as advanced chemical processes using oxidation e.g., ozonation, UV oxidation, and Fenton and Fenton-like (conventional) processes (Zhang et al., 2022). In Fenton oxidation highly oxidizing hydroxyl species are responsible for the degradation of organic pollutants. Fenton oxidation processes have been tested and showed promising results in removal of β-blockers and antibiotics (Annabi et al., 2016; Veloutsou et al., 2014). Hydroxyl species can also be produced in water containing H_2O_2 under UV light for removal of PPCPs (Guo et al., 2018). UV cannot alone destroy chemical bonds of organic pollutants through pyrolysis but are effective in removal of PPCPs in combination with H_2O_2 (Lai et al., 2017). H_2O_2/UV is effective, but is costly and UV irradiation can be responsible for formation of by-products with higher polarity and water solubility then the parent compound (Yang et al., 2016).

2.4.3 Biological processes

Activated sludge process (ASP) is commonly used in STPs and has been reported to be effective in removal of several PPCPs. The removal mechanisms of PPCPs in a sewage treatment plant can be divided in to biodegradation (45%), sorption to sewage sludge (33%), and UV irradiation (22%) (Salgado et al., 2012). Fenoprofen, ketoprofen, naproxen and triclosan is effectively removed in ASP, while DFC and CBZ are persistent in this process.

It is difficult to predict degradation of PPCPs in ASP because the results from one plant cannot be compared to other plants directly due to the variation in sludge characteristics (Chen et al., 2015). PPCPs in the sludge after the process are not necessarily eliminated and can cause secondary pollution during sludge disposal. Approximately 50% of the treated sludge in Europe is applied to soil and can lead to chronic environmental risks (Martín et al., 2015).

Membrane Bioreactor (MBR) has shown good removal efficiency for sulfamethoxazole, ethinyl oestradiol, progesterone and metoprolol. MBR is a combination of suspended growth bioreactor as a biological treatment process and a membrane filtration system as a filtration process (Musson et al., 2010). Attached growth bioreactors are an alternative to suspended growth systems for PPCPs removal. The use of biofilters have been proposed due to their low space and energy requirements (Zhang et al., 2022). Biofiltration can be combined with other treatment processes by adding sand and granular activated carbon (GAC) to biofilters or integrate ozonation.

The removal rate of several of the five selected PPCPs used in this experiment have been studied in STPs. CBZ had less than 20% removal in 11 STPs with ASP in 2004 (Clara et al., 2004). DEET was removed with 5%-93% in sedimentation followed by ASP (Gao et al., 2016) and 7% was removed by UV (Gao et al., 2016; Wang et al., 2014). Physical treatment of DFC with sedimentation and ASP had a removal rate between -13 and 18% (Papageorgiou et al., 2016) and -57 to 96% with grit removal and activated sludge (Kosma et al., 2014). Several other studies reported DCF removal between 22 and 55 % with activated sludge (Archer et al., 2017; Kramer et al., 2018; Patrolecco et al., 2015). It has been observed degradation of OCT in activated sludge (Liu et al., 2012).

2.5 Carbonaceous materials (CMs)

Carbonaceous materials (CMs) are materials containing a significant amount of carbon such as activated carbon (AC) and biochar (BC). They have a large surface area, developed pore structure and abundant functional groups. The properties of CMs give them ability to sorption, hence they can be used for removal of organic pollutants in water and wastewater (Zhang et al., 2022). CMs have also been used to increase soil fertility and crop production (Ahmed et al., 2016).

2.5.1 Activated Carbon

Activated Carbon (AC) is ideal for removing contaminants from water, but can be costly to make (Mohan et al., 2014). Commercial ACs are produced from carbon-rich organic materials such as coal, lignite and wood (Baker et al.). The AC is activated by either thermal activation or chemical activation and are produced in granular, powdered, or shaped products. The large surface area, high micro pore content and surface functional groups on AC makes it a good sorbent (Lee et al., 2013).

2.5.2 Biochar

Biochar is a stable carbon-dominant product produced by thermal conversion of organic products under complete or partial absence of oxygen; pyrolysis (Zhang et al., 2022). BC is produced by pyrolysis and pyrolysis processes are listed in Table 3. BC is an alternative sorbent to AC due to its properties, low-cost and environmentally friendly production. BC has large specific surface area, developed pore structure and abundant functional groups that makes it a good sorbent for various pollutants (Zhu et al., 2022). The characteristics of BC will depend on pyrolysis temperature, heating rate, residence time and type of raw materials. It will affect the yield, surface area, pore volume, ash, element composition, viscosity, calorific value and water content (Ahmed et al., 2016). BC can be made from multiple feedstocks, for example agricultural materials, wood, solid waste, food waste, and animal litters.

Pyrolysis produces several products including biochar, bio-oil, solid fuel and synthetic gas (Ahmed et al., 2016). BCs are mostly produced in slow pyrolysis also called conventional carbonization, whereas flash carbonization, torrefaction, fast pyrolysis and gasification is used to produce bio-oil, solid fuel and synthetic gas yields.

TABLE 3: DIFFERENT PYROLYSIS PROCESSES (AHMED ET AL., 2016)

Thermochemical process	**Temperature range (°C)**	**Yield (%)**	**Residence time**	**Heating rate**
Slow pyrolysis	100-1000	15-40	Minutes to hours	Slow (<10°C/min)
Fast pyrolysis	300-1000	10-25	< 2 s	Very fast (1000 °C/s)
Torrefaction	200-300	61-77	Minutes to hours	Slow (<10°C/min)
Gasification	700-1500	10	Second to minutes	Moderate-very fast
HTC	175-300	20-72	30 min to 16 h	Slow

Microwave pyrolysis	550-700	34	5-20 min	Slow
Flash carbonization	300-600	37-50	30 min	Slow

BC can also be activated (designed BC) to improve the sorption capacity further. Properties of BC can be divided in to: Specific surface area and pore size and surface functional groups. Both is important when evaluating different use of BC.

2.5.3 Activated carbon and biochar properties

CMs like AC and BC can be characterised from different properties of the material. The properties will depend on the feedstock and pyrolysis temperature. Specific surface area (SSA), pore size and pore distribution and elemental composition are important properties to predict sorption capacities of the material.

Specific surface area and pore size

Specific surface area is often linked to the sorption characteristics of a sorbent. For instance, a large specific surface area (SSA) is important to increase the sorption sites for contaminants and larger SSA can usually contribute to higher sorption capacity. The SSA is positively correlated with the pyrolysis temperature due to the escape of volatile substances from biomass and thus formation of channel structure during pyrolysis (Ahmed et al., 2016). These channels improve the specific surface area and pore structure of the BC. Yield will decrease with pyrolysis temperature, while pore volume, ash and SSA will increase. Wood materials have shown high surface area and carbon content and will be well suited as sorbent material (Dzihora et al., 2021). The increased sorption capacity due to larger surface area and pore size was demonstrated in a study where rice husk BC pyrolyzed at 700 °C showed much higher capacity of sorption then rice husk BC produced at 300 °C (Zeng et al., 2018). AC has typically a high SSA (Tong et al., 2016).

The distribution of pore size effects the sorption efficiency. Pores can be divided in micropores (pore diameter < 2 nm), mesopores (2 nm < pore diameter < 50 nm) and macropores (pore diameter > 50 nm) (Liu et al., 2014). Micropores provide sorption sites while mesopores and macropores act as diffusion channels, shortening sorption time (Liu et al., 2014). The pore size is important in the sorption of PPCPs, as micro-pores can be size-exclusive to PPCPs with larger molecular wight (Zhang et al., 2022). AC consists of mainly micropores, while the pore size and distribution on BC varies a lot due to a wide range of feedstock possibilities.

Elemental composition

The elemental composition is an important property of BC and AC. Carbon, oxygen, and hydrogen can be plotted against the pyrolysis temperature. The carbon content of BC will increase with increasing pyrolysis temperature. Hydrogen and oxygen contents decrease with increasing pyrolysis temperature. The H/C ratio is used as a degree of carbonization due to hydrogen being associated with the organic matter biomass (Ahmed et al., 2016). The ratio also indicates that there are more alkyl groups present in BCs if this ratio becomes higher. A higher O/C ratio in BCs may be indication of more oxygenated functional groups, representing more negative surface charge (Ahmed et al., 2016). High H/C and O/C molar ratios indicates that the BC contain higher alkyl as well as oxygenated groups in the core structure. Lower O/C and H/C ratio indicates lower functional group in the BC core structure. An increase in oxygen-containing functional groups on BC can be beneficial to the sorption of PPCPs containing amino groups, carbon-carbon double bonds, benzene rings or other groups that can be used as electron donors (Zhang et al., 2022). For sorption of PPCPs on BC, the one which is electron-rich can act as a donor to the electron-poor acceptor, resulting in a specific non-covalent force, the π-π EDA interaction (Chen et al., 2007). AC has typically a high carbon content, due to carbon rich feedstock material for AC.

2.5.4 Biochar in PPCPs removal

The sorption capacity of BC for PPCPs will vary depending on the properties of the PPCPs and the characteristics of the BC (Ming Zhang, 2020). Pyrolysis process has an effect on the structural morphology and functional groups of BC, and therefore, resulting in different sorption capacities for PPCPs (Ming Zhang, 2020). BC with higher SSA is more effective in adsorbing contaminants such as organic pollutants from water (Ahmed et al., 2016). It is a wide variation on surface area, carbon content, hydrogen content and oxygen content in BCs from different feedstocks. In addition, modification of the BC can be performed to increase the SSA and opening and creating new pores. For example can BC be modified with HCl and gain a better sorption capacity for Triclosan (Tong et al., 2016). The sorption capacity (Qm) of CBZ by pomelo biochar was increased with an increase in SSA and pore volume and had the sorption capacity of up to 286.5 mg/g (Chen et al., 2017). Studies have proven that pore-size is significant in sorption of PPCPs. Micro- and mesoporous carbons were tested for sorption of three antibiotics with different sizes; small-sized sulfamethoxazole could de adsorbed to the microporous material, but tetracycline and tylosin would not occupy the pores due to size-exclusion effect (Ji et al., 2010).

2.5.5 Activated carbon in PPCPs removal

ACs have been applied to remove a broad spectrum of dissolved organic pollutants due to its large surface area, developed pore structures and industrial availability. The wide use of AC comes from the wide range of physical and chemical surface properties of commercially available and specifically treated carbon materials (Mohan et al., 2014). AC has been used in a PPCPs removal experiments where 26 pharmaceuticals were treated in a large-scale experiment with powdered activated carbon (PAC) (Mailler et al., 2015). Six of the pharmaceuticals were poorly removed (<60%) including ibuprofen, paracetamol and estrone. Some of the contaminants including beta-blocker and CBZ, were removed with a removal efficiency higher than 80%, whereas some other compounds including DFC and naproxen, were experienced removal efficiency between 60% and 80% (Mailler et al., 2015). AC has also been studied in combination with other technologies. For examples was dielectric barrier discharge plasma combined with AC fibres for a 93% removal of Triclosan (Xin et al., 2016). PAC in combination with ultrafiltration has been shown to result in the removal of 60-95% of emerging contaminants (Löwenberg et al., 2014).

2.5.6 Regeneration of CMs

To make the production and use of CMs economical it is necessary to be able to regenerate the product after use. Regeneration can be done by thermal regeneration, chemical and solvent regeneration, microwave, microbiological, electrochemical, ultrasonic and wet air oxidation regeneration method (Ahmed et al., 2016). Thermal regeneration of CMs can be done by pyrolysis, pyrolysis-gasification and gasification. The adsorption capacity may drop slightly during regeneration cycle. Regenerated BC from pomelo peel has 58.5% capacity retention at the fourth cycle for the sorption of CBZ (Chen et al., 2017). The potential emissions of PPCPs in the regeneration of CMs with thermal or solvents, should be considered, and waste gas and waste solvents from the regeneration need to be handled (Zhang et al., 2022)

Aims and objectives

Freshwater demand is increasing, and reuse of wastewater can be necessary to cover the demand in large parts of the world. To be able to do so, the quality of the treated wastewater needs to be sufficient for its use. At the same time, there has been an increasing focus on contaminants of emerging concern. PPCPs have shown to be resistant in the environment and possible harmful for human and animal health and a possible threat to already vulnerable fresh water sources. Traditional wastewater treatment is not sufficient in PPCPs removal and previous studies have shown how they end up in the environment.

Both biochar and activated carbon have a high capacity for organic contaminants removal and are products worth considering when promoting green and sustainable wastewater treatment methods. Biochar is an easily accessible product, with a wide range of raw material possibilities which can be adapted to available waste products. Sewage sludge is a promising feedstock for the production of biochar, considering safe sewage sludge management is a challenge in many places in the world.

The main objective of this master's thesis is to evaluate sewage sludge biochar as a potential sorbent for the removal of the five selected PPCPs; Acetaminophen, Carbamazepine, DEET, Diclofenac and Octocrylene, and to compare sewage sludge biochar with activated carbon in a greywater batch experiment. PPCPs removal rate will be measured from the effluent of sorption columns filled with either BC or AC. Possible release of other compounds such as heavy metals and nutrients is also considered.

3. Materials and methods

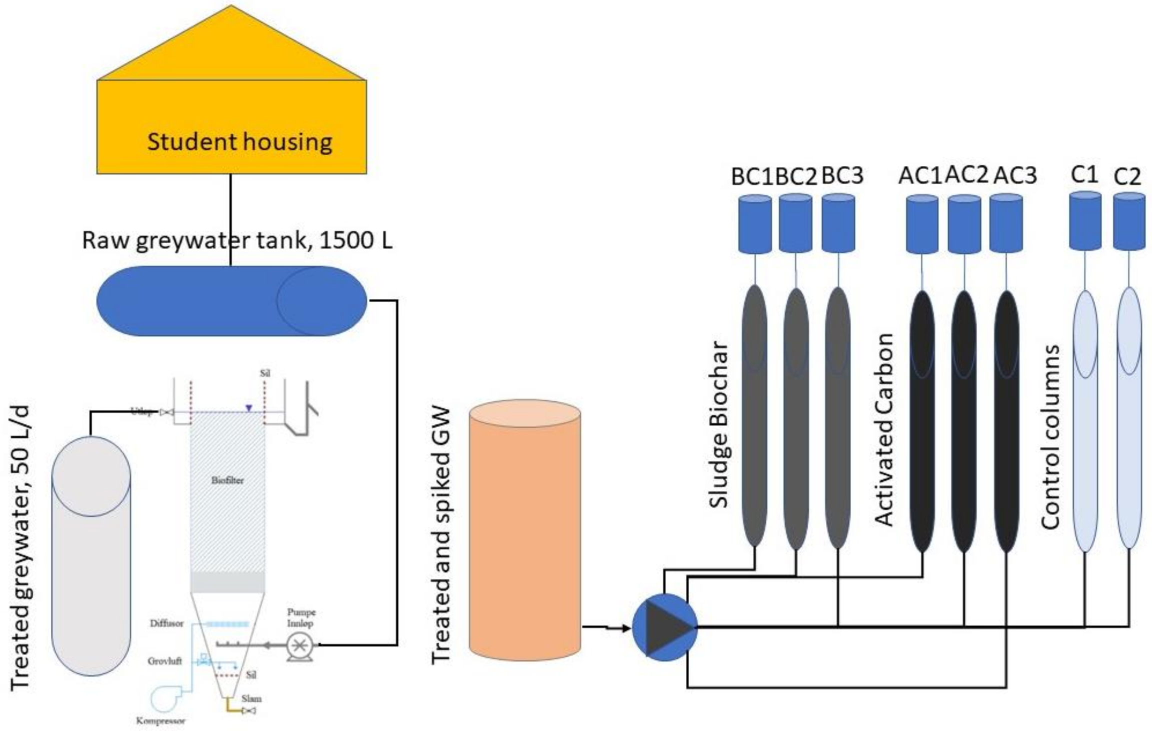


Figure 2: Greywater line from student housing to sample collection after polishing step in this study. Details of the greywater treatment is shown in Figure 3.

In this experiment, the greywater (GW) was collected from the student housing at Kajaveien at NMBU. Figure 2 shows the experimental setup from raw greywater source in the student housing at Kajaveien to sample collection after the polishing step in the laboratory.

3.1 Greywater

Kajaveien student housing consists of 24 student apartments, with 48 permanent residents (Todt et al., 2015). GW from the student housing is led by gravity drained pipe to a drain and then pumped to a 1500 L container in the Fløy 4 laboratory at the Faculty of Science and Technology, NMBU. The tank has a slow stirrer (30 rpm) and the retention time in the pipeline and tank is calculated to be between 36-48 hours. Raw GW quality was measured from February 2022 to June 2022. Water quality parameters measured include biochemical oxygen demand (BOD_5), total suspended solids (TSS), turbidity, total nitrogen (TN), total phosphorus (TP), pH, and chemical oxygen demand (COD_T).

GW is then pumped from the 1500 L tank to a biological aerated filter (BAF) reactor for pre-treatment. It was pumped with a peristaltic pump (Bredel SPX10) with a flowrate on 50 L/d.

3.1.1 Greywater pre-treatment

The greywater treatment setup with BAF treatment (Figure 3) is based on Simon Rummelhoff's setup for his master's thesis in 2019 (Rummelhoff, 2019). GW was pumped from the 1500 L tank to the reactor with a hydraulic load of 50 L/day. The reactor has a up flow stream with submerged biofilter. Filter material used is a floating biomedia (BWT S^{TM}) from Biowater with a protected growth surface on 650 m^2/m^3. The specification of the Biomedia BWT S^{TM} is indicated in Table 4. A mix of new and used biomedia was added to the tank to speed up biofilm development.

TABLE 4: BIOMEDIA BWT S^{TM}.

Spesific weight [kg/L]	0.95
Protected biofilm surface area [m^2/m^3]	650
Material	Polyethylene, high density
Weight of BWT S^{TM} [kg/m^3]	122

The reactor column is round with an inner diameter of 0.24 m. Table 5 shows dimensions and measurements for the biofilter in the reactor.

TABLE 5: DIMENSIONS AND MEASUREMENTS FOR BIOFILTER (RUMMELHOFF, 2019).

Filter depth [m]	0.9
Degree of filling [%]	74
Reactor volume [L]	54
Total protected growth area [m^2]	26
Filter area [m^2]	0.044
Filter volume [L]	40
Total liquid volume [L]	50.6

As shown in Figure 3, air is added through two perforated pipes connected to a compressor and volume flow regulator to move through and mix the biofilter. The greywater inflow pipe is situated 10 cm under the air flow inlet. The effluent of biofiltrated greywater was collected using outflow pipe from the top of the column. The BAF treatment system is shown in Figure 3, and the specifications for the filter with a hydraulic load on 50 L/d are presented in Table 6.

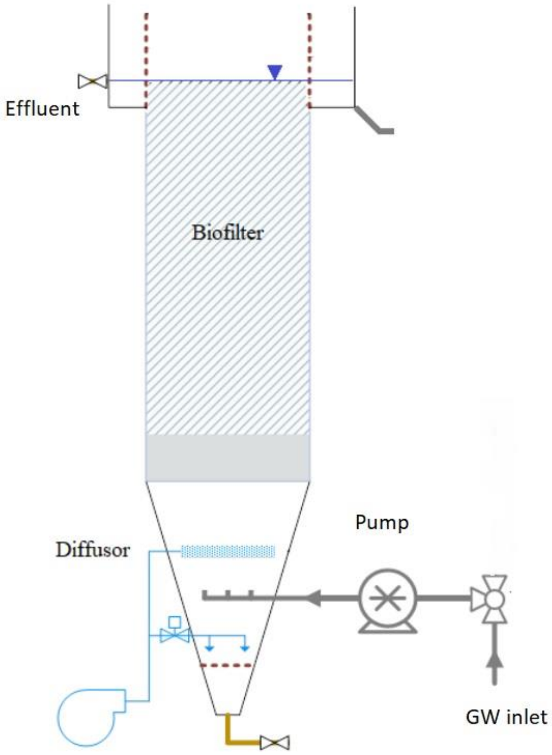


FIGURE 3: FIGURE FROM PREVIOUS MASTER'S THESIS (RUMMELHOFF, 2019)

TABLE 6: CONDITIONS FOR BIOFILTER WITH HYDRAULIC LOAD ON 50 L/DAY

Hydraulic load [L/d]	50
Filter velocity [m/h]	0.05
Theoretical retention time [h]	24.3

The BAF treatment of GW started 18.02.2022 but had to be stopped 31.02.2022 due to problems with aeration. The BAF was restarted and was in use from the beginning of March and a backwash was performed every three weeks. Backwash of the filter was done with disconnection of the GW inlet and connection of hose with tap water. At the same time aeration was turned up to make a mixing in the biofilter media. Washing was performed for approximately 5 minutes. BOD_5, turbidity, TSS and pH was measured five times from inlet and outlet, and additional five turbidity measurements from outlet upon batch collection to estimate treatment efficiency and time for backwash.

Treated GW for spiking was collected between 23.04.2022 and 27.04.2022 at the end of the washing cycle. 150 L of treated GW was collected in a steal tank. The BAF treated GW was then spiked with five selected PPCPs.

3.2 PPCPs spiking of greywater

3.2.1 Preparation of PPCPs solutions

All chemicals were purchased through Merck (Darmstadt, Germany). Acetaminophen and Diclofenac was each dissolved in ethanol 96% from VWR (Radnor, PA, USA) to a concentration of 40ppm. Carbamazepine and Octocrylene were each dissolved in 99.8% anhydrous methanol from VWR (Radnor, PA, USA) to a concentration of 40ppm. DEET was dissolved in ethanol 96% to a concentration of 30ppm. Table 7 presents the preparation and final concentrations.

3.2.2 Spiking

To make the 150 L of spiked GW batch for the experiment 100 L of treated greywater was transferred to the batch steel container before spiking. 3.75 mL of each 40ppm solution of PPCPs was then added with pipette to the container, and 5 mL of the 30ppm solution. Then 50 L of treated greywater was added for mixing. The concentration of each PPCPs in the batch tank of 150 L was 1 mg/L with a total of 5 mg PPCP/L.

TABLE 7: PREPARATION OF PPCPS SOLUTIONS

PPCPs	Amount of PPCPs	Dissolvent	Solution concentration	Solution added batch	Batch concentration
Acetaminophen (ACET), BIOXTRA, ≥99,0% from Sigma-Aldrich (Burlington, MA, USA)	1 g	25 mL ethanol	40 mg/mL	3.75 mL	1 mg/L
Carbamazepine (CBZ) Sigma-Aldrich (Burlington, MA, USA)	1 g	25 mL methanol	40 mg/mL	3.75 mL	

DEET, 98.5% Supelco (Bellefonte PA, USA)	750 mg	25 mL ethanol	30 mg/mL	5 mL
Diclofenac (DFC) sodium salt ≥98% Sigma-Aldrich (Burlington, MA, USA)	1 g	25 mL ethanol	40 mg/mL	3.75 mL
Octocrylene (OCT) 97% Sigma-Aldrich (Burlington, MA, USA)	1 g	25 mL methanol	40 mg/mL	3.75 mL

3.3 Sorption columns

Eight columns were used in this batch experiment. Three columns with biochar, three columns with activated carbon and two empty control columns. Each column was made of PVC with an inner diameter of 42 mm and hight 310 mm. Top and bottom were made of PVC and has 1/8’’ inlet in bottom and outlet on top.

3.3.1 Filter material preparation

Biochar used in this experiment was pyrolyzed by Scanship AS at Lindum AS (Drammen, Norway). Feedstock material for the biochar was sewage sludge-biorest, digestate from a biogas plant in Drammen handling sewage sludge. The biorest was dried to >90% TS and pelletized to 8 mm pellets in diameter. The pyrolysis was done with FoU pyrolysis in a ETIA (conventional pyrolysis technology) to produce biochar on 600 °C with 20 minutes retention time. Activated carbon from WATTS (North Andover, MA, USA), bought from ECOWATER (Drøbak, Norway), was used to compare the performance efficiency of sludge biochar in the removal of PPCPs in treated greywater.

Biochar and activated carbon were further prepared the same way for this experiment. The material was first sieved with 2 mm mesh followed by sieve with 1 mm mesh to collect material with particle size 1-2 mm. Biochar and activated carbon were then carefully washed in cold water until washing water was clear. The material was then dried at 105 °C for 24h. The amount of BC and AC used to fill the columns is presented in Table 8.

TABLE 8: AMOTNH OF BC AND AC FILLED IN EACH COLUMN, IN WEIGHT AND VOLUME. DIAMETER, HIGHT AND VOLUME ARE THE SAME FOR ALL COLUMNS.

Column	Particle size [mm]	Weight [g]	Volume [mL]	Diameter [mm]	Hight [mm]	Volume [L]
Biochar 1 (BC1)	1-2	436.5	475	42.5	310	1.76
Biochar 2 (BC2)	1-2	435.5	470			
Biochar 3 (BC3)	1-2	442.4	485			
Activated Carbon 1 (AC1)	1-2	305.3	455			
Activated Carbon 2 (AC2)	1-2	308.1	460			
Activated Carbon 3 (AC3)	1-2	313.1	475			
Control 1 (C1)	-	-	-			
Control 2 (C2)	-	-	-			

3.3.2 Biochar characterisation

The characterisation of the BC used in this sorption experiment can be found in Table 9 and is based on the characterisation done by Yuliia Dizhora (2021), who characterised BC from the same feedstock, pyrolyzed at the same temperature from the same company (Lindum AS) for her Master thesis at NMBU in 2021.

TABLE 9: SLUDGE-DERIVED BC CHARACTERISTICS (DZIHORA ET AL., 2021)

Property	Sludge-Biochar, 600°C from Lindum AS
pH	8.08
Ash content [%]	85.9
Specific surface area $a_{s\ BET}$ [m^2/g]	77.97

Average pore diameter [nm]	7.14
Total pore volume [cm^3/g]	1.1391
Micropore volume	0.165
Total C [%]	14.69
Total H [%]	1.10
Total N [%]	0.96
Total O [%]	55.49

3.4 Batch experiment and sampling

3.4.1 Experimental setup

Each column was connected to a Ismatec BVP peristaltic pump (Wertheim, Germany) with eight channels. Spiked GW was pumped from batch tank to each column with an up-stream flow (Figure 4). With effluent on the top of each column. The experiment started 28.04.2022 (day 0) with first sampling day 29.04.2022 (day 1). The flowrate was approximately 1 L/day. The experiment was running for 18 days, with 16 sampling days. Due to problems with the pump on day 3, 4 and 5, it was decided to mix samples from those days because the total volume passing through the columns these days was approximately 1 L.

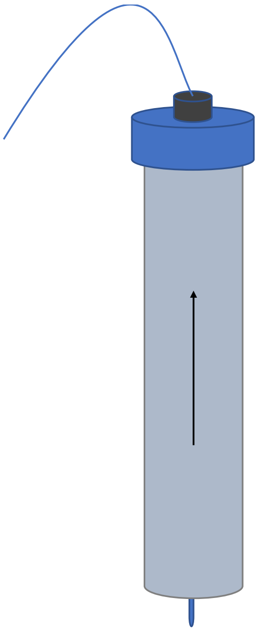


FIGURE 4: ILLUSTRATION OF COLUMN DESIGN, INLET FROM BOTTOM AND EFFLUENT ON TOP.

3.4.2 Sampling

Samples were collected from the effluent of each column every day for 16 days. Approximately 1 L was collected after 24 h in glass bottles. 1L samples from tank were collected on day 1-6, 10 and 16. Volume was measured every day. TSS, BOD_5, turbidity, conductivity, and pH were measured every day for the first six days, then on day 10 and 16. Samples for PPCPs, heavy metals, COD_T, total phosphorus (TP) and total nitrogen (TN) was stored in glass containers in the freezer.

3.5 Analysis methods

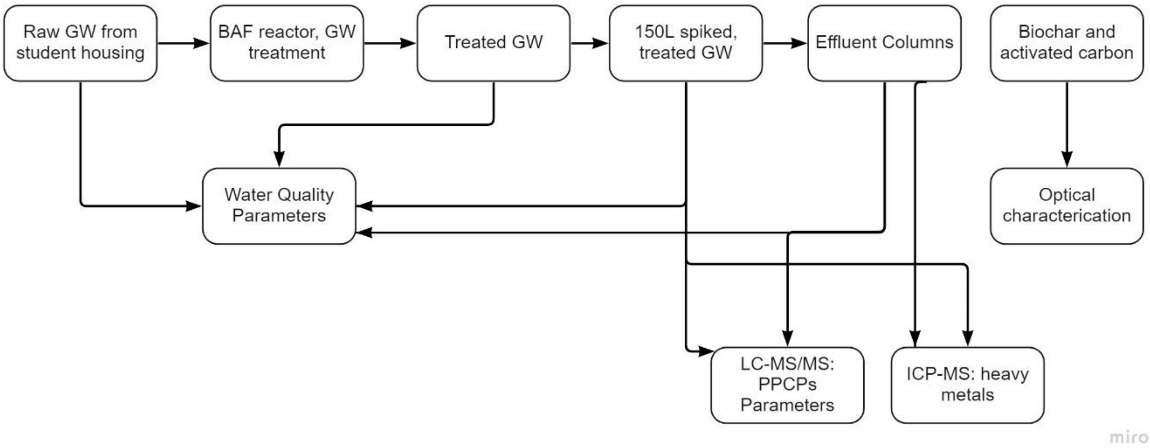


FIGURE 5: FIGURE PRESENTS SAMPLING POINTS AND ANALYSIS METHODS.

Water samples collected from the column effluents were analysed for selected water quality parameters, PPCPs and heavy metals. LC-MS/MS was used to determine PPCPs concentrations, and ICP-MS/MS was used to analyse for heavy metals. Figure 5 shows the treatment steps with sampling points and analysis methods. Scanning Electronic Microscopy (SEM) and X-Ray Diffraction was performed to decide element composition on the surface of the biochar and activated carbon. An overview of the selected parameters and sampling days can be found in Appendix (A1).

3.5.1 Water quality parameters

Table 10 shows selected water quality parameters, analytical method and equipment used.

TABLE 10: WATER QUALITY PARAMETERS, ANALYTICAL METHODS AND EQUIPMENT USED.

Parameter	Analytical method	Name
TSS	Vacuum filtration	Whatman GF/C^{TM}, 1.2 µm glass fibre filter 47mm
BOD_5	Manometric	Oxitop OC 100, control measuring system
COD(T)	Photometric	Hach Lange LCK1414
Turbidity	Optical	Hach, 2100N IS Turbidimeter
pH	Glass electrode	pH-meter PH20 VWR
Conductivity	Four-electrode conductivity	WTW TetraCon 325
Total Nitrogen	Photometric	Hack Lange LCK138
Total Phosphorus	Photometric	Hach Lange LCK349

Total suspended solids (TSS)

Total suspended solids were measured with filtrating water sample through glass fibre filter with pore size 1.2 µm from Whatman GF/C^{TM} (Little Chalfont, Buckinghamshire, UK) with vacuum pump. Filter was weighed before filtration, sample filtrated, and filter was dried for 24h on 105 degrees before weighed again. TSS was calculated with Equation 1.

$$TSS = \frac{(m_{after} - m_{before})}{V} 10^6 \; [\frac{mg}{L}]$$

EQUATION 1: CALCULATION OF TSS

Where m_{before} is filter mass before filtration in grams (g) and m_{after} is oven dried sample and filter weight after filtration in grams (g). V is filtrated sample volume in millilitres (mL).

Biochemical oxygen demand (BOD)

BOD was measured with WTW OxiTop OC 100 from Xylem (Washington, D.C., USA). 164-432 mL of sample was added 5-6 drops of nitrification inhibitor and 2-3 NaOH-pellets. Samples were then incubated at 20°C with constant stirring for five days. BOD_5 measures oxygen demanded by aerobic biological organisms to break down organic material present in the water sample after five days.

Chemical Oxygen Demand (COD)

COD was measured using Hach Lange test kit (LCK1414) and DR3900 spectrophotometer (Dusseldorf, Germany). Unfiltered samples from BC1-3 and AC1-3 were added 1/1 to the cuvettes, samples from C1-2, tank and raw water were diluted 1/2 or 1/10. Cuvettes were heated with LT200 from Hach Lange GMBH (Dusseldorf, Germany) on 148 °C for 2 hours. Total COD_T represent both easy and heavy degradable solids and the non-biological degradable organic matter.

Turbidity

Turbidity was measured with “2100N IS turbidimeter” from HACH (Dusseldorf, Germany). The instrument calculates the turbidity (NTU) from the scattering of the light rays.

pH and conductivity

pH was measured with a pH20 from VWR (Radnor, PA, USA). The pH-meter was calibrated before use every day. Conductivity was measured with WTW TetraCon 325 from Xylem (Washington, D.C., USA).

Total Nitrogen and Total Phosphorus

Total nitrogen was measured with Total nitrogen kit LCK138 from Hach Lange (Dusseldorf, Germany). Total Phosphorus was measured with Total Phosphorus kit LCK349 from Hach Lange (Dusseldorf, Germany). All samples were unfiltrated, some samples were diluted with deionized water.

3.5.2 PPCPs parameters

LC-MS/MS was used to measure the concentrations of the selected PPCPs in effluent from all columns from day 1-6, 10 and 16. Spiked tank samples were analysed on day 1, 6, 10 and 16. PPCPs were analysed on a LC-MS/MS using a method based on the method developed by Dr. Aasim Ali (Ali et al., 2018) . The samples were added internal standards (details, table AX) and diluted with 50 % (v/v) methanol (HiPerSolve Chromanor, HPLC gradient grad, VWR, Radnor, PA, USA) to a resulting internal standard concentration of 62.5 ng/mL. The samples were then filtered using centrifuge filters (1.5 mL, 0.2 µm, nylon membrane, VWR, Radnor, PA, USA) at 10.2 rpm for 1 min (MicroCL 17 centrifuge, Thermo scientific, Waltham, MA, USA). The filtered sample was transferred directly to HPLC vials and analysed. An Agilent 1200 HPLC-system with Eclipse plus C18 (1.8 µm, 100 x 2.2 mm, Agilent technologies, Santa Clara, CA, USA) column was coupled with an Agilent jetstream-ESI ion source used in positive mode and 6490 triple quadrupole mass spectrometer (Santa Clara, CA, USA). Mobile phase A was 0.1 % (v/v) formic acid (reagent grade, ≥ 95 %, Sigma-Aldrich, now Merck, Readington Township, NJ, USA) in water and B was 100% acetonitrile (HiPerSolve Chromanorm, isocratic grad, VWR, Radnor, PA, USA). 5 µL of sample was injected with a starting mobile phase composition of 0 % B. This was increased linearly to 100% over 11 minutes and then kept at 100% B for 1 minute, before the mobile phase was returned to 0 % B in 1 min, and the column conditioned for 3 min. Details from the analysis and parameters can be found in Appendix (A2). Sample preparation was performed by me and analysis with LC-MS/MS was performed by Head engineer Lena Foseid.

3.5.3 Heavy metals

ICP-MS/MS was used to detect selected heavy metals (Cr, Ni, Cu, Zn, As, Cd, Pb) from the effluent of the columns at day 1 and 16. An Agilent Technologies SPS 4 autosampler with 8800 ICP-MS Triple Quad. Samples were added 2% (v/v) ultra-pure nitric acid and 4 µg/mL internal standard (IV-ICPMS-71D) from Inorganic Ventures (Christiansburg VA, USA). Indium was used as internal standard for all elements. Calibration solutions were made with IV-ICPMS-71A from Inorganic Ventures (Christiansburg VA, USA), and checked against a control solution (1643S, an in-house standard from the Faculty of Environmental Sciences and Natural Resource Management, NMBU. This standard is checked against certified reference materials). Details of elemental analysis is shown in Appendix (A3). Analysis was performed by Head engineer Lena Foseid.

3.5.4 Optical characterisation

Scanning Electronic Microscopy (SEM) was performed with a Zeiss (UK) EVO 50 EP scanning electronic microscope. The samples were placed in the microscope chamber under low vacuum at 48-49 Pa in order to perform X-Ray diffraction (XDR) at the same time as imaging. Analysis was performed by Senior Engineer Hilde Raanaas Kolstad at Faculty of Biosciences, NMBU.

4. Results and discussion

4.1 Greywater characterisation

The characteristics of greywater from different parts of the world vary depending on social and cultural conditions. Water quality parameters measured in this experiment can be found in Table 11. BOD_5 concentrations from raw greywater was in average 231.8 mg O_2/L from the student housing, BOD_5 is reported to be 205-449 mg O_2/L in Europe (Meinzinger & Oldenburg, 2009). COD_T for raw greywater water was only tested once, and the 303 mg O_2/L is a little bit below the reported 350-783 mg O_2/L, but matches well with the 250-300 mg O_2/L estimation from average Norwegian greywater (Todt et al., 2015). TSS concentration was 69.5 mg/L in this study, and therefore, it was below average TSS concentration reported for European greywater characteristics with 228 mg/L, but close to the values measured (Todt et al., 2015) in Norway with 66-89 mg/L. Total nitrogen (TN) and total phosphorus (TP) in European greywater was 6.7-22 mg N/L and 0.4-8.2 mg P/L, respectively; and are corresponding well to raw water measurements in this study found in Table 11. Measured raw water quality from the student housing used in this experiment is similar to what has been found in studies of European greywater characteristics.

TABLE 11: WATER QUALITY PARAMETERS MEASURED FOR RAW GREYWATER, EFFLUENT OF BAF REACTOR AND THE COLLECTED GW FOR THE BATCH EXPERIMENT AT EXPERIMENT START.

Water quality parameter	**Inlet BAF reactor**	**Effluent BAF reactor**	**Removal [%]**	**Column experiment batch**	**Removal [%]**
pH	6.7	7.43	-	7.25*	-
Turbidity [NTU]	70.2	18.5	76.6	23.4*	70.5
COD_T	303*	-	-	97.6*	67.8
TSS [mg/L]	69.5	54.7	21.4	60*	13.8
Conductivity [µS/cm]	385*	-	-	468*	-
Total Phosphorus [mg/L]	1.4*	-	-	1.24*	11.4

Total Nitrogen [mg/L]	8.9*	-	-	7.92*	11.01
BOD$_5$	231.8	50.7	78.1	39.5*	82.3

* - MARKED VALUES REPRESENT THE PARAMETERS ONLY MEASURED ONCE.

4.2 Water quality parameters after biochar and activated carbon polishing step

The concentration variations in water quality parameters measured in the tank and the column effluents can be explained by some practical issues during the experiment. The tank was not supplied with aeration and not covered in the first 6 days of the experiment, and it started to smell. Aeration was implemented from day 6 to day 16 to avoid anaerobic conditions. The particles in the batch tank sedimented early in the experiment, and tank samples from day 1, 6 and 10 were collected from the middle layer approximately. On the other hand, the tubes connected to the columns were close to the bottom of the tank during the whole experiment and would likely have pumped more particulate water into the columns than the samples taken from the tank sampling. The water quality parameters measured from the effluents of the control columns are decreasing and reduced compared to tank values for most parameters. The water was pumped into the bottoms of the columns with the effluent from the top. A lot of the particles and sludge sedimented in the bottom of the control columns due to gravity. Most of the water quality parameter concentrations are dependent on the particulate bonded organic matter and nutrients and therefore not detected in the control effluents. The sedimented particles and sludge can also work as a filter and remove more of the concentrations.

4.2.1 pH and conductivity

pH and conductivity were measured from the effluent of each column on Day 0-6, Day 10 and Day 16 (Figure 6 and Figure 7). The tank was measured on day 0, 6, 10 and 16.

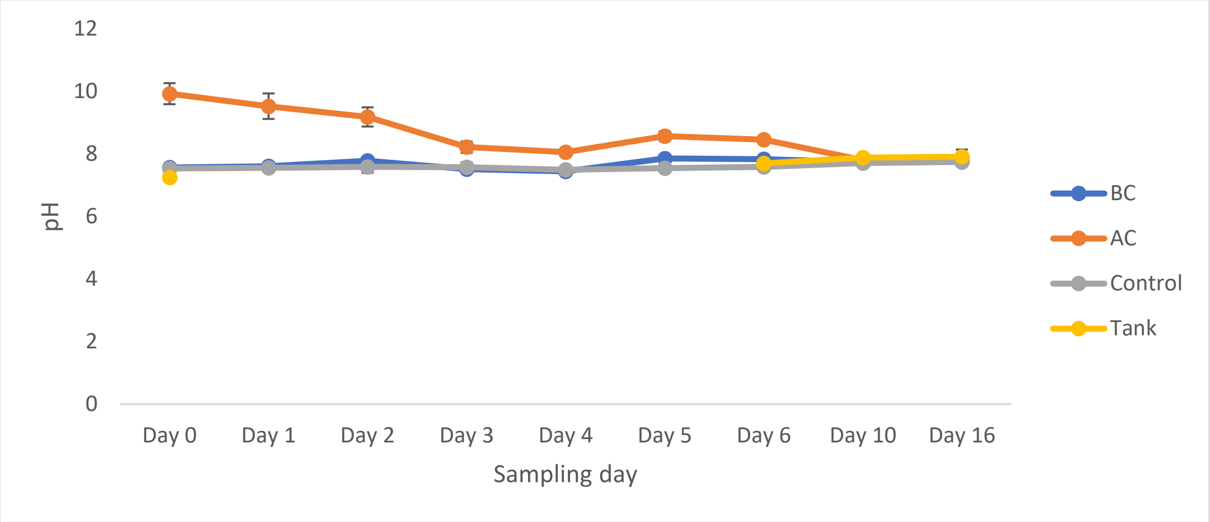


FIGURE 6: MEASURED PH VALUES FROM DAY 0-6, DAY 10 AND 16. ERROR BARS REPRESENT STANDARD DEVIATION (N=3 FOR AC AND BC, N=2 FOR CONTROL). NOTE THAT FOR SOME OF THE REPLICATES THE STANDARD DEVIATION IS SO SMALL THAT THE ERROR BAR IS NOT VISIBLE IN THE FIGURE. FOR TANK N=1.

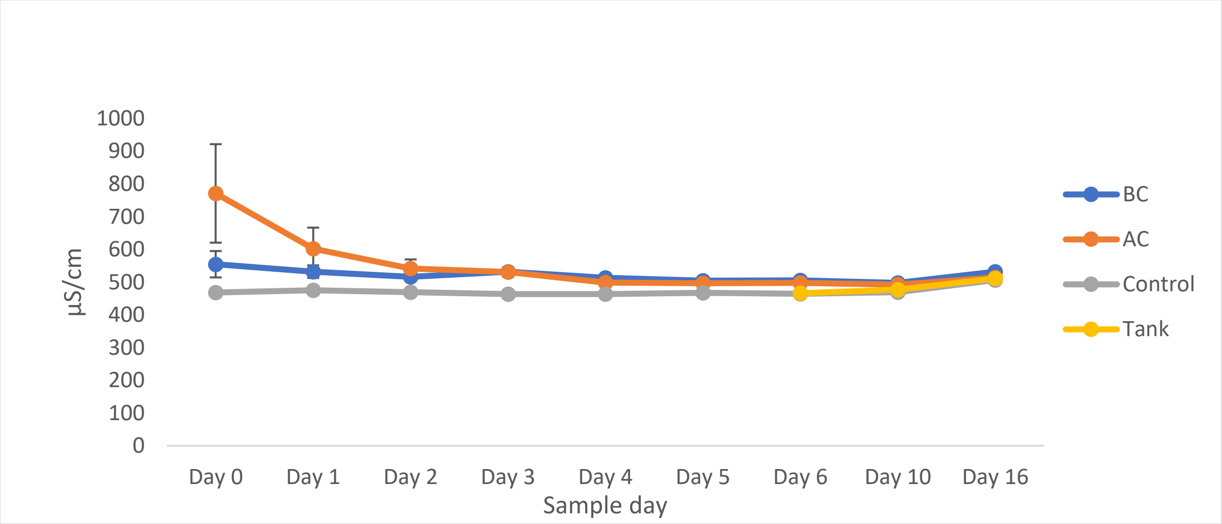


FIGURE 7: MEASURED CONDUCTIVITY FROM ALL COLUMNS. ERROR BARS REPRESENT STANDARD DEVIATION (N=3 FOR AC AND BC, N=2 FOR CONTROL). NOTE THAT FOR SOME OF THE REPLICATES THE STANDARD DEVIATION IS SO SMALL THAT THE ERROR BAR IS NOT VISIBLE IN THE FIGURE. FOR TANK N=1.

As it can be seen in Figure 6, pH for the AC columns decreased from day 0 to day 10 and reaching more stable pH after day 10. For the BC columns, the controls, and the tank (influent for all columns) pH were around 7.5 during the whole experiment, and a similar pattern could be observed for conductivity as can be seen in Figure 7. The effluent from the AC columns has higher pH and conductivity in the beginning, which can be explained by the ash content of BC and AC. In general, fresh BC and AC are alkali products and can have initial pH of 9.5 to 10.5 (Desilva, 2001). During this experiment, soluble ash is rinsed out of the media during the first days, which can explain the stabilized pH and conductivity. BC1 and AC1 was used to adjust the flowrate with tap water through the columns before the experiment started and can explain the standard deviations in the measurements from day 0 and 1 due to ash was rinsed out. It is no differences in effluent from AC and BC columns after day 2 (conductivity) and day 10 (pH). The AC and BC material don't affect the conductivity of the GW after day 3 for both materials, but pH for AC was first stabilized at day 10. A more thorough wash of the AC before use can prevent the increase in pH.

4.2.2 TSS

TSS measured in the experiment is shown in Figure 8. Average BC, AC and control measurements can be read from left axis while tank values are shown on right axis in yellow. We observed a stable reduction in TSS concentration in BC effluent from day 1 to 16, with a removal rate of 85.8% on day 1 and 98.9% on day 16. TSS for AC effluent is increasing from day 1 to day 6, then decreasing to values similar to BC. AC has a removal rate on >90% on day 1 and day 16 but has higher TSS than tank on day 6. The TSS values are decreasing in control columns, which was likely due to sedimentation because of the up-flow set-up. The increase in TSS from AC columns can, like pH and conductivity, be explained by the rinse out of the AC materials for the first days (Desilva, 2001).

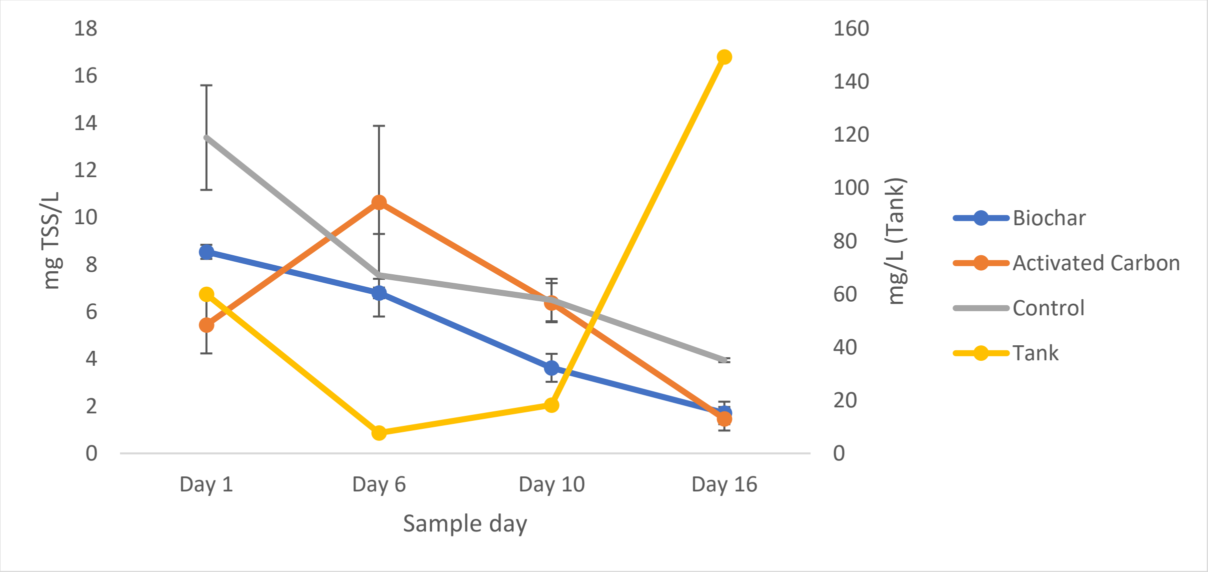


FIGURE 8: AVERAGE MEASURED TSS IN COLUMN EFFLUENT CAN BE READ ON LEFT AXIS, WHILE TANK VALUES CAN BE SEEN IN YELLOW AND READ ON THE RIGHT AXIS. ERROR BARS REPRESENT STANDARD DEVIATION (N=3 FOR AC AND BC, N=2 FOR CONTROL). NOTE THAT FOR SOME OF THE REPLICATES THE STANDARD DEVIATION IS SO SMALL THAT THE ERROR BAR IS NOT VISIBLE IN THE FIGURE. FOR TANK N=1

4.2.3 Turbidity

Turbidity in the effluent of AC columns is increasing until day 6. Effluent from BC columns are increasing until day 3 before decreasing. Both effluents reach NTU between 1.7 and 1.8 on day 16. The increase in the effluents from day 1 can be seen in Figure 9, and can also be explained by rinse out of the column materials for the first days. At the same time measured turbidity in the tank is increasing, with a turbidity of 58 NTU on day 16. Control columns are increasing until day 4 and decrease to similar values as AC and BC. Tank values goes up probably because of sedimentation at the bottom of the tank. Meanwhile, it was visually observed accumulation of sediments in the control and that was probably working as a filter after day 4. The accumulation indicates that the particles are reaching the columns, but the control columns are not working as control columns for turbidity concentrations. The increase in turbidity in the tank and the decrease in measured turbidity from AC and BC effluents indicates increasing removal.

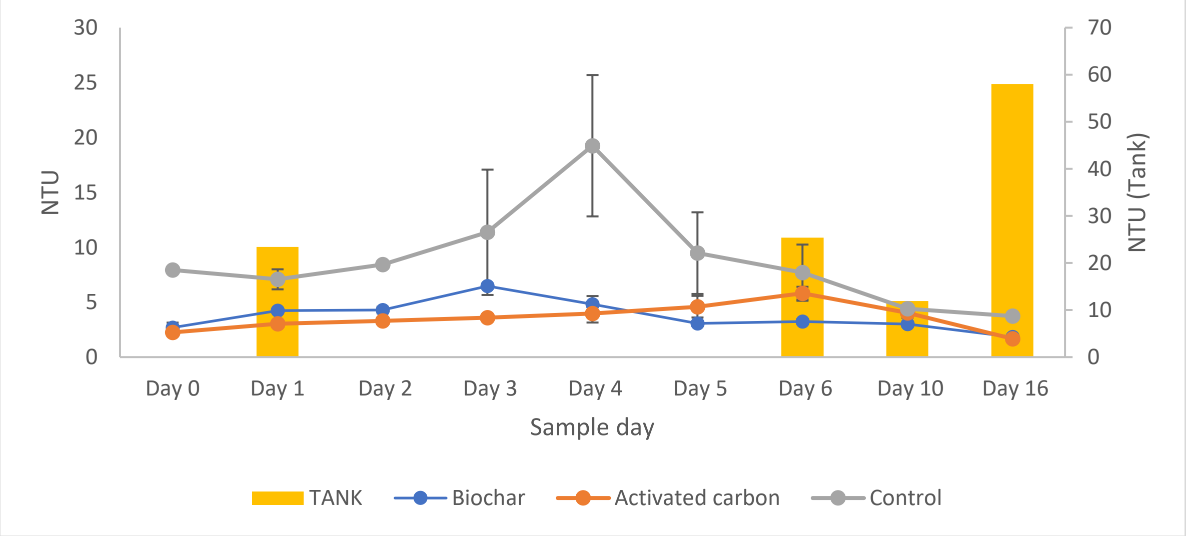


FIGURE 9: MEASURED TURBIDITY FROM TANK AND COLUMN EFFLUENTS. NTU MEASURED FOR ALL COLUMNS CAN BE READ ON THE LEFT AXIS, WHILE TANK VALUES CAN BE SEEN IN YELLOW AND READ OF THE RIGHT AXIS. ERROR BARS REPRESENT STANDARD DEVIATION (N=3 FOR AC AND BC, N=2 FOR CONTROL). NOTE THAT FOR SOME OF THE REPLICATES THE STANDARD DEVIATION IS SO SMALL THAT THE ERROR BAR IS NOT VISIBLE IN THE FIGURE. FOR TANK N=1

4.2.4 COD_T

Tank values for COD_T are increasing from day 1 to day 6, then there is a decrease in COD_T on day 10, before COD_T is again increasing on day 16 with three times measured COD_T compared to day 1. COD is the amount of oxygen required to oxidize organic compounds, therefore COD_T is likely increasing due to sludge in bottom of the tank. The values shown in Table 12 and

Figure 10, are the average measured COD_T values. The measured values correspond to an average removal rate of 22% at day 1 with BC and 44% for AC columns, compared to the measured tank values. Removal rate for both materials is increasing to more than 90% on day 16. Control columns have a decrease in COD_T measured, most likely due to sedimentations in columns working as a filter. The COD_T measurements from tank, AC, BC and control correlates with the TSS measurements.

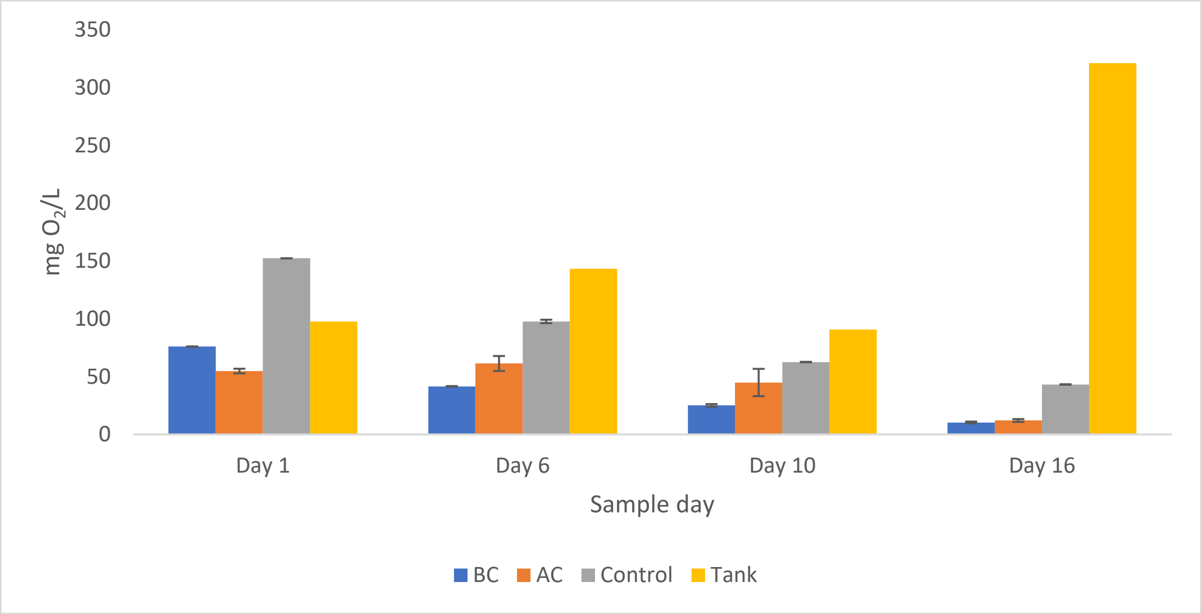


Figure 10: Column effluents are decreasing on day 16. Error bars represent standard deviation (n=3 for AC and BC, n=2 for control). Note that for some of the replicates the standard deviation is so small that the error bar is not visible in the figure. For tank n=1

Table 12: Average COD_T concentration from each column and in tank (influent) on day 1, 6, 10 and 16. Removal rate is calculated from tank values to effluent from the columns.

	BC$_{av}$		**AC$_{av}$**		**Control$_{av}$**		**Tank**
	Effl. [mg O_2 /L]	Removal [%]	Effl. [mg O_2 /L]	Removal [%]	Effl. [mg O_2 /L]	Reduction [%]	[mg O_2 /L]
Day 1	76.0	22.1	54.8	43.9	152.3	-56.0	97.6
Day 6	41.6	71.0	61.4	57.1	99.2	31.8	143.2
Day 10	25.1	72.3	44.9	50.4	62.6	30.9	90.6
Day 16	10.4	96.8	12.1	96.2	43.2	86.5	321

4.2.5 Total phosphorus and Total Nitrogen

TP and TN were only measured on day 1 and day 16. Both TP and TN values were lower in the tank from day 1 compared to day 16 (Table 13). The higher TN and TP concentrations on day 16 might be related to the particle bound N and P content in the sediments. The reduction in C1 column is showing the same, with a reduction rate more than 50% compared to the tank concentrations. It can be explained with the particles pumped into the control columns sedimented in the bottom and not reach effluent and making the TP and TN measured in control column representing the dissolved P and N.

The TP concentrations in AC and BC effluents on day 1 vary. BC2 effluent shows three times higher TP concentrations than BC1 and the AC columns have similar results. Measured TP from BC2 and AC2 are most likely the representable measurements for the effluent, since BC1 and AC2 had been washed through with more tap water before use to test and adjust a similar flowrate in each column. More P from the material surface was likely washed off before experiment started and could explain the variation in the columns containing the same material. The TN reduction from tank to columns is stable from day 1 and 16 for both materials, but the TN released in the effluent is higher on day 16. It can be explained with the high concentration of TN pumped from the tank or desorption of the nitrogen already inside the columns or in the carbon material.

The removal rate from the BC material is a little bit better for both TN and TP removal compared to AC. BC has proved to be effective in removal of nutrients and organic matter, with up to 73% removal rate of phosphorus (Tong et al., 2016). Similarly, orthophosphate and dissolved organic carbon removal efficiencies reaching up to 90% and 82%, respectively, were reported by (Kocatürk-Schumacher et al., 2017). The BC removal rate in this study shows similar finding.

TABLE 13: TP AND TN MEASURED FROM TANK AND COLUMN EFFLUENTS. THE REMOVAL RATE FOR BC AND AC IS CALCULATED FROM AVERAGE BC AND AC CONCENTRATIONS AND TANK VALUES. THE REDUCTION IN CONTROL COLUMN IS THE DIFFERENCE BETWEEN TANK AND CONTROL.

	Total Phosphorus		**Total Nitrogen**	
	Day 1	**Day 16**	**Day 1**	**Day 16**
Tank [mg/L]	**1.24**	**1.87**	**7.92**	**16.8**
BC1 [mg/L]	0.466	0.377	1.388	2.75
BC2 [mg/L]	1.5	0.378	1.61	3.08
BC_{av}	0.983	0.377	1.474	2.915
STD	0.517	0.0005	0.136	0.165
Removal [%]	**20.7**	**79.8**	**81.4**	**82.6**
AC1	0.466	0.657	1.638	3.78
AC2	1.5	0.757	2.18	3.53
AC_{av}	0.983	0.707	1.909	3.655
STD	0.517	0.05	0.271	0.125
Removal [%]	**20.7**	**62.2**	**75.9**	**78.2**
C1	0.554	0.644	3.93	4.59
Reduction [%]	**55.3**	**65.6**	**50.4**	**72.7**

4.2.6 BOD_5

Measured BOD in the tank was decreasing from day 1 to day 10, before increasing from day 10 to 16 and is shown in Table 14.. The sample from day 16 contained sediments, which could be the reason for increasing BOD concentrations. BOD concentrations in the effluents from control columns are decreasing, samples from day 1 was detected to exceed the measurement limit at 40 mg O_2/L. The BOD concentrations on day 16 is very low despite the high concentrations in the tank and that can be explained by the accumulation of sludge in the control columns due to sedimentation. Accumulated sludge in the control columns might have worked as a filter and prevented particles to reach the effluent.

Measured BOD from AC1 column is decreasing steadily from day 1 to day 16, while AC2 and AC3 has a smaller decrease between day 6 and 10 before reaching more than 90% removal. BC1 and BC2 are decreasing between day 1 and 6, before increasing between day 6 and 10. After day 10 all the BC effluent concentrations are decreasing before reaching more than 95% removal of BOD_5 at day 16. The BC columns perform better removal before day 16 compared to AC columns. The measured BOD_5 concentrations from AC2 and AC3 effluents were higher than measured tank value on day 10 and has no logical explanations.

TABLE 14: MEASURED BOD_5 VALUES FROM TANK AND COLUMNS BETWEEN DAY 1 AND 16. BC AND CONTROL COLUMNS HAD DETECTED VALUES HIGHER THAN 40 MG O_2/L RANGE ON DAY 1. ON DAY 16 SEVERAL OF BC AND AC EFFLUENTS HAD BOD LOWER THAN THE DETECTION RANGE. REMOVAL AND REDUCTION ARE THEN CALCULATED WITH THE DETECTABLE VALUES FROM THE EFFLUENTS AND IS MARKED WITH (*).

	Day 1	**Day 6**	**Day 10**	**Day 16**
Tank [mg O_2/L]	**39.5**	**36.6**	**19.7**	**45**
BC1 [mg O_2/L]	31.4	2.8	9.3	<1.7
BC2 [mg O_2/L]	>40	8.5	11.2	<1.7
BC2 [mg O_2/L]	>40	12.7	8.4	1.7
Removal [%]	20.5*	78.1	51.1	96.2*
AC1 [mg O_2/L]	34	15.5	9	<1.7
AC2 [mg O_2/L]	33.4	29.6	27.8	<1.7
AC3 [mg O_2/L]	34	25.4	28.1	2.8
Removal [%]	14.4	35.8	-9.8	93.7*
C1 [mg O_2/L]	>40	40.9	14	6.2
C2 [mg O_2/L]	>40	38	16.6	3.4
Reduction [%]	-	-7.8	22.3	89.3

4.2.7 Greywater quality after treatment and limits for reuse

IWA published in 2009 a guide on water quality parameters with limits for reuse purposes (Li et al., 2009). The limits are based on earlier studies and can be found in Table 15. Recreational, unrestricted reuses are referring to lakes and pounds for swimming. Recreational, restricted reuses are referring to lakes and ponds without body contact. Urban, unrestricted reuses are referring to toilet flushing, laundry, landscape irrigation and irrigation of food crops and vegetables (consumed uncooked). Urban, restricted reuses are referring to landscape irrigation where public access is infrequent and controlled, subsurface irrigation of non-food crops and food crops and vegetables (consumed after processing) (Li et al., 2009). Regulation (EU) 2020/741 on minimum requirements for water reuse will come into effect in June 2023 and can be found in Table 15 (EEA, 2020).

The BAF reactor has a removal rate more than 70 % for turbidity and BOD_5 (Table 11), but GW treated with the BAF reactor alone is exciding the limits for reuse according to the limits for reuse purposes suggested by IWA and EU for all purposes. Exception is the limits for restricted reuse from EU, where irrigation of fruit threes is allowed. Based on the GW characteristics data in this study, additional treatment step such as a polishing step would be necessary to reach suggested water quality for reuse.

Table 15: Water quality parameter limits for reuse of greywater (EEA, 2020; Li et al., 2009).

	Recreational, impoundments, lakes			**Urban reuses**		
	Unrestricted reuse	**Restricted reuse**		**Unrestricted reuse**		**Restricted reuse**
	IWA	**IWA**	**EU**	**IWA**	**EU**	**IWA**
BOD_5 [mg/L]	10	30	≤ 240	10	≤10	30
TP [mg/L]	0.05	0.05	-	-	-	-
TN [ng/L]	1	1	-	-	-	-
Turbidity [NTU]	2	-	-	2	≤5	-
pH	6-9	6-9	-	6-9		6-9
SS [mg/L]	-	30	≤140	-	≤10	30

Table 16 shows the strictest suggested limits for reuse of greywater from Table 15, concentrations detected from the BAF reactor effluent and the average effluent from BC columns and AC columns on day 1 and 16. The concentrations detected satisfying the limits are marked in green. The BAF reactor alone is not enough to reuse greywater with the suggested limits, but both BC and AC filter material show good results. TP and TN concentrations is too high to meet the limits from IWA, but EU has no suggested limits for TP and TN. TP and TN are nutrients good for fertilization in agriculture, and the reuse for such purposes should be investigated. For agricultural reuse, additional microbiological testing should be performed to look at the hygienic perspective.

Table 16: Suggested limits for reuse of greywater. Average concentrations detected form BAF reactor effluent and column effluents. Green values meets the limits of reuse.

	Limits for reuse	**BAF effluent**	**Day 1**		**Day 16**	
			BC effl.	**AC effl.**	**BC effl.**	**AC effl.**
BOD	10	50.7	>40	33.8	1.7	2.8
TP	0.05	1.24	0.983	0.983	0.3775	0.707
TN	1	7.92	1.474	1.909	2.915	3.655
Turb	2	18.5	4.22	3.03	1.83	1.67
pH	6-9	7.43	7.6	9.5	7.8	7.9
TSS	30	54.7	8.5	5.45	1.71	1.5

4.3 Properties of sludge biochar and activated carbon

CMs have shown high sorption capacity in several studies over the last decade. The interest in BCs has increased due to its promising properties and as an environmentally friendly and economic alternative to AC in sorption of different contaminants in water. The feedstock and the pyrolysis temperature are decisive for the sorption properties of the BC. Therefore, to understand the sorption mechanisms, properties like specific surface area, hydrophobicity and functional groups must be characterised for the specific BC.

Due to time limitations on this master thesis, the biochar was not characterised, and characteristics are based on characterisation done by Yuliia Dzihora (2021) who characterised BC from the same feedstock pyrolyzed at the same temperature, from the same company (Lindum AS) as the BC used in this thesis. It is reasonable to conclude that the characteristics of the BC from 2021 are similar to the characteristics of the BC used in this experiment in 2022. Properties of the BC from Dzihora, two sludge BC from other studies and commercial AC is listed in Table 17 to compare the differences.

The three columns with commercial AC used in this experiment were not characterised and was used to compare with the removal efficiency of the selected BC. BC is typically less carbonized than AC due to the feedstock material. More hydrogen and oxygen remain in the BC structure along with the ash orientating from the biomass (Mohan et al., 2014). AC has been used as an effective adsorbent for hydrophobic organic contaminants due to its adsorption capacity. Most commercial AC consists of micropores (<2nm) with irregular-shaped, closed pore structures and therefore some organic contaminants can be size-excluded and be less removable.

TABLE 17: BC PROPERTIES OF SLUDGE BC REPORTED BY (DZIHORA ET AL., 2021), COMPARED TO SLUDGE BC PROPERTIES FOUND IN OTHER STUDIES AND COMMERCIAL AC PROPERTIES FOUND IN OTHER STUDIES.

Property	**Sludge-BC600 from Lindum (Dzihora et al., 2021)**	**Sludge-BC600, (Chen et al., 2014)**	**Sludge-BC600 (Zhang et al., 2015)**	**Activated carbon (Tong et al., 2016)**
pH	8.08	9.04	10.8	
Ash content [%]	85.9	77.9	63.24	10
Specific surface area $a_{s\ BET}$ [m^2/g]	77.97	20.27	12.22	755
Average pore diameter [nm]	7.14	3.75	-	-
Total pore volume [cm^3/g]	1.1391	0.052	-	-
Micropore volume	0.165	-	-	-
Total C [%]	14.69	18.4	26.5	82
Total H [%]	1.10	0.34	1.12	0.9
Total N [%]	0.96	1.38	3.54	0.5
Total O [%]	55.49	7.35	5.29	5.8

Ash-content

Sewage sludge-based BC has a high ash content percentage compared to other biosolid BCs, due to high mineral content. For example, increased pyrolysis temperature for sewage sludge BC will increase the ash content, while in wood BC an increase of pyrolysis temperature will decrease the ash content (Dzihora et al., 2021), due to sludge BCs contains more minerals that is still stable at high temperatures. Ash content in the BC batch from Lindum in 2021 was 85.9% when pyrolyzed at 600°C and is close to the ash content found by (Chen et al., 2014), but higher than (Zhang et al., 2015). Compared to commercial AC, sludge-BC has very high ash content.

Metal oxides and minerals will remain as ash content in the BC and the alkaline substances and pH value of the BC induce alkalinity (Chen et al., 2014).

Specific surface area and pore size

Specific surface area is an important characteristic for adsorption and will depend in the shape, texture and porosity of the BC. Sludge BC has typically lower specific surface area compared to other BC, e.g. wood BC, and much lower than commercial AC (Table 17). The BC from Lindum have a specific surface area of 77.97 m^2/g and is lager then other sludge BC listed in Table 17. BCs with large specific surface area are typically better sorption material, but sorption properties will also depend on chemical compositions and functional groups on the BC surface. The BC from Lindum had average pore diameter at 7.1359 nm, total pore volume at 0.1391 cm^3/g and micropore volume at 0.0165 cm^3/g (Table 17). The BC from Lindum was reported to have all kinds of pore sizes, but was low in micropore volume (Dzihora et al., 2021). The average pore diameter and pore volume is also higher then reported from Chen et al. (2014) with 3.75 nm average pore diameter and 0.052 cm^3/g pore volume. Commercial AC typically contains micropores (<2nm), and sludge BC contains more mesopores (Chen et al., 2014).

Chemical properties (C-H-N)

Sludge BC typically has lower carbon content and higher oxygen and hydrogen content compared to other BCs. The sludge BC has a high mineral content and therefore require higher temperature to break down the compounds. The sludge BC from Lindum had a total C% of 14.69, H% at 1.10, N% of 0.96 and total O% of 55.49. The C, H, N and O content can be used to calculate the aromaticity index (H/C), nitrogen availability (C/N), hydrophilicity (O/C), and polarity index ((O+N)/C).

The Aromaticity index (H/C) indicates aromaticity and carbonization of the BC (Gaffar et al., 2021). The H/C index is decreasing with temperature, and a low H/C ratio is an indication of a higher carbonization degree. The H/C ratio for the Lindum BC was calculated to 0.889 and can indicate pyrolysis deficiencies due to low carbonisation. H/C ratio found by (Chen et al., 2014) was 0.22 and 0.51 by (Zhang et al., 2015).

Hydrophilicity index (O/C) suggests that sludge BCs are hydrophilic due to high O% and lower C%. The sludge BC from Lindum had a O/C ratio at 3.040. O/C ratio BC show good performance as a filtration material for water treatment (Dzihora et al., 2021). The hydrophilicity index for sludge BC from Lindum is much higher than the two other BCs compared with in Table 17. O/C ratio for sludge BC is higher than most commercial AC, due to high C content in AC.

Polarity index ((O+N)/C) indicates the availability of polar functional groups and hydrophobicity. The polarity index for the BC was calculated to 3.096. For most BCs the increase in carbonisation with increased pyrolysis temperature will reduce polarity and increase the hydrophobicity. For sludge BCs, which is highly mineralized, the pyrolysis temperature might not make any difference in polarity index due to the protection of polar groups by minerals (Qiu et al., 2014).

The properties of the sludge BC pyrolyzed at 600 °C were presented in Table 17 and shows the great variations in sludge-derived BCs. It is great variations in the properties of BC produced at the same temperature with sludge as the feedstock and can be explained with the variations in the sludge characteristics before the pyrolysis process. It shows the importance of characterisation of a specific BC, even when the BC is produced from similar feedstocks.

4.3.1 Optical characterisation

Optical characterisation of the BC and AC was performed with SEM and XRD. The SEM was used to look at the morphology and X-ray diffraction was performed to get the element distribution on the surface. The element distribution is based on element ratio on the specific sample surface, and it is therefore not possible to estimate the amount of the elements found with this method alone. The optical characterisation in this experiment was performed to look at the visual differences in morphology on the surface of the two materials and to find the elements precent on the surface before the sorption experiment. The results can be found in Appendix (A4).

The visual differences in shape of the BC and the AC are shown in Figure 11. The AC (left) has a smoother and more monotonous surface with less variations. The BC (right) has higher variation in shape and visual elements. Figure 12 shows the differences in morphology of the two materials. The image shows great variations in folds and structure on the BC surface, while the morphology on the AC is less visual in this scale possibly due to smaller pore sizes and folds in the surface.

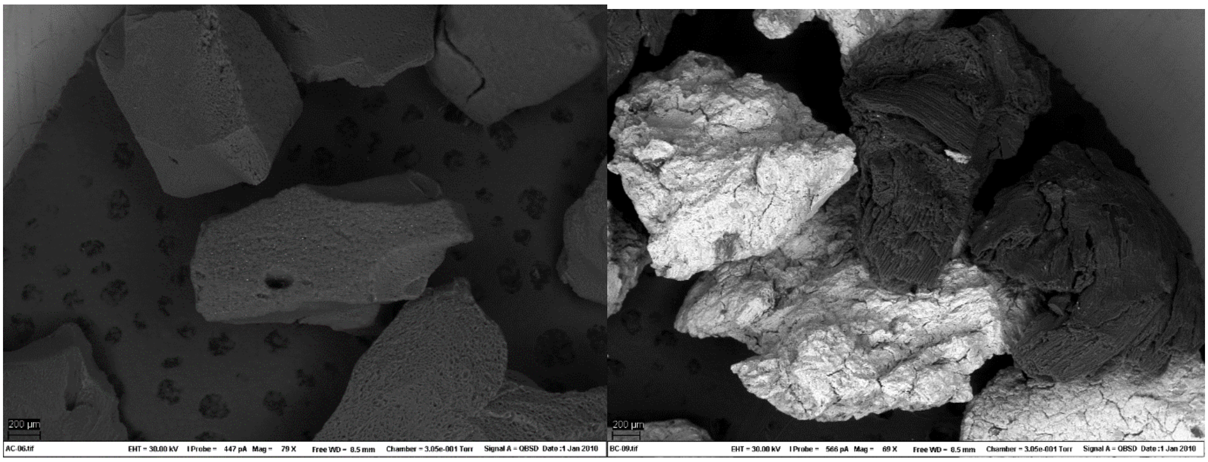


Figure 11: Activated carbon (left) and biochar (right) at 200μm scale.

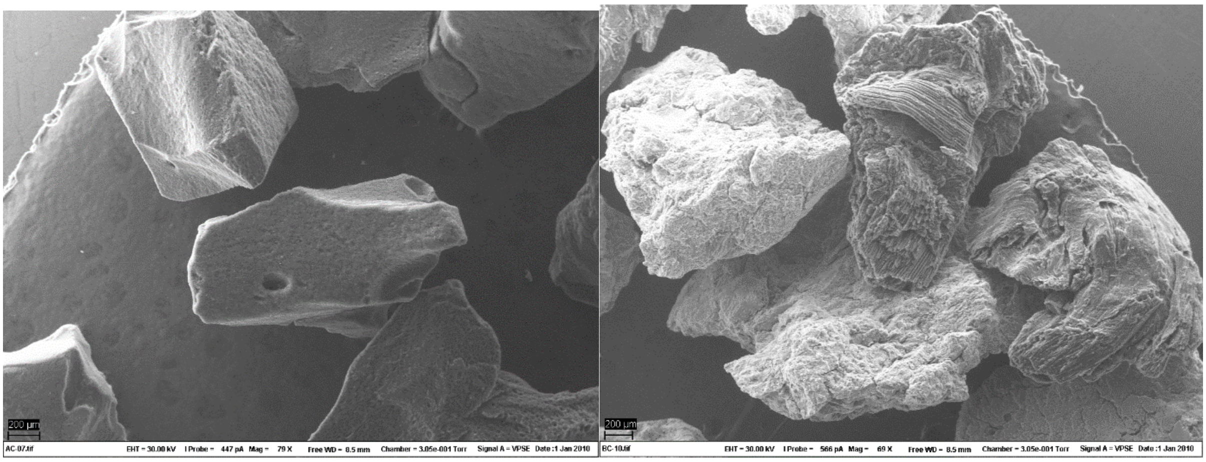


Figure 12: Activated carbon (left) and Biochar (right) at 200μm scale

Optical characterisation of the BC in 2021, unwashed and washed, discovered that elements such as Ca, Mg, P, Na and K were washed away and not strongly attached to the surface (Dzihora et al., 2021). It can explain high TP concentrations on the first day in the effluent of BC2. The sludge BC look highly mineralized with many small sediments attracted to the surface, some tightly attached and some more easy to fall off. The results of the X-ray diffraction of spots on the material surface can be found in Appendix (A4). In general, a high Si, K and Ca element ratio were found on the AC surface, with some lower element ratio of Fe and Na and some traces of Cu and Br. The BC had high elemental ratio of Fe, Si, Al and Ca, some P and Na and traces of Ti. Fe and Al are normally used in coagulants in STPs and can explain the high elemental ratio detected on the sludge BC surface. Optical characterisation of the material should be performed after the sorption experiment to find differences in the surface and the elemental ratio after sorption. It can determine the sorption of organic matter and the sorption mechanisms for the materials. It can also determine the risks of unwanted pollutions from the sorption material.

4.4 PPCPs removal in sorption columns

PPCPs concentrations measured in the tank are shown in Table 18. Carbamazepine (CBZ) and Diclofenac (DFC) have relatively even concentrations measured every sampling day and can be explained by their solubility properties. Acetaminophen (ACET) was detected close to spiked values until day 6 before decreasing until not detectable on day 16. Decreasing ACET concentrations can be explained with biodegradation of the pharmaceutical due to microbial activities in the tank. Previous studies have shown ACET biodegrade over time, in microbiological conditions (Yang et al., 2020). Concentration of Octocrylene (OCT) on day 1 is under limit of quantification and was probably not dissolved properly in the tank. The OCT could be observed as a white layer on the surface right after it was added. OCT is highly hydrophobic with log K_{ow} = 7.3 and can explain why it was not detected on day 1. OCT can then have sedimented to the bottom of the tank early in the experiment. OCT concentrations are then increasing on day 6, decreasing on day 10 before increasing to high concentrations on day 16. Another explanation could be that OCT has adsorbed to solids on the bottom of the tank, OCT has shown high adsorption to sludge and particles in earlier studies of sludge in STPs (Langford et al., 2015). The TSS and turbidity measurements from the tank were lower in the beginning and OCT attached to particles could be difficult to detect in the sample. The samples were filtrated using centrifuge filters before the LC-MS/MS and could make it difficult to measure OCT if it was attached to particles. But the samples were added methanol before the centrifuge filtration, and the methanol and centrifugation can have detached the OCT from the particles. On day 16 OCT is measured to concentrations higher then spiked and has likely accumulated in the sludge on the bottom of the tank sampled at day 16. Measured PPCPs concentrations in the tank can be read in Table 18.

TABLE 18: DETECTED PCPPS CONCENTRATIONS IN THE SPIKED TANK FOR DAY 1, 6, 10 AND 16.

	Day 1	Day 6	Day 10	Day 16
Acetaminophen [ng/mL]	960	970	170	<LOD
Carbamazepine [ng/mL]	830	800	790	840
DEET [ng/mL]	<LOQ	<LOQ	<LOQ	1082
Diclofenac [ng/mL]	880	890	880	870
Octocrylene [ng/mL]	<LOQ	670	320	1700

The LC-MS/MS method was not working for measuring the concentrations of DEET. The LOD and LOQ calculated for DEET were higher than desired due to traces of DEET in the blank samples. DEET was likely stuck in the LC-MS/MS system. LOD were calculated to 20 ng/mL and LOQ to 100 ng/mL (Appendix A5). DEET Concentrations in the tank and control samples could therefore not be calculated when tank samples were diluted 1/10. The samples should have been run again with less dilution but could not be done due to time limitations.

Two control columns were used to control the PPCPs concentrations reaching the columns. Figure 13 presents average PPCPs concentrations measured in the two control columns. Concentrations in the control columns show the same pattern as the tank concentrations for ACET, CBZ, and DFC, with ACET decreasing after day 6, which might be explained by biodegradation. OCT is detectable from day 1 in the control columns, but in lower concentrations then the spike concentration. It supports the explanation of sorption to solids if the solids sedimented to the bottom of the tank early, where the intake tubes to the columns where situated. After day 6 the TSS and turbidity measurements from the control columns effluent decreased due to sedimentation in the columns and OCT is therefore also not detectable if attached to particles. The peak in OCT concentrations on day 16 from the tank is not detected in control column effluent and can also be explained with the decrease in solids in the control effluent after day 6. All concentrations measured can be found in appendix (A5).

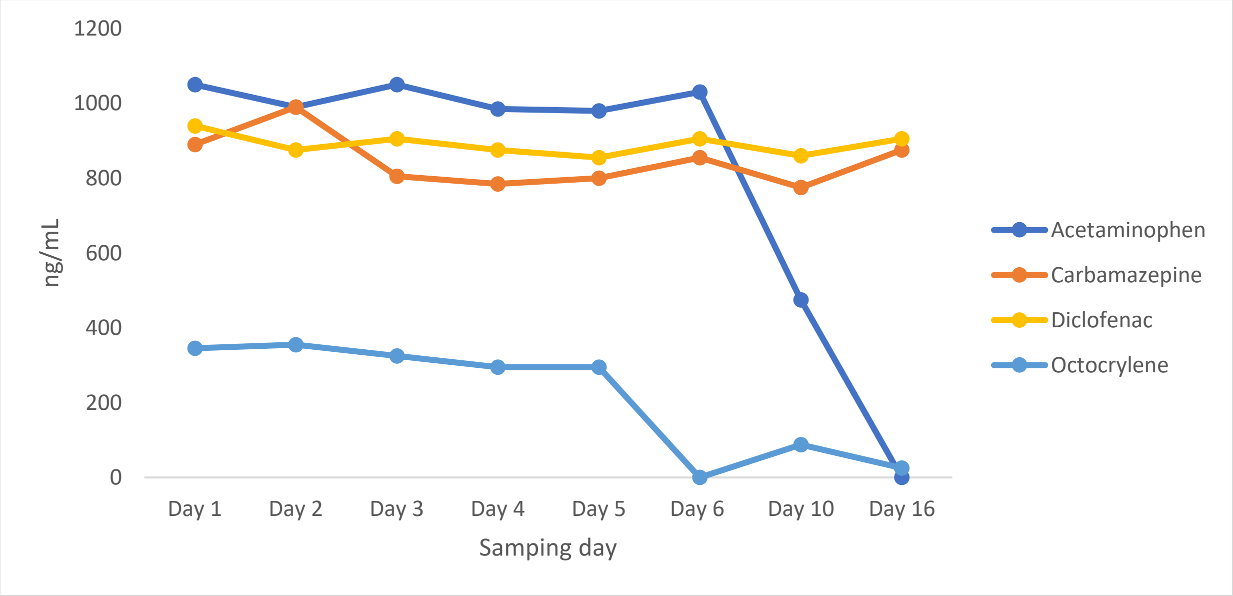


FIGURE 13: PPCP CONCENTRATIONS FROM THE CONTROL COLUMN EFFLUENTS ON DAY 1-6, 10 AND 16.

4.4.1 PPCPs removal with biochar and activated carbon

PPCPs concentrations from column effluents were measured for day 1-6, 10 and 16. Most of the concentrations were under limit of detection (LOD) or limit of quantification (LOQ). LOD and LOQ calculated for each PPCP can be found in Table 19. Removal rate for each day and each PPCP are then calculated using effluent concentrations from control columns for each day and either LOD, LOQ or measured concentration, dependent on the highest detected concentration in effluent of BC and AC columns. This to be sure the concentrations reaching the columns are correct and minimum removal rate are displayed in Table 19. The removal of DEET was not possible to measure due to high LOD and LOQ, but the measured concentrations from BC and AC effluents were < 20 ng/mL (LOD).

Highest measured effluent concentration was 2.4 ng/mL ACET from AC1 column on day 2 (appendix A5). All other measurements were under LOD or LOQ, therefore were LOD and LOQ the highest possible effluent concentrations to calculate removal rate with for AC and BC columns from day 1 to day 16. The lowest possible removal rate was OCT day 16 (≥80 %) due to low concentrations in the control effluents. ACET, CBZ and DFC are removed with more than 99 % every day. OCT was removed with more than 93 % everyday, except day 16. The AC and BC columns are showing equally good sorption.

Table 19: LOD and LOQ calculated for each PPCP. Removal rate [%] for each PPCP by activated carbon (AC) or Biochar (BC), calculated from LOD or LOQ based on control column effluent concentrations each day. Minimum removal rate is displayed for each material each day.

		Acetaminophen [ng/mL]	**Carbamazepine [ng/mL]**	**Diclofenac [ng/mL]**	**Octocrylene [ng/mL]**
LOD		**0.25**	**0.1**	**0.1**	**5**
LOQ		**1**	**1**	**0.5**	**20**
Day 1	**AC**	≥ 99.98 %	≥99.99 %	≥ 99.95 %	≥ 94.20 %
	BC	≥ 99.98 %	≥ 99.99 %	≥ 99.95 %	≥ 94.20 %
Day 2	**AC**	≥ 99.75 %	≥ 99.99 %	≥ 99.94 %	≥ 94.37 %
	BC	≥ 99.97 %	≥99.99 %	≥ 99.99 %	≥ 94.37 %
Day 3	**AC**	≥ 99.98 %	≥ 99.99 %	≥ 99.99 %	≥ 93.85 %
	BC	≥ 99.98 %	≥ 99.99 %	≥ 99.99 %	≥ 93.85 %
	AC	≥ 99.97 %	≥ 99.99 %	≥ 99.99 %	≥ 93.22 %

Day 4	**BC**	≥ 99.97 %	≥ 99.99 %	≥ 99.99 %	≥ 93.22 %
Day 5	**AC**	≥ 99.97 %	≥ 99.99 %	≥ 99.99 %	≥ 93.22 %
	BC	≥ 99.90 %	≥ 99.99 %	≥ 99.99 %	≥ 98.31 %
Day 6	**AC**	≥ 99.98 %	≥ 99.88 %	≥ 99.99 %	- *
	BC	≥ 99.98 %	≥ 99.88 %	≥ 99.94 %	- *
Day 10	**AC**	≥ 99.95 %	≥ 99.99 %	≥ 99.99 %	≥ 94.32 %
	BC	≥ 99.95 %	≥ 99.99 %	≥ 99.99 %	≥ 94.32 %
Day 16	**AC**	- *	≥ 99.99 %	≥ 99.99 %	≥ 80.00 %
	BC	- *	≥ 99.99 %	≥ 99.99 %	≥ 80.00 %

* OCT (day 6) and ACET (day 16) had LOQ/LOD in both control column effluent and BC/AC effluent, removal rate is therefore not calculated.

4.4.2 Removal mechanisms

Removal of PPCPs by BC and AC as carbonaceous sorbents can be related to several possible sorption mechanisms. Sorption mechanisms and capacity depend on both the properties of the CM and PPCP. It is not possible to determine the sorption mechanisms in the removal of PPCPs by BC and AC in this experiment without isolated sorption experiments and analysis of the sorption material after the experiment. But the known properties of the sludge BC and AC, PPCPs properties and greywater quality can help to understand the high removal rate for the PPCPs by the CMs. The properties of the sludge biochar used in this experiment are listed in Table 9 and the properties of the five selected PPCPs are listed in Table 2. The quality of the greywater containing the PPCPs pumped into the columns can also interact with the sorption and sorption capacity and can be found in Table 11. Zhang et al. (2022) has divided sorption mechanisms of PPCPs by BCs into:

- π-π interactions
- Hydrophobic Interaction
- Electrostatic interaction
- Hydrogen bonds
- Pore-filling
- Others: Lewis acid-base interaction and partition non-carbonized phase

An earlier study done by Tong et al. (2016) indicated that sorption of triclosan onto sludge BC mainly occurred due to high surface area, hydrophobicity and potential interactions including hydrogen bonding.

Pore size distribution and specific surface area

An important property for PPCPs removal by AC and BC is the pore size distribution. The sludge BC has a wide range of pore sizes which can be an advantage in sorption of PPCPs with different molecule sizes. A study based on machine learning reported that average pore diameter larger than the diameter of the PPCP molecule by 1.5-2.5 folds performed best in adsorption (Zhu et al., 2022). The variation in pore diameters on the sludge BC can be an advantage in removal of PPCPs with different molecule sizes and can be a better solution for wastewater treatment. AC normally contains micropores (<2nm) and can size-exclude PPCPs with higher molecule masses in the sorption process (Ji et al., 2010). An example is antibiotics, which often have bulky molecules and is size-excluded in the adsorption process with AC (Ji et al., 2010). Diffusion onto BC and AC can occur during diffusion of sorbates into pores during pore filling or into the organic matter matrix of the BC’s non-carbonized fractions (Kończak et al., 2021). The sludge BC has low a carbon content and sorption into other fractions on the BC can be an important sorption mechanism.

In general, a higher SSA will increase the possible adsorption sites on the CMs and is important for the sorption capacity of the material. The high surface area of AC can benefit the physical adsorption with more accessible adsorption sites to enhance the interactions between the PPCPs and the AC surface. The specific surface area and micropore volume of BC is reported to be much smaller than commercial AC, and it is likely to think that pore volume and SSA is less important in the sorption of the PPCPs onto the BC in this experiment.

Hydrophobic interactions

The octanol-water distribution coefficient (K_{ow}) of a PPCP can be used to predict the hydrophobic interaction between sorbates and sorbents, where a high K_{ow} indicates highly hydrophobic interactions (Chen et al., 2017). Therefore, the sorption capacity of BC and AC for PPCPs can be related to the hydrophobicity of the PPCPs. The five selected PPCPs in this experiment have different $\log K_{ow}$ values, and hydrophobic interactions alone cannot explain the high removal rate for all the compounds. $\log K_{ow}$ for ACET is 0.46 (Table 2), relatively hydrophilic. The weak hydrophobic interactions can therefore not explain the high sorption capacity of ACET alone. LogK_{ow} value for CBZ and DFC are 2.45 and 1.9. Hydrophobic adsorption was reported to be the main sorption mechanism of CBZ and DFC onto loblolly pine chips-derived BC (Jung et al., 2013). OCT has logK_{ow} value of 7.3 and is likely to be adsorbed by hydrophobicity interaction.

Ash content

The high ash content in the sludge BC can be an advantage in sorption of PPCPs. A high ash content can lead to increase in the adsorption ability of polar molecules and therefore an advantage in the PPCPs removal processes due to PPCPs properties (Xia et al., 2019). ACET has two hydrogen bonds and one dipole-dipole making it more polar. DFC is polar due to the -COOH group, -NH and -Cl. The high removal rate of ACET and DFC by the BC can possibly be explained by the high ash content. DEET is slightly polar with C=O group and N.

Hydrogen-bond

Hydrogen-bonding is another possible sorption mechanism and has been tested for sorption of CBZ onto BC. Hydrogen-bonding was the main sorption mechanism in sorption of CBZ on to BC in a study by Chen et al. in (2017). Hydrogen bond can form between functional groups of aromatic compounds and BC (Chen et al., 2017). It is not possible to confirm if H-bonding is happening in this sorption experiment. H-bonding mechanism can be tested with increase and decrease of pH in the water. An increase in pH will reduce H^+ and the PCPP will interact with the BC and result in increase of PPCP sorption onto the BC. In reverse, a decrease in pH will reduce the sorption of a PPCPs onto BC if the main sorption mechanism is H-bonding (Chen et al., 2017).

PPCPs load on the biochar and activated carbon

The CM has to be saturated to be able to evaluate the capacity of the BC and the AC and compare the two sorption materials. It was therefore decided to spike the tank with higher concentrations than expected in STPs to find the saturation point for the BC and AC. But the removal efficiency was equally high in the end of the experiment and the saturation point was not reached. The PPCPs loading on the BC and AC can be calculated with PPCPs concentration in the batch tank (5 mg PPCP/L) and the amount of water filtrated through each column divided by the amount of AC or BC in the column. The calculated loading can be seen in Table 20.

TABLE 20: CALCULATED PPCPS LOAD ON THE BC AND AC MATERIAL

Column	Spiked GW filtrated [L]	Material [g]	Load [mg PPCP/g]
BC1	14	436.5	0.16
BC2	15.3	435.5	0.18
BC3	14.2	442.4	0.16
AC1	16.4	305.3	0.27
AC2	15.2	308.1	0.25
AC3	15.7	313.1	0.25

The PPCPs load on each gram BC is low compared to the AC due to the lower wight of AC. A study of maximum adsorption capacity of CBZ onto AC showed capacity of 45.3 mg CBZ/g AC (Chen et al., 2017). It can indicate a much higher sorption capacity of PPCPs onto AC than tested in this experiment, but the AC and BC in this experiment were also loaded with other organic and inorganic matter from the GW. The organic matter in the greywater will have a suppression effect on the sorption of the PPCPs onto the BC and AC (Tong et al., 2016). The greywater matrix with the presence of TSS and organic matter can result in sorption competition. This was tested by Tong et al. (2016) by testing sorption of Triclosan onto sludge BC in Milli-Q water and treated secondary effluent from wastewater. The sorption capacity was reduced from 518 µg triclosan/g BC in Milli-Q water to 239 µ triclosan/g BC in wastewater.

4.5 Heavy metal leach and removal

Several studies have reported high heavy metal content in sludge-derived BC (Chen et al., 2014). The metal content in the BC from Lindum was measured by Dzihora et al. in (2021) and can be found in Table 21, together with heavy metals content in commercial AC and sludge-BC analysed by Chen et al. (2014). The amount of heavy metal content in sorbents is important, as the heavy metals might leach from the BC, which can then determine the suitability of the sludge-derived BCs for water treatment to prevent additional pollution from treatment effluent. Despite high heavy metal content, the leaching is reported to be low from sewage sludge biochar (Chen et al., 2014) and matches with the findings in this study. ICP-MS/MS was used to measure the heavy metal (Cr, Ni, Cu, Zn, As, Cd, Pb) concentrations in the effluent from the BC, AC and control columns on day 0, 6, 10 and 16. The heavy metal concentrations in the tank was measured for day 0,6 and 10. Day 16 is not tested for the tank due to problems with the sample from that day.

The guidelines for trace metals in irrigation water from Food and Agriculture Organization of the United Nations (FAO) can be found in Table 21 (WHO, 2001). Effluent concentrations from all columns on the tested days were below the guidelines for trace metals in irrigation water and meet the requirements. Concentrations measured can be found in appendix (A6).

TABLE 21: HEAVY METAL CONTENT IN THE SLUDGE BC FROM LINDUM, ANALYSED BY (DZIHORA ET AL., 2021) AND (CHEN ET AL., 2014), COMMERCIAL AC BY (CHEN ET AL., 2014). FAO'S GUIDELINES FOR TRACE METALS IN IRRIGATION WATER (WHO, 2001).

Mineral	Sludge biochar		Activated carbon	FAO guidelines for trace metals in irrigation water
	(Dzihora et al., 2021)	(Chen et al., 2014)	(Chen et al., 2014)	(WHO, 2001)
Cr [mg/kg]	51	100.94	9.35	0.10
Ni [mg/kg]	43	-	-	0.20
Cu [mg/kg]	260	208.5	3.18	0.20
Zn [mg/kg]	680	-	-	2.0
As [mg/kg]	4.8	-	-	0.10
Cd [mg/kg]	0.067	3.7	0.07	0.10
Pb [mg/kg]	25	51.5	-	5.0

Only Cr had noticeable higher concentrations in the effluent from AC and BC compared to the tank on day 0 (Figure 14). But since the control column on day 0 had same concentrations as AC and BC it is less likely to be related to desorption. Lower concentrations in effluent from BC and AC columns compared to control can indicate some removal of Cr on day 10 and 16. Pb concentrations (Figure 15) from AC and BC effluents is higher than tank and control on day 0 and 6 and can be a leach from the filter materials. The concentration is then decreasing, to lower values than control and tank. In general, the tank concentrations increased by day, and correlates with the TSS measurements from the tank. The increase in the tank concentrations can also be related to elements in the steel container. Steel can be alloyed with different alloying elements to gain different properties. Alloying elements such as Cr and Ni are added to make the steel harder (Cunat, 2004).

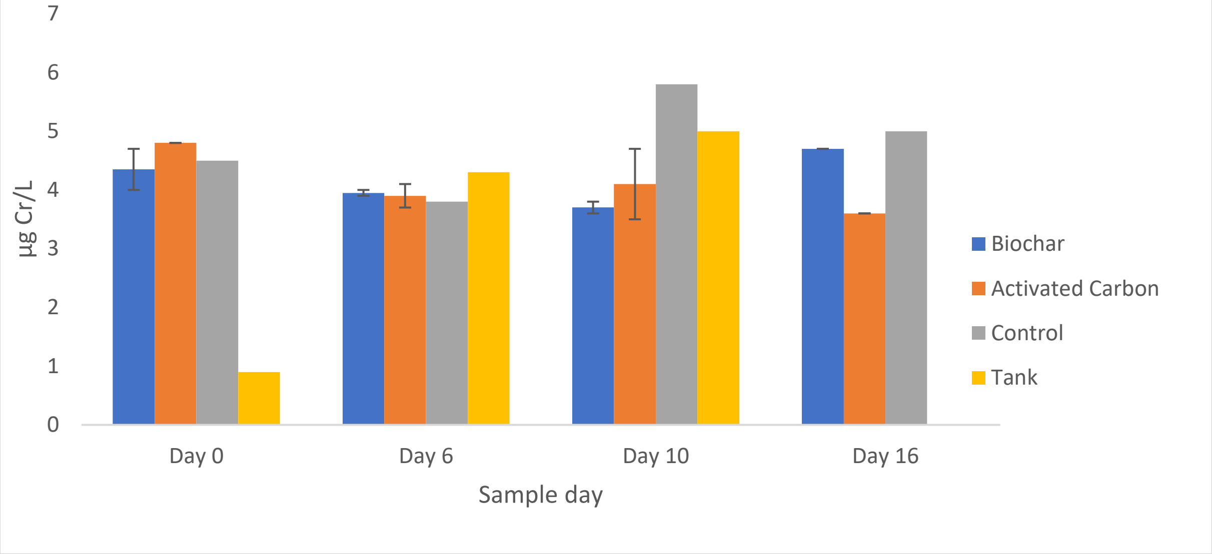


FIGURE 14: CR CONCENTRATIONS. ERROR BARS REPRESENT STANDARD DEVIATION (N=2 FOR AC AND BC). NOTE THAT FOR SOME OF THE REPLICATES THE STANDARD DEVIATION IS SO SMALL THAT THE ERROR BAR IS NOT VISIBLE IN THE FIGURE. FOR CONTROL AND TANK N=1

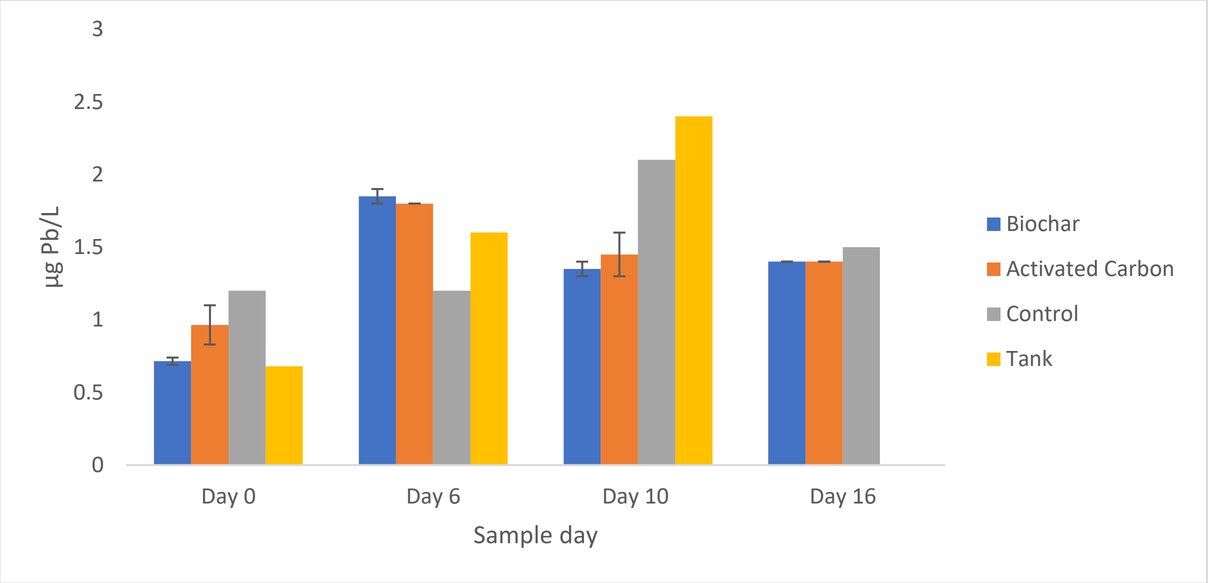


FIGURE 15: PB CONCENTRATIONS. ERROR BARS REPRESENT STANDARD DEVIATION (N=2 FOR AC AND BC). NOTE THAT FOR SOME OF THE REPLICATES THE STANDARD DEVIATION IS SO SMALL THAT THE ERROR BAR IS NOT VISIBLE IN THE FIGURE. FOR CONTROL AND TANK N=1

Ni, As (at day 6 and 10), Cu and Zn had all lower effluent concentrations than tank and control effluent and is likely adsorbed in the AC and BC columns. Ni (Figure 16) and Zn (Figure 17) had the highest removal rate. The removal of Ni is high for both BC and AC materials from day 0 to 10. Ni concentrations in the BC effluent have then increased on day 16 to concentrations similar to control and can indicate a Ni saturation of the BC material. Zn concentrations are decreasing from the AC and BC effluents from day 6, while the tank and control concentrations are increasing, likely due to adsorption of Zn. Measured Cu concentrations indicates adsorption by the BC and AC material, with some better removal rate for the BC columns (Figure 18). As concentrations measured from the tank has lower values than in BC, AC and control effluents on day 0. It is less likely to be leaching from the AC and BC due to similar control values, and more likely too low concentrations in tank sample taken from the top of the tank (Figure 19). The As concentrations measured indicated some sorption of As by the BC and AC between day 6 and 16.

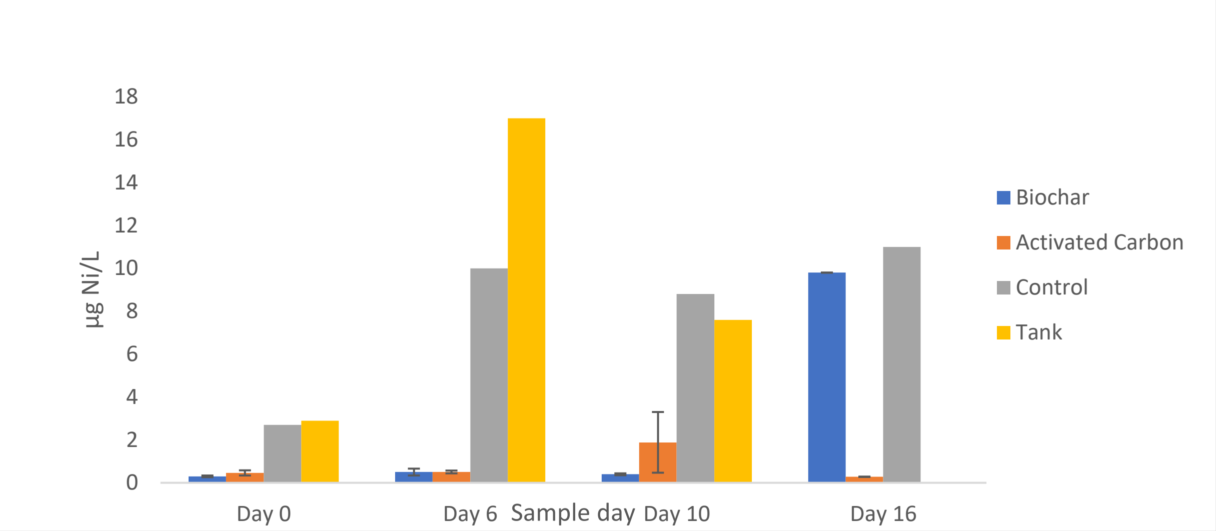


FIGURE 16: NI CONCENTRATIONS. ERROR BARS REPRESENT STANDARD DEVIATION (N=2 FOR AC AND BC). NOTE THAT FOR SOME OF THE REPLICATES THE STANDARD DEVIATION IS SO SMALL THAT THE ERROR BAR IS NOT VISIBLE IN THE FIGURE. FOR CONTROL AND TANK N=1

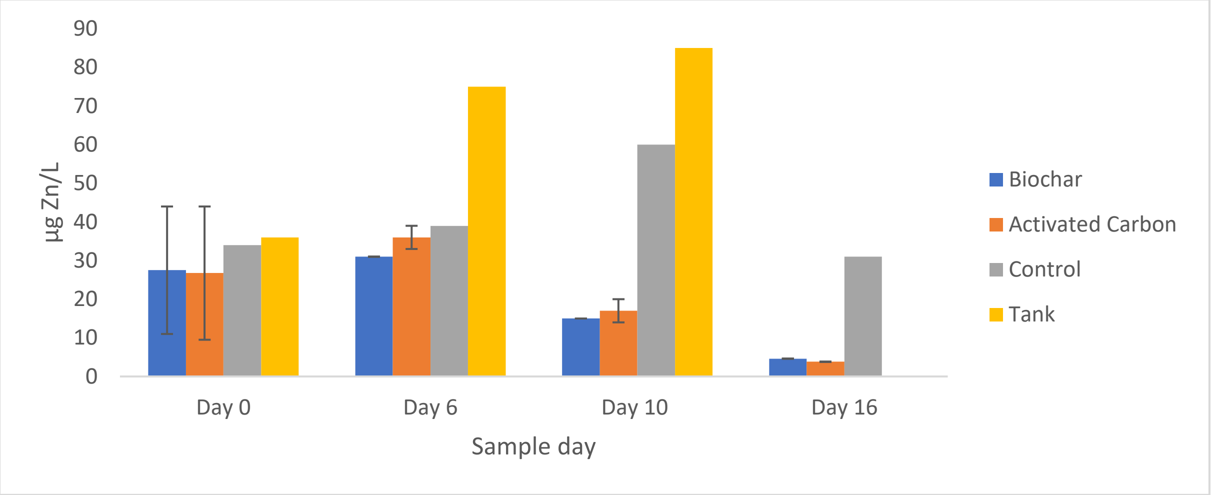


FIGURE 17: ZN CONCENTRATIONS. ERROR BARS REPRESENT STANDARD DEVIATION (N=2 FOR AC AND BC). NOTE THAT FOR SOME OF THE REPLICATES THE STANDARD DEVIATION IS SO SMALL THAT THE ERROR BAR IS NOT VISIBLE IN THE FIGURE. FOR CONTROL AND TANK N=1

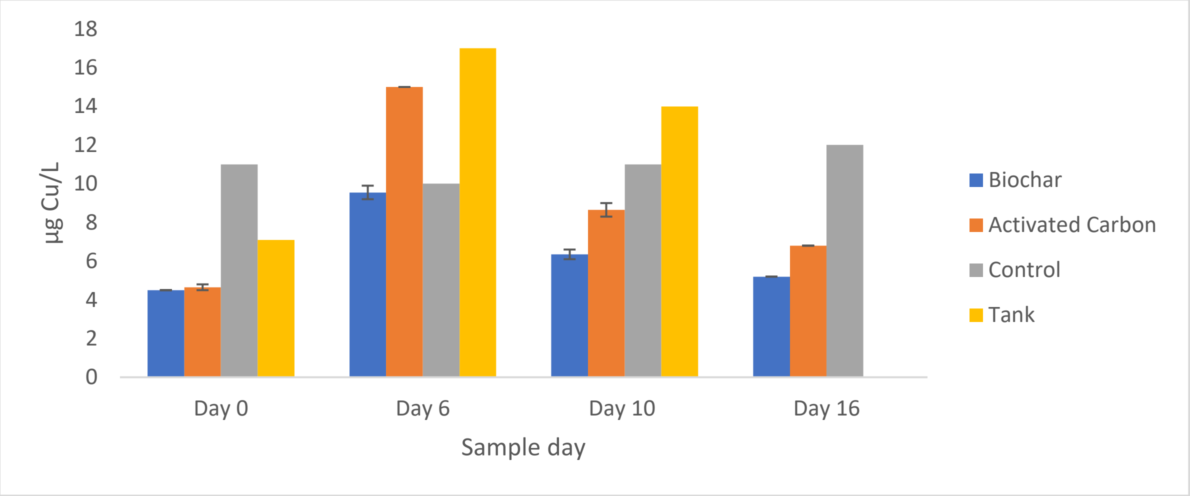


FIGURE 18: CU CONCENTRATIONS. ERROR BARS REPRESENT STANDARD DEVIATION (N=2 FOR AC AND BC). NOTE THAT FOR SOME OF THE REPLICATES THE STANDARD DEVIATION IS SO SMALL THAT THE ERROR BAR IS NOT VISIBLE IN THE FIGURE. FOR CONTROL AND TANK N=1

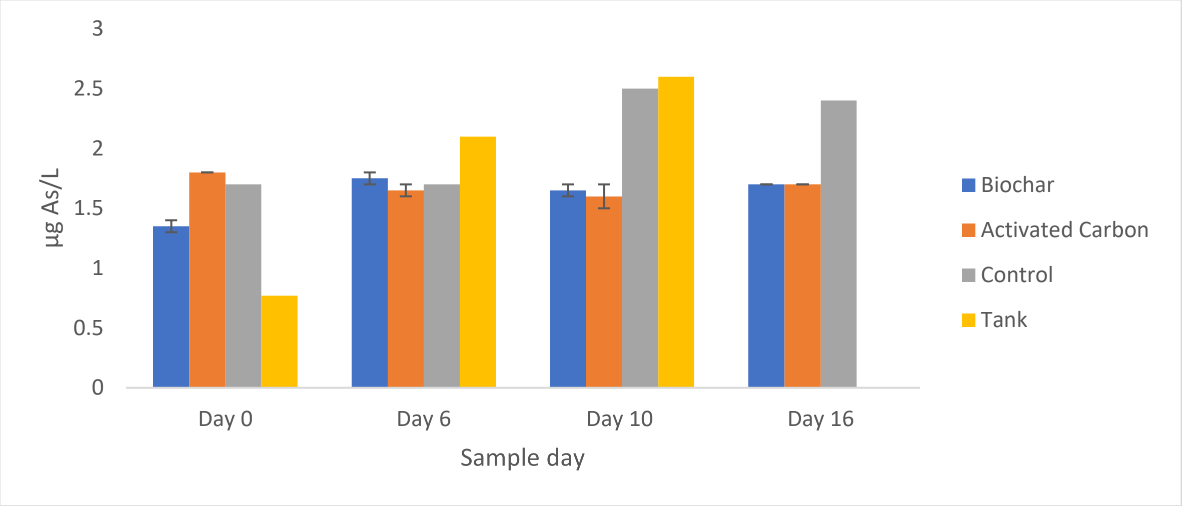


FIGURE 19: AS CONCENTRATIONS. ERROR BARS REPRESENT STANDARD DEVIATION (N=2 FOR AC AND BC). NOTE THAT FOR SOME OF THE REPLICATES THE STANDARD DEVIATION IS SO SMALL THAT THE ERROR BAR IS NOT VISIBLE IN THE FIGURE. FOR CONTROL AND TANK N=1

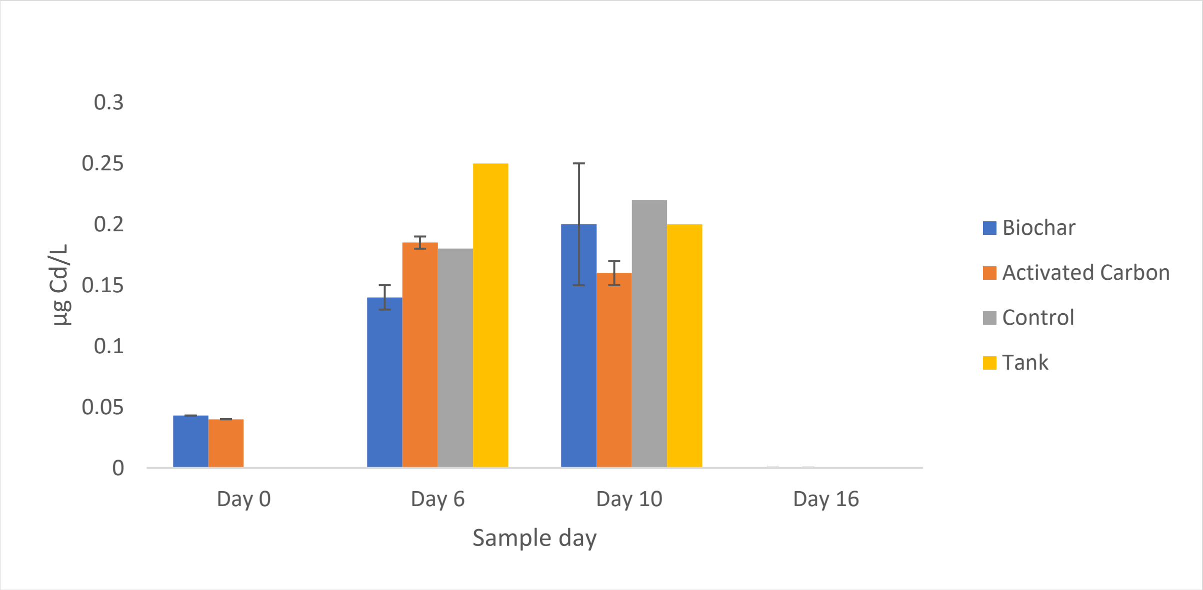


FIGURE 20: CD. ERROR BARS REPRESENT STANDARD DEVIATION (N=2 FOR AC AND BC). NOTE THAT FOR SOME OF THE REPLICATES THE STANDARD DEVIATION IS SO SMALL THAT THE ERROR BAR IS NOT VISIBLE IN THE FIGURE. FOR CONTROL AND TANK N=1

The Cd concentrations measured are in general very low, samples from day 16 and the tank from day 0 were under limit of quantification. It is therefore not possible to determine sorption of Cd onto AC and BC, but the results show no evidence of leaching from the material.

The specific surface area of the sludge BC is much smaller than of AC, but the sorption of heavy metals is equally good in this experiment. A study done by Chen et al. (2014) reported that the sorption of heavy metals onto sludge BC was better than AC. The study found out that the high sorption capacity of heavy metals onto sludge BC was explained with the porous structure with more mesopores than micropores with higher fractional dimensions (Chen et al., 2014).

In general, it was found no or very little leach from the BC and AC. The heavy metal content in the BC is much higher than AC, but the effluent concentrations is close to the same every day. It is therefore likely to think the effluent concentrations is related to the heavy metals in the water and not in the CMs. It is not possible to conclude on the sorption mechanisms of heavy metals onto the BC and AC in this experiment due to low concentrations of heavy metals in the GW used in this experiment. The concentrations measured from the effluents can still indicate no or little leach from the carbon material, despite high heavy metal content in the BC, and effluent concentrations below the guideline for irrigation water given by FAO.

5 Conclusion

The BAF treatment of the greywater alone was not enough to meet the water quality limits for reuse of greywater suggested by IWA and EU. Sludge BC pyrolyzed at 600°C improved the treated greywater quality in the polishing step. It was no differences in the water quality parameters TSS, BOD_5, COD_T, turbidity, total phosphorus and total nitrogen measured from the biochar column effluents and the activated carbon column effluents. The BC effluents had a pH of approximately 7.5 during the whole 16 days experiment and did not affect the pH in the GW, while the effluents from the AC columns had an increase in the pH from day 1 to 10. The water quality parameters were below the suggested limits for reuse after the polishing-step. Future work should include microbiological testing of the effluent water to determine the disinfection effect by BC.

The sludge BC and AC performed equally good in the PPCPs removal, with a removal rate of more than 93% off all the PPCPs for all sampled days. Acetaminophen, carbamazepine and diclofenac were removed with more than 99% and octocrylene was removed with more than 93%. The PPCPs load on the AC and the BC were in average 0.26 mg PPCP /g for AC columns and 0.15 mg PPCP/g for BC columns in addition to the organic load from the greywater. The saturation of the materials was not reached, and it was therefore not possible to compare the sorption capacity of the AC and the BC material. It was not possible to decide the main removal mechanisms in the sorption of each PPCP by the BC in an experiment with water containing other organic compounds and without analysing the material after use. But the properties of the BC and PPCPs can indicate that the variation in the pore structure and pore size on the sludge BC surface can be an advantage in sorption of PPCPs with different properties. Future investigations should focus on the sorption capacity of PPCPs onto sludge BC and the main sorption mechanisms.

Heavy metal concentrations from the column effluents indicated no or little leach of heavy metals from the AC and the BC material, despite high metal content in the sludge BC. It was observed some sorption of Zn and Ni by both materials. The measured concentrations were below the limits of trace materials in irrigation water from FAO and could therefore be suitable for treatment of irrigation water. Regeneration of BC used for PPCPs removal should be investigated, due to the risk of release of the organic compounds in the regeneration process.

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Appendix

A1 - Analysis performed each day

	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10	Day 11	Day 12	Day 13	Day 14	Day 15	Day 16
TSS	x					x				x						x
BOD_5	x					x				x						x
COD_T	x					x				x						x
Turb.	x	x		x	x	x				x						x
pH	x	x	x	x	x	x				x						x
Cond.	x	x	x	x	x	x				x						x
Tot. P	x															x
Tot. N	x															x
Volume	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Acetam.	x	x	x	x	x	x				x						x
Carb.	x	x	x	x	x	x				x						x
DEET	x	x	x	x	x	x				x						x
Diclof.	x	x	x	x	x	x				x						x
Octoc.	x	x	x	x	x	x				x						x
Heavy metals	x					x				x						

A2 – LC-MS/MS

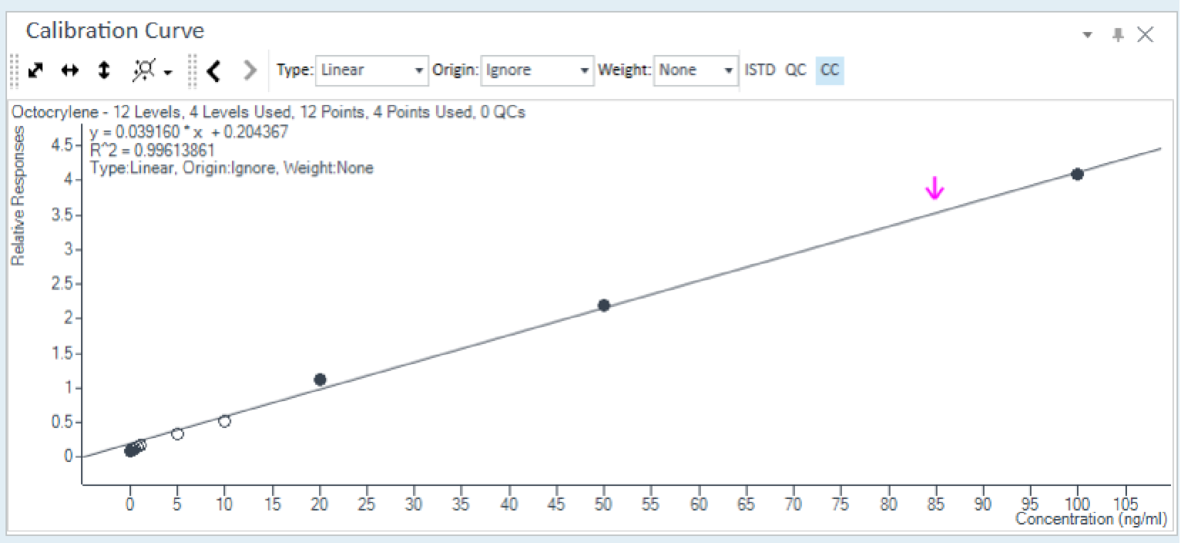
LC-MS/MS internal standards used:

Analyte	**Internal Standard**
Acetominophene	Acetaminophen D4 (Sigma Aldrich, Burlington, MA, USA)
Carbamazapine	Carbamazepine 13C6 (Sigma Aldrich, Burlington, MA, USA)
DEET	Diclofenac 13C6 (Sigma Aldrich, Burlington, MA, USA)
Diclofenac	Diclofenac 13C6 (Sigma Aldrich, Burlington, MA, USA)
Octocrylene	Octocrylene D15 (Sigma Aldrich, Burlington, MA, USA)

LC-MS/MS sample preparation

	Sample [µL]	ISTD [µL]	MeOH [µL]	Greywater [µL]	Total Volume [µL]	Dilution
A+B	400	50	350	-	800	1/2
C + Tank	80	50	335	335	800	1/10

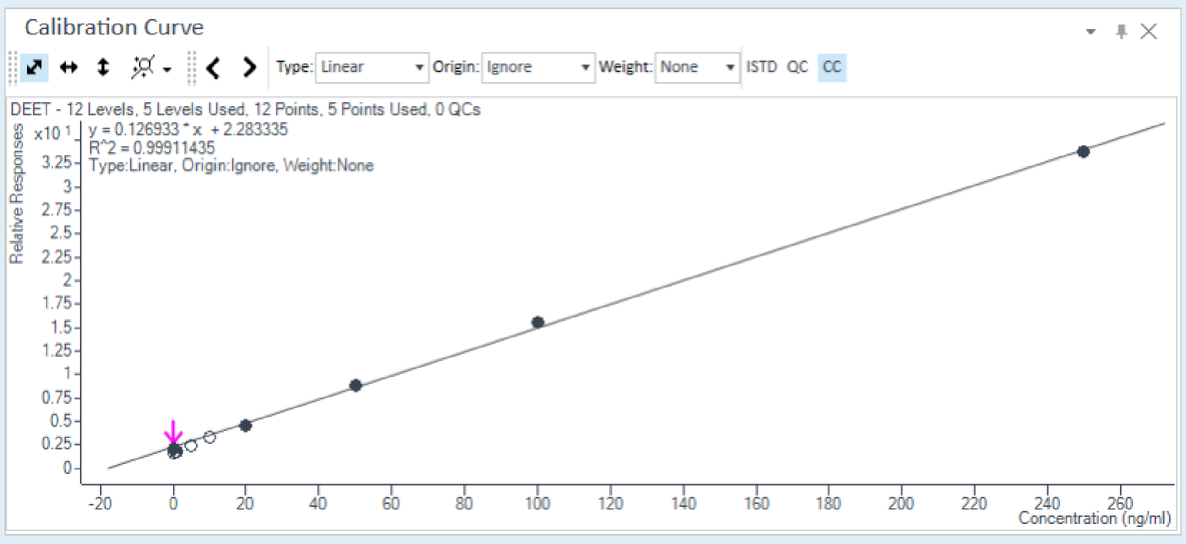
Calibration curves for high concentrations:



Type: Linear
Origin: Ignore
Weight: None

Octocrylene - 12 Levels, 4 Levels Used, 12 Points, 4 Points Used, 0 QCs

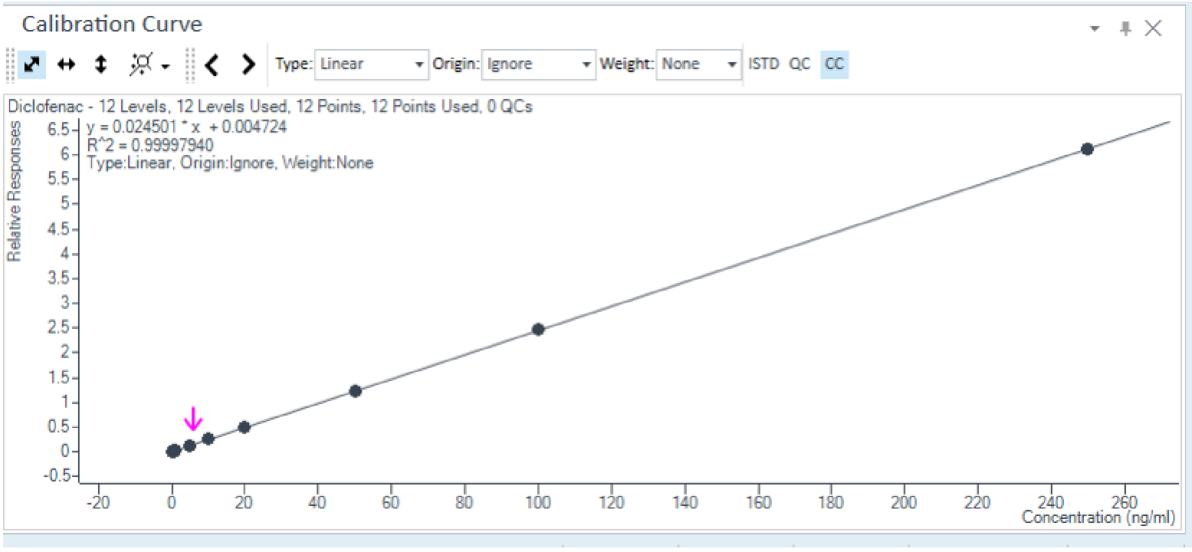
y = 0.039160 * x + 0.204367
R^2 = 0.99613861
Type:Linear, Origin:Ignore, Weight:None



Type: Linear
Origin: Ignore
Weight: None

DEET - 12 Levels, 5 Levels Used, 12 Points, 5 Points Used, 0 QCs

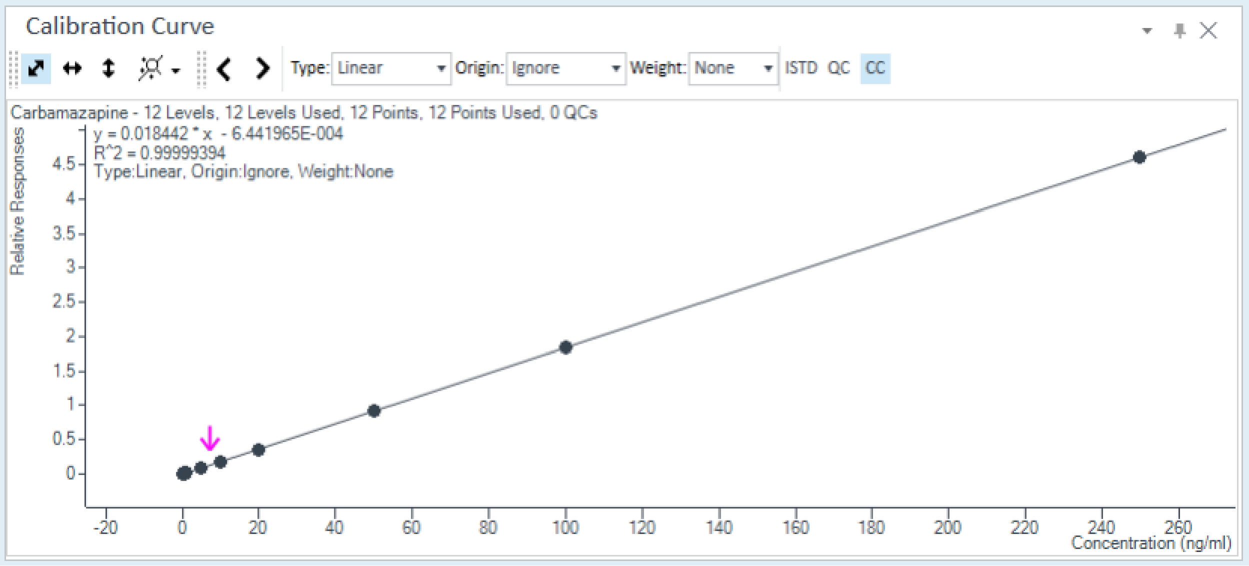
y = 0.126933 * x + 2.283335
R^2 = 0.99911435
Type:Linear, Origin:Ignore, Weight:None



Type: Linear
Origin: Ignore
Weight: None

Diclofenac - 12 Levels, 12 Levels Used, 12 Points, 12 Points Used, 0 QCs

y = 0.024501 * x + 0.004724
R^2 = 0.99997940
Type:Linear, Origin:Ignore, Weight:None



Calibration Curve

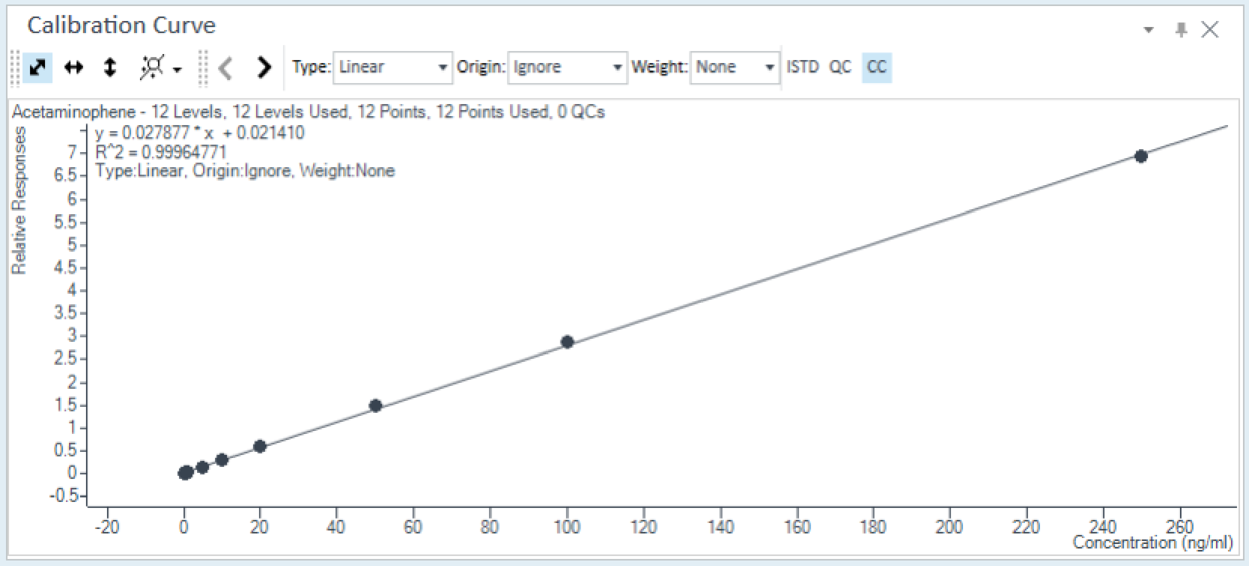
Type: Linear Origin: Ignore Weight: None

Carbamazapine - 12 Levels, 12 Levels Used, 12 Points, 12 Points Used, 0 QCs

y = 0.018442 * x - 6.441965E-004

R^2 = 0.99999394

Type:Linear, Origin:Ignore, Weight:None



Calibration Curve

Type: Linear Origin: Ignore Weight: None

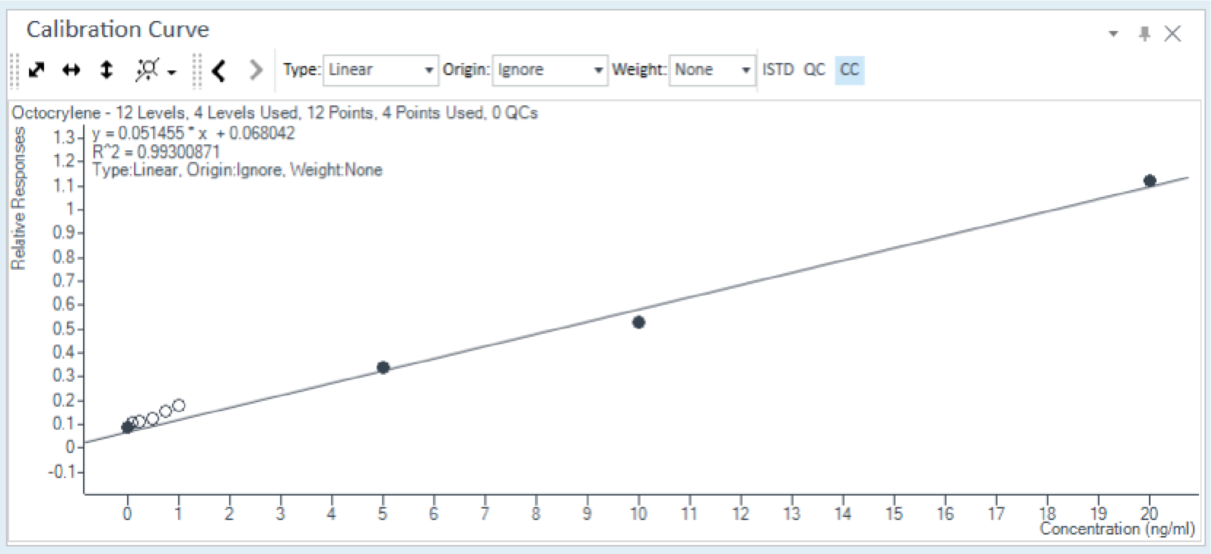
Acetaminophene - 12 Levels, 12 Levels Used, 12 Points, 12 Points Used, 0 QCs

y = 0.027877 * x + 0.021410

R^2 = 0.99964771

Type:Linear, Origin:Ignore, Weight:None

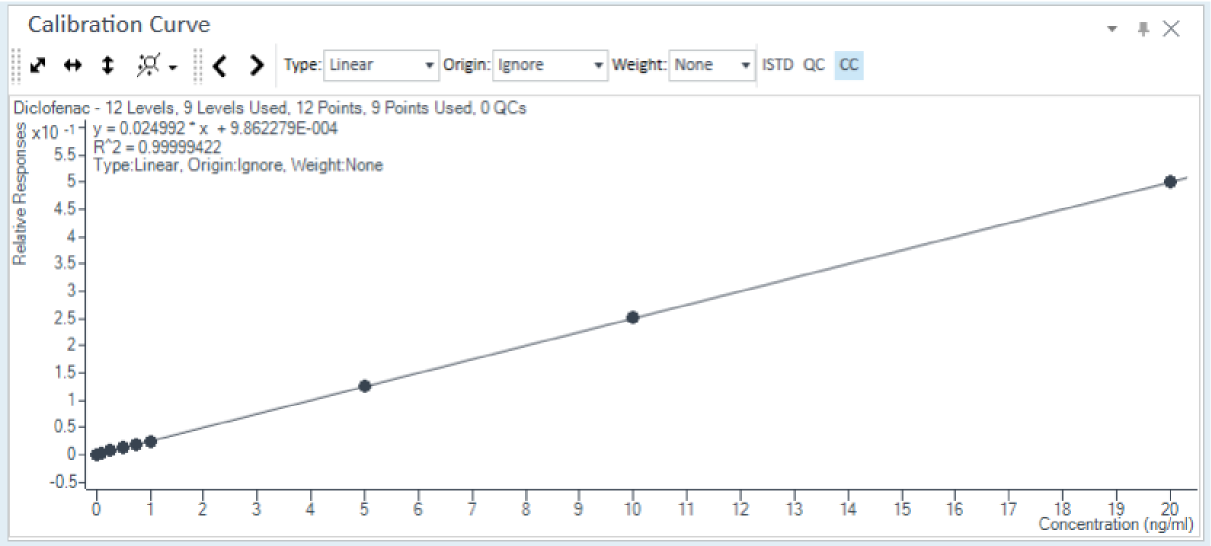
Calibration curve for low concentrations:


Calibration Curve

Type: Linear Origin: Ignore Weight: None ISTD QC CC

Octocrylene - 12 Levels, 4 Levels Used, 12 Points, 4 Points Used, 0 QCs

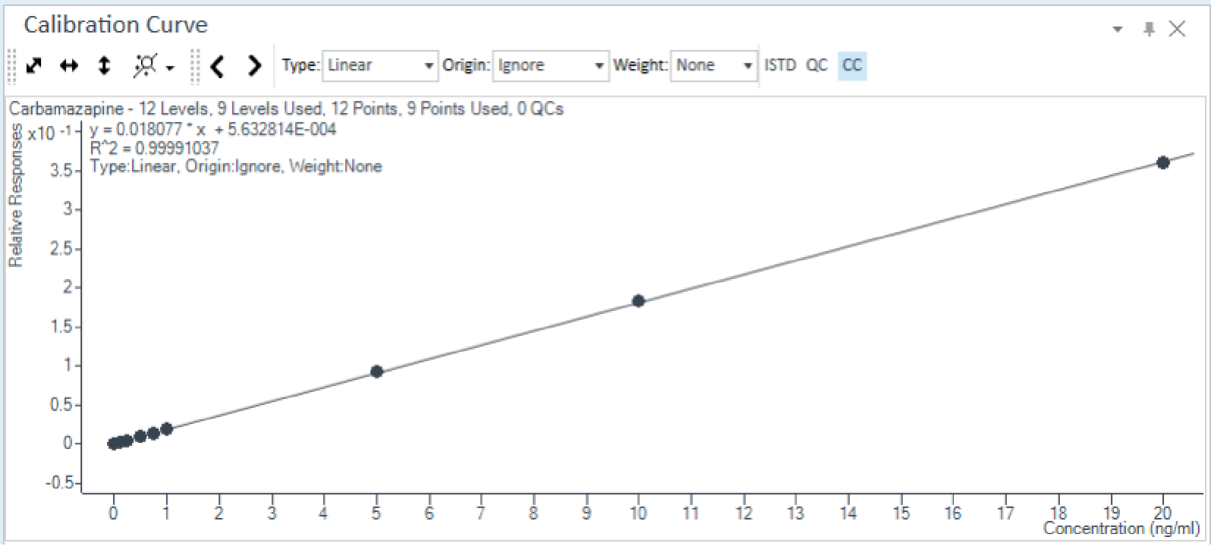
y = 0.051455 * x + 0.068042
R^2 = 0.99300871
Type:Linear, Origin:Ignore, Weight:None


Calibration Curve

Type: Linear Origin: Ignore Weight: None ISTD QC CC

Diclofenac - 12 Levels, 9 Levels Used, 12 Points, 9 Points Used, 0 QCs

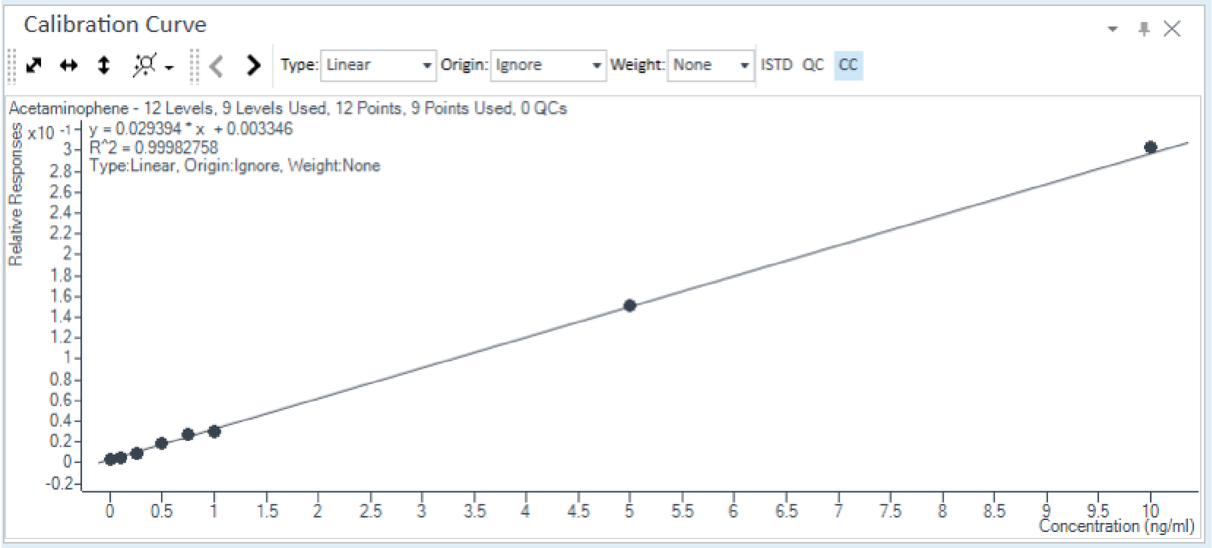
y = 0.024992 * x + 9.862279E-004
R^2 = 0.99999422
Type:Linear, Origin:Ignore, Weight:None


Calibration Curve

Type: Linear Origin: Ignore Weight: None ISTD QC CC

Carbamazapine - 12 Levels, 9 Levels Used, 12 Points, 9 Points Used, 0 QCs

y = 0.018077 * x + 5.632814E-004
R^2 = 0.99991037
Type:Linear, Origin:Ignore, Weight:None



Type: Linear
Origin: Ignore
Weight: None

Acetaminophene - 12 Levels, 9 Levels Used, 12 Points, 9 Points Used, 0 QCs

y = 0.029394 * x + 0.003346
R^2 = 0.99982758
Type:Linear, Origin:Ignore, Weight:None

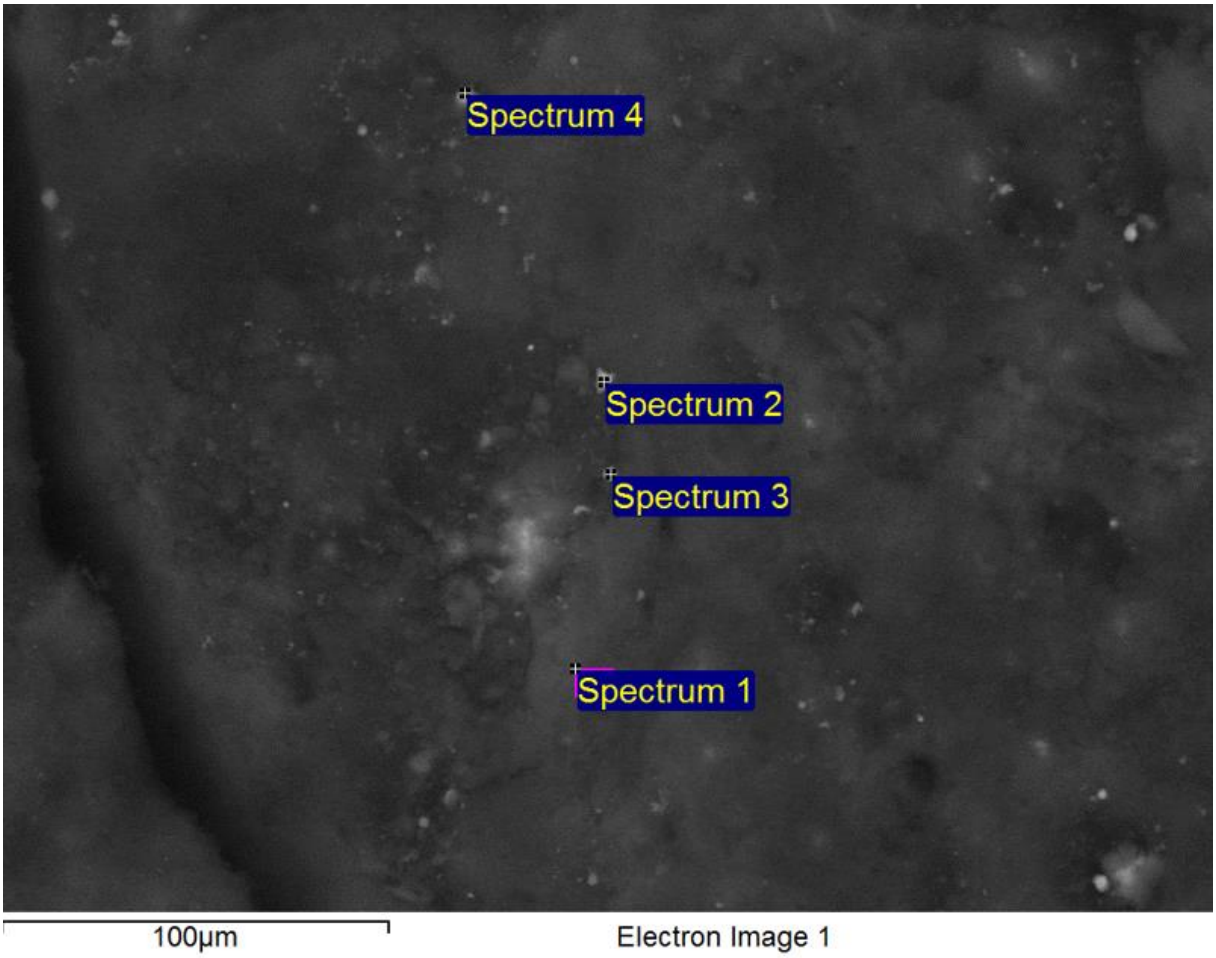
A3 - ICP-MS/MS

Calculated LOD and LOQ.

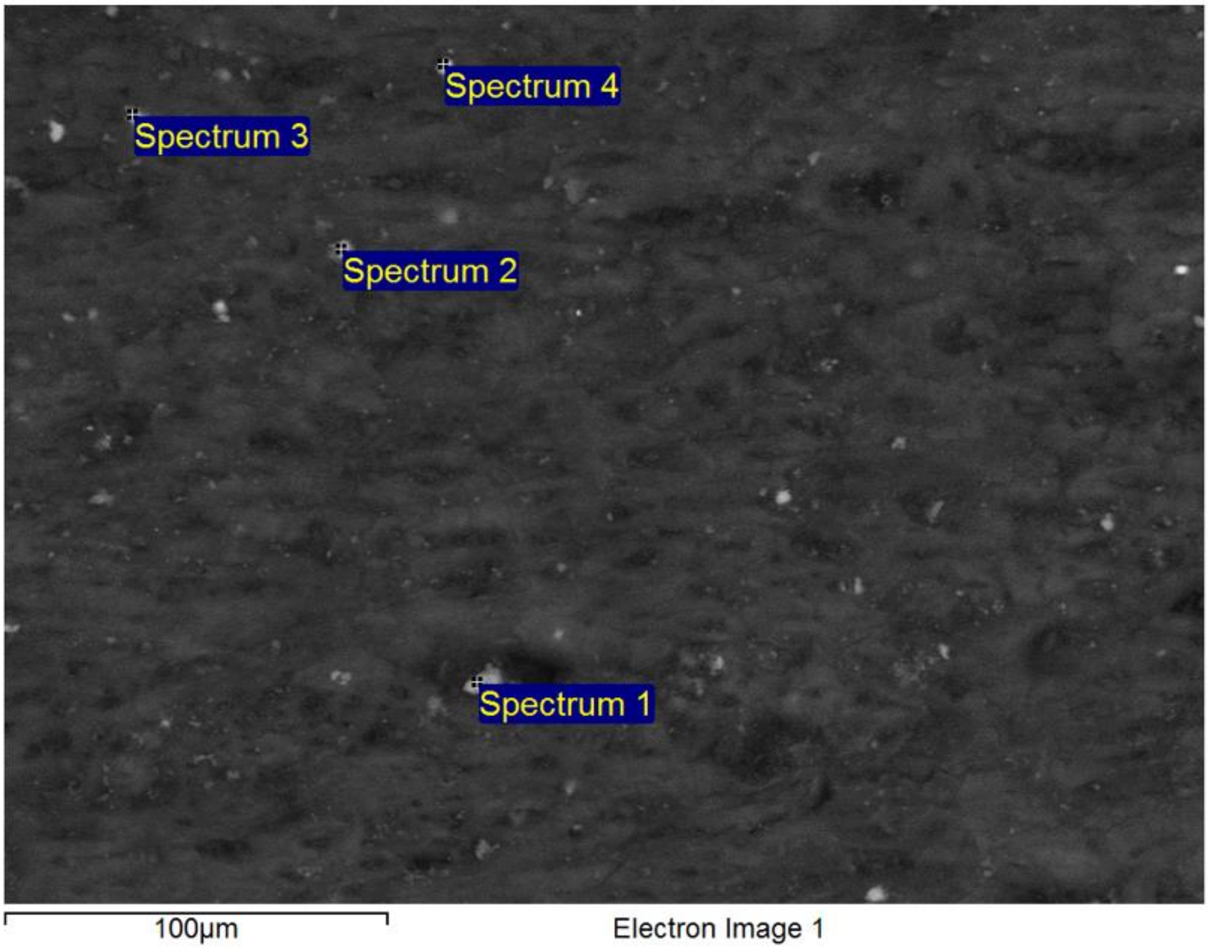
Element	**Isotope transition**	**Collision gas**	**LOD [µg/L]**	**LOQ [µg/L]**
Cr	52-52	He	0.087	0.29
Ni	60-60	He	0.041	0.14
Cu	65-65	He	0.0083	0.028
Zn	66-66	He	0.16	0.55
As	75-91	O_2	0.043	0.14
Cd	114-114	O_2	0.011	0.038
Pb	Sum of 206. 207, 208	O_2	0.0077	0.026

A4 - Optical characterisation of AC and BC

Activated carbon:

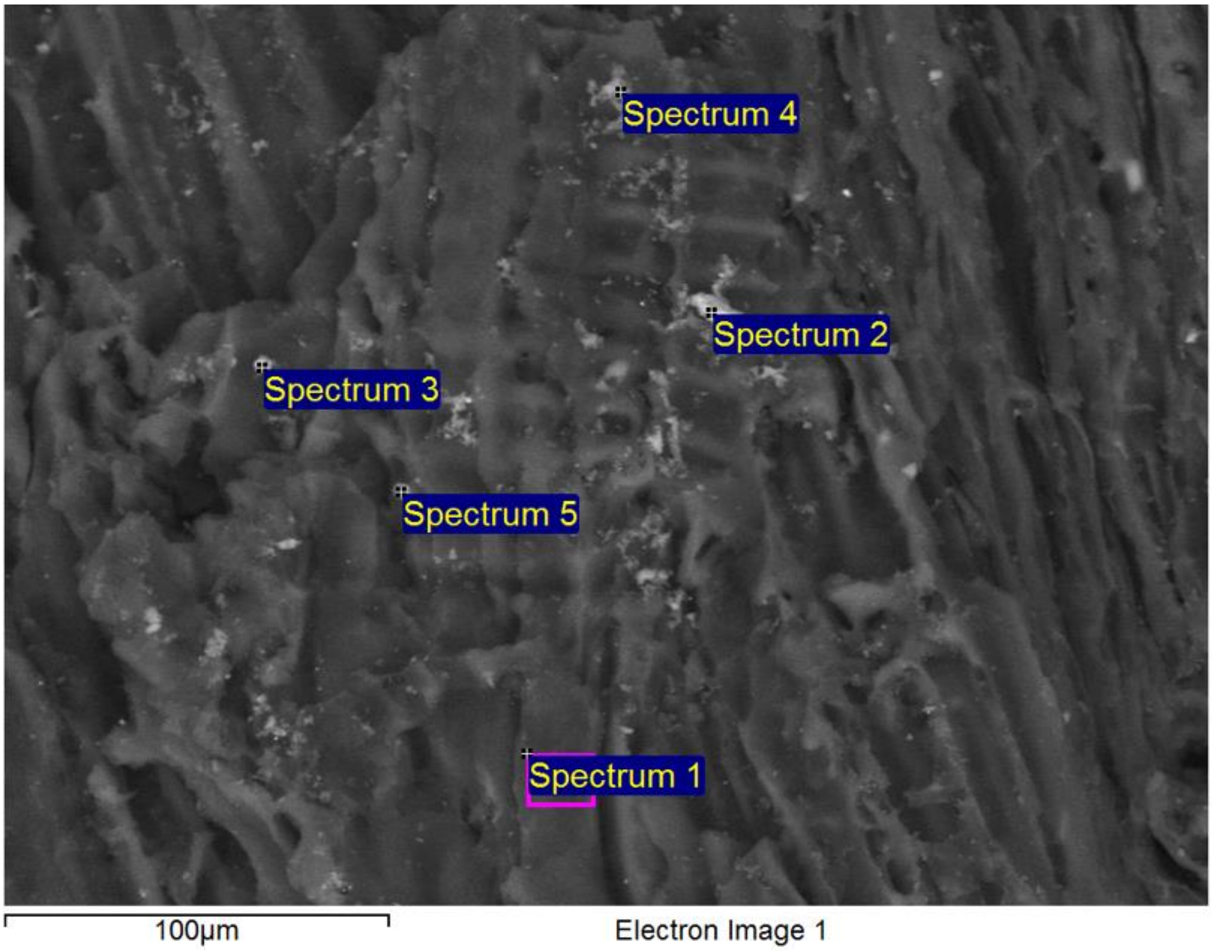


Spectrum	In stats.	Na	Mg	Al	Si	P	K	Ca	Mn	Fe	Br
Spectrum 1	Yes				30		49	13		6	1
Spectrum 2	Yes	5			4		3	88		1	0
Spectrum 3	Yes	17	6	2	47	2	8	4	1	13	
Spectrum 4	Yes	13	7	18	38	6	5	8		5	
Max.		17	7	18	47	6	49	88	1	13	1
Min.		5	6	2	4	2	3	4	1	1	0

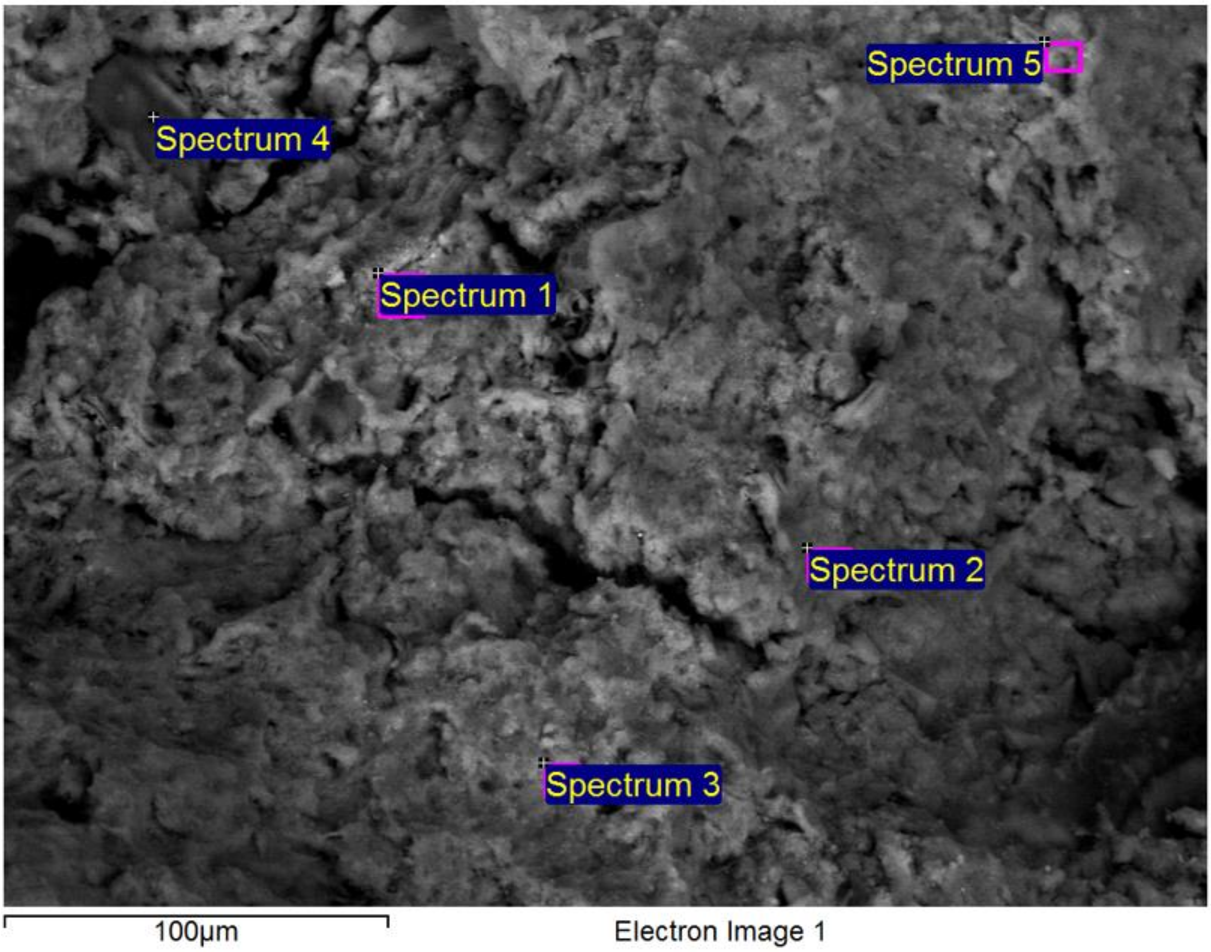


Spectrum	In stats.	Na	Mg	Al	Si	P	Cl	K	Ca	Mn	Fe	Cu
Spectrum 1	Yes	8	3	16	32	8		9	21		3	
Spectrum 2	Yes	8	6	7	43	3	0	8	16	0	8	0
Spectrum 3	Yes		2	3	35		4	35		0	12	9
Spectrum 4	Yes	8		3	33		2	29		1	17	8
Max.		8	6	16	43	8	4	35	21	1	17	9
Min.		8	2	3	32	3	0	8	16	0	3	0

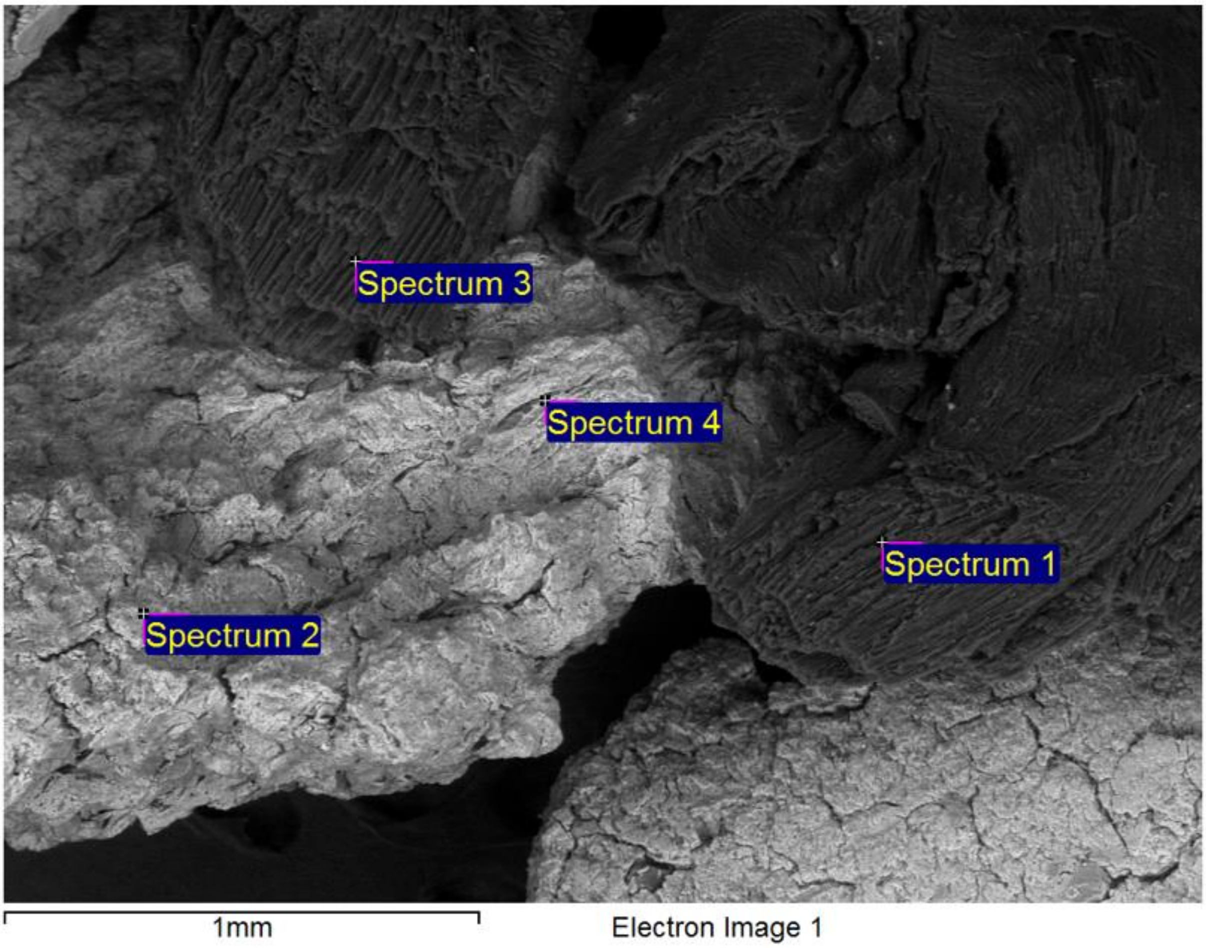
Biochar:



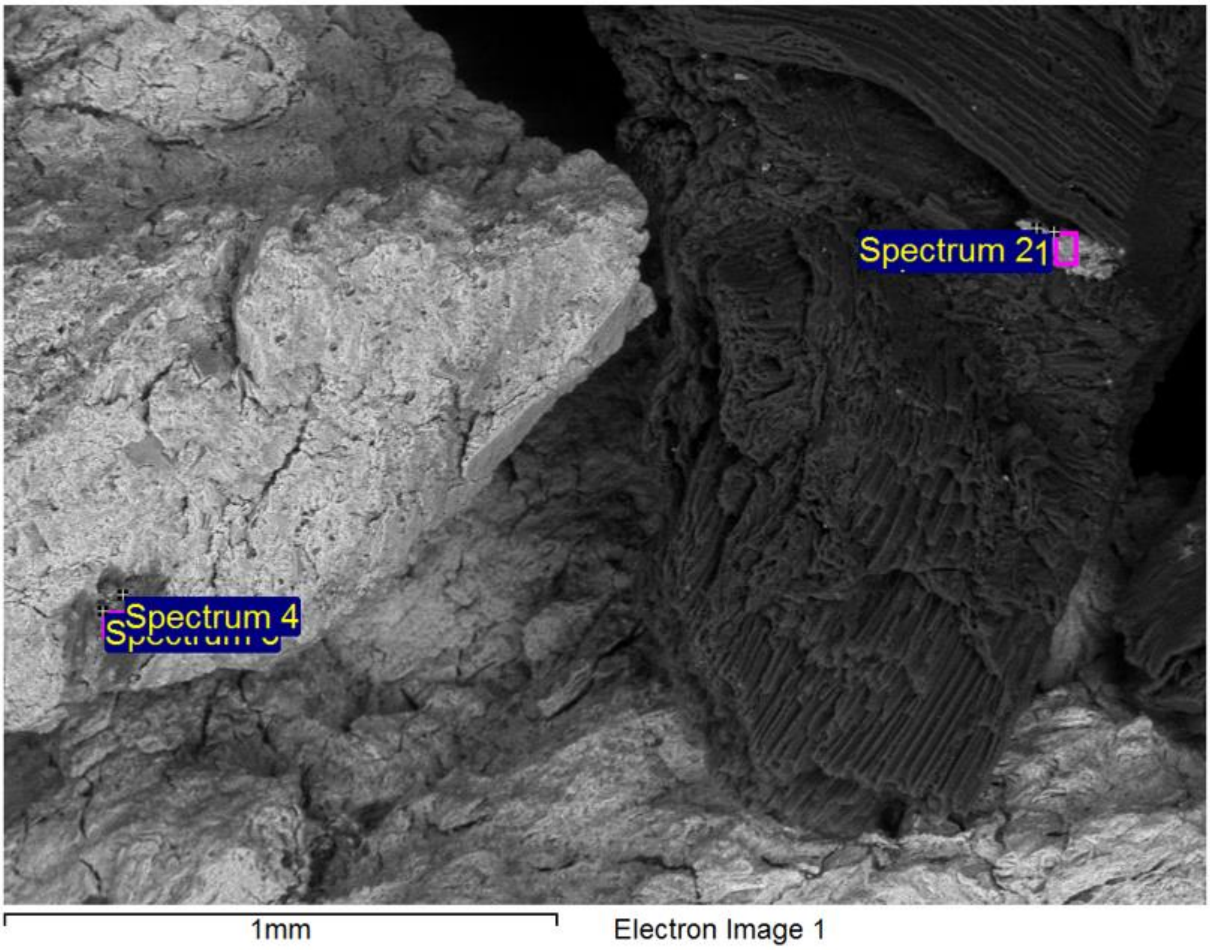
Spectrum	In stats.	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Br
Spectrum 1	Yes	12			12		11	8	14	18	23	1
Spectrum 2	Yes	11	2	11	6	8	15	5	15	5	25	
Spectrum 3	Yes	10	3	17	7	10	11	2	6	5	29	
Spectrum 4	Yes	17	3	5	4	3	14	15	21	9	8	
Spectrum 5	Yes	4	5	22	42	2	5	3	13	1	3	
Max.		17	5	22	42	10	15	15	21	18	29	1
Min.		4	2	5	4	2	5	2	6	1	3	1



Spectrum	In stats.	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe
Spectrum 1	Yes	1	1	7	7	4	5	1	4	0	70
Spectrum 2	Yes	2	5	20	16	12	5	1	5	1	33
Spectrum 3	Yes		1	7	6	3	1	1	3	1	76
Spectrum 4	Yes			3	79	4	1		2		11
Spectrum 5	Yes		4	15	10	10	4	1	6	1	51
Max.		2	5	20	79	12	5	1	6	1	76
Min.		1	1	3	6	3	1	1	2	0	11



Spectrum	In stats.	Mg	Al	Si	P	S	K	Ca	Ti	Fe
Spectrum 1	Yes	4	37	10		15	3	12		19
Spectrum 2	Yes		29	10	5	1	1	3		51
Spectrum 3	Yes	6	48	12		6	2	10		17
Spectrum 4	Yes	2	17	9	9	4	1	5	1	53
Max.		6	48	12	9	15	3	12	1	53
Min.		2	17	9	5	1	1	3	1	17



Spectrum	In stats.	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe
Spectrum 1	Yes	3	2	21	18	14	3		1	5	1	33
Spectrum 2	Yes	2	2	22	13	15	5		1	5	0	33
Spectrum 3	Yes	3	5	18	30	10	4		2	10	1	17
Spectrum 4	Yes	3	4	14	30	6	3	1	2	24	0	12
Max.		3	5	22	30	15	5	1	2	24	1	33
Min.		2	2	14	13	6	3	1	1	5	0	12

A5 - Measured PPCPs concentrations

Tank and control columns, measure 09.05.2022.

* These were under LOQ, and where therefore not corrected for the 10 times dilution. Idealy these should have been re-analysed with a lower dilution factor, but due to carry over of DEET in the instrument, this was not done.

	Acetaminophene	**Carbamazapine**	**Diclofenac**	**Octocrylene**
	ng/mL	**ng/mL**	**ng/mL**	**ng/mL**
LOD (ng/mL)	0.25	0.1	0.1	5
LOQ (ng/mL)	1	1	0.5	20
SAMPLES				
Tank_dag1	960	830	880	<LOQ*
1-3.05.22_C1	1100	850	940	350
1-3.05.22_C2	1000	760	870	300
04.05.22_C1	1000	790	900	280
05.05.22_C1	990	810	880	300
05.05.22_C2	970	790	830	290
06.05.22_C1	960	810	890	<LOQ*
06.05.22_C2	1100	900	920	<LOQ*
06.05.22_tanken	970	800	890	670
29.04.22_C1	1100	930	980	340
29.04.22_C2	1000	850	900	350
30.04.22_C1	980	820	870	330
30.04.22_C2	1000	830	880	380

Tank and control columns, measured 19.05.2022

* These were under LOQ, and where therefore not corrected for the 10 times dilution. Idealy these should have been re-analysed with a lower dilution factor, but due to carry over of DEET in the instrument, this was not done.

	Acetominiphene	**Carbamazapine**	**Diclofenac**	**Octocrylene**
Name	**ng/mL**	**ng/mL**	**ng/mL**	**ng/mL**
LOD	0.25	0.1	0.1	5
LOQ	1	1	0.5	20
Samples				

10.05.22_C1	470	780	870	66
10.05.22_C2	480	770	850	110
10.05.22_tank	170	790	880	320
16.05.22_C1	<LOD*	830	880	22
16.05.22_C2	<LOD*	920	930	28
16.05.22_tank	<LOD*	840	870	1700
04.05.22_C2	970	780	850	310

AC and BC effluents measured 09.05.2022

	Acetominiphene	**Carbamazapine**	**Diclofenac**	**Octocrylene**
	ng/mL	**ng/mL**	**ng/mL**	**ng/mL**
LOD	0.25	0.1	0.1	5
LOQ	1	1	0.5	20
Samples				
29.04.22_A1	<LOD	<LOD	<LOQ	<LOD
29.04.22_A2	<LOD	<LOD	<LOQ	<LOQ
29.04.22_A3	<LOD	<LOD	<LOQ	<LOQ
29.04.22_B1	<LOD	<LOD	<LOQ	<LOD
29.04.22_B2	<LOD	<LOD	<LOQ	<LOQ
29.04.22_B3	<LOD	<LOD	<LOD	<LOQ
30.04.22_A1	12	<LOD	<LOQ	<LOQ
30.04.22_A2	<LOD	<LOD	<LOD	<LOQ
30.04.22_A3	<LOD	<LOD	<LOD	<LOQ
30.04.22_B1	<LOD	<LOD	<LOD	<LOQ
30.04.22_B2	<LOD	<LOD	<LOD	<LOQ
30.04.22_B3	<LOD	<LOD	<LOD	<LOQ
30.04.22_A1	12	<LOD	<LOQ	<LOQ
30.04.22_A2	<LOD	<LOD	<LOD	<LOQ
30.04.22_A3	<LOD	<LOD	<LOD	<LOQ
30.04.22_B1	<LOD	<LOD	<LOD	<LOQ
30.04.22_B2	<LOD	<LOD	<LOD	<LOQ
30.04.22_B3	<LOD	<LOD	<LOD	<LOQ

1-3.05.22_A1	<LOD	<LOD	<LOD	<LOD
1-3.05.22_A2	<LOD	<LOD	<LOD	<LOD
1-3.05.22_A3	<LOD	<LOD	<LOD	<LOQ
1-3.05.22_B1	<LOD	<LOD	<LOD	<LOQ
1-3.05.22_B2	<LOD	<LOD	<LOD	<LOQ
1-3.05.22_B3	<LOD	<LOD	<LOD	<LOQ
04.05.22_A1	<LOD	<LOD	<LOD	<LOQ
04.05.22_A2	<LOD	<LOD	<LOD	<LOQ
04.05.22_A3	<LOD	<LOD	<LOD	<LOQ
04.05.22_B1	<LOD	<LOD	<LOD	<LOQ
04.05.22_B2	<LOD	<LOD	<LOD	<LOQ
04.05.22_B3	<LOD	<LOD	<LOD	<LOQ
05.05.22_A1	<LOD	<LOD	<LOD	<LOD
05.05.22_A2	<LOD	<LOD	<LOD	<LOQ
05.05.22_A3	<LOD	<LOD	<LOD	<LOQ
05.05.22_B1	<LOD	<LOD	<LOD	<LOD
05.05.22_B2	<LOD	<LOD	<LOD	<LOD
05.05.22_B3	<LOQ	<LOD	<LOD	<LOD
06.05.22_A1	<LOD	<LOD	<LOD	<LOQ
06.05.22_A2	<LOD	<LOQ	<LOD	<LOQ
06.05.22_A3	<LOD	<LOD	<LOD	<LOQ
06.05.22_B1	<LOD	<LOD	<LOD	<LOD
06.05.22_B2	<LOD	<LOD	<LOD	<LOD

AC and BC effluents measured 19.05.2022

	Acetaminophene	**Carbamazapine**	**Diclofenac**	**Octocrylene**
	ng/mL	**ng/mL**	**ng/mL**	**ng/mL**
LOD	0.25	0.1	0.1	5
LOQ	1	1	0.5	20
SAMPLES				
10.05.22_A1	<LOD	<LOD	<LOD	<LOD
10.05.22_A2	<LOD	<LOD	<LOD	<LOD

10.05.22_A3	<LOD	<LOD	<LOD	<LOD
10.05.22_B1	<LOD	<LOD	<LOD	<LOD
10.05.22_B2	<LOD	<LOD	<LOD	<LOD
10.05.22_B3	<LOD	<LOD	<LOD	<LOD
16.05.22_A1	<LOD	<LOD	<LOQ	<LOD
16.05.22_A2	<LOD	<LOD	<LOD	<LOD
16.05.22_A3	<LOD	<LOD	<LOD	<LOD
16.05.22_B1	<LOD	<LOD	<LOD	<LOD
16.05.22_B2	<LOD	<LOD	<LOD	<LOD
16.05.22_B3	<LOD	<LOD	<LOD	<LOD
06.05.22_B3	<LOD	<LOD	<LOQ	<LOQ

A6 - Heavy metals

	Cr	**Ni**	**Cu**	**Zn**	**As**	**Cd**	Pb (sum of 206, 206 and 208)
	µg/L	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**
Cal curve							
Cal Blank	0	0	0	0	0	0	0
Std1	7.13	7.48	7.32	7.09	6.99	7.02	7.20
Std2	69.99	69.95	69.97	69.99	70.00	70.00	69.98
Controle							
Kontroll x 1.02 (ISTD dilution correction)	18.42	59.81	21.69	72.70	60.25	6.00	19.14
True value	18.5	59.8	21.66	74.4	57.42	5.89	18.448
% deviation	0.45	0.01	0.12	2.34	4.69	1.89	3.60
LOD (x3)	0.087	0.041	0.0083	0.16	0.043	0.011	0.0077
LOQ (x10)	0.29	0.14	0.028	0.55	0.14	0.038	0.026
Samples							

28.04 A1	4.8	0.34	4.5	9.5	1.8	0.04	1.1
28.04 A2	4.8	0.58	4.8	44	1.8	<LOQ	0.83
28.04 B1	4.7	0.26	4.5	44	1.3	<LOQ	0.69
28.04 B2	4	0.34	4.5	11	1.4	0.043	0.74
28.04 C1	4.5	2.7	11	34	1.7	<LOQ	1.2
06.05 A1	4.1	0.44	15	33	1.7	0.18	1.8
06.05 A2	3.7	0.57	15	39	1.6	0.19	1.8
06.05 B1	4	0.66	9.9	31	1.8	0.13	1.8
06.05 B2	3.9	0.34	9.2	31	1.7	0.15	1.9
06.05 C1	3.8	3.7	10	39	1.7	0.18	1.2
06.05 Tank	4.3	5.6	17	75	2.1	0.25	1.6
27.04 gw before spike	0.9	2.9	7.1	36	0.77	<LOQ	0.68
16.05 A3	3.6	0.28	6.8	3.8	1.7	<LOQ	1.4
16.05 B3	4.7	9.8	5.2	4.6	1.7	<LOQ	1.4
16.05 C2	5	11	12	31	2.4	<LOQ	1.5
10.05 A1	4.7	3.3	9	14	1.7	0.15	1.6
10.05 A2	3.5	0.47	8.3	20	1.5	0.17	1.3
10.05 B1	3.6	0.35	6.6	15	1.7	0.25	1.3
10.05 B2	3.8	0.44	6.1	15	1.6	0.15	1.4
10.05 C1	5.8	8.8	11	60	2.5	0.22	2.1
10.05 Tank	5	7.6	14	85	2.6	0.2	2.4

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