Aalto-yliopisto
Insinööritieteiden
korkeakoulu

Pietu Pankkonen

Urban stormwater microplastics – Characteristics and removal using a developed filtration system

Master's thesis for the degree of Master of Science in Technology submitted for inspection

Espoo 27th March 2020
Supervisor: Professor Harri Koivusalo
Advisors: D.Sc. (Tech) Julia Talvitie and
D.Sc. (Tech) Nora Sillanpää

Aalto University
School of Engineering

Aalto University, P.O. BOX 11000, 00076
AALTO
www.aalto.fi

Abstract of master's thesis

Author	Pietu Ville Ilmari Pankkonen
Title of thesis	Urban stormwater microplastics – Characteristics and removal using a developed filtration system
Master programme	Water and Environmental Engineering **Code** ENG29
Thesis supervisor	Prof. Harri Koivusalo
Thesis advisor(s)	D.Sc. (Tech) Julia Talvitie and D.Sc. (Tech) Nora Sillanpää
Date	27.3.2020 **Number of pages** 46+6 **Language** English

Abstract

Microplastics (MP) in urban stormwater runoff and the management methods for their efficient removal are subjects receiving increasing attention. In addition, the means to decrease the microplastic load in stormwater lacks information. This study presents results for this issue from a Finnish case study thus providing a basis to resolve an emerging environmental problem.

A concrete-based filtration system with two comparative fine filtration media (sand and biochar) was built to filtrate stormwater before entering a seawater bay in a separate stormwater sewer network in Helsinki, Finland. The research examines the microplastic quality and quantity of three rain-induced stormwater runoff before and after the filtration process. Due to lack of sampling methods for stormwater runoff, a passive sampling device was designed and tested *ex-situ* and *in-situ*. Collected samples were processed based on universal enzymatic purification protocol and analyzed with an FPA-based FT-IR spectroscopy and data analysis. From the data, microplastic particle types, quantity and mass estimations were produced with data analysis using spectra correlation.

The results indicate that the stormwater runoff contained 29 MP particles (90 µm – 5 mm) per litre of stormwater runoff although the concentration varied greatly between the three rain events. Both sand and biochar as fine filtration media removed significantly microplastics from influent stormwater. The results indicated that sand filtration was able to remove up to 96 % of microplastics from stormwater runoff and biochar 93 %. Polyethylene (PE) and polypropylene (PP) accounted for 99 % of all microplastic types in all samples from the three rain events. The average polymer mass was 14.8 µg/l for influent stormwater, 0.2 µg/l after sand filtration and 1.9 µg/l after biochar filtration.

To more accurately assess urban stormwater runoff microplastic quality and quantity, regular monitoring from rain events through the filtration system is suggested. However, the received data and results from this study are important information for follow-up studies.

Keywords filtration, microplastic, runoff, stormwater, urban

Aalto University
School of Engineering

Aalto University, P.O. BOX 11000, 00076
AALTO
www.aalto.fi

Abstract of master's thesis

Tekijä Pietu Ville Ilmari Pankkonen		
Työn nimi Kaupunkiympäristön hulevesien mikromuovien laatu ja määrä sekä käsittely suodatinarkkulaitteiston avulla		
Maisteriohjelma Water and Environmental Engineering		**Koodi** ENG29
Työn valvoja Prof. Harri Koivusalo		
Työn ohjaaja(t) TkT Julia Talvitie ja TkT Nora Sillanpää		
Päivämäärä 27.3.2020	**Sivumäärä** 46+6	**Kieli** englanti

Tiivistelmä

Kaupunkiympäristön hulevesien mikromuovien laatu ja määrä, näytteenotto- ja tutkimusmenetelmät sekä hallintamenetelmät niiden poistamiseksi hulevesistä ovat kasvavan huomion kohteena. Tästä tutkimuksesta saadut tulokset hulevesien mikromuovipitoisuuksista ja -laadusta sekä niiden käsittelystä tarjoaa perustan kasvavan ympäristöongelman ratkaisemiseksi.

Betonisista valmisosista koottu suodatinarkkulaitteisto rakennettiin hulevesien hallitsemiseksi ja suodattamiseksi ennen niiden päätymistä vastaanottavaan vesistöön erillisviemäröidyssä viemärijärjestelmässä. Tutkimuksessa tarkasteltiin kolmen sadetapahtuman mikromuovien laatua ja määrää hulevedessä ennen suodatusprosessia ja sen jälkeen kahden eri suodatinmateriaalin läpi (hiekka ja biohiili). Hulevesien mikromuovien näytteenottomenetelmien puuttumisen vuoksi passiivisuodatukseen perustuva näytteenottolaite suunniteltiin ja testattiin. Valuntatapahtumista kerätyt näytteet prosessoitiin entsymaattisella puhdistusmenetelmällä ja analysoitiin FPA-pohjaisella FT-IR-spektroskopialla. Tuotetulle spektriaineistolle tehtiin korrelaatio referenssikirjaston muovityyppeihin, mistä saatiin tietoa näytteiden mikromuovien lukumäärästä, muovityypeistä sekä massoista.

Tulevassa hulevedessä oli keskimäärin 29 mikromuovipartikkelia (90 µm – 5 mm) litraa hulevettä kohti, vaikkakin vaihteluväli sadetapahtumien välillä oli suuri. Hiekka oli hieman biohiiltä parempi suodatinmateriaali mikromuovien poistamiseksi hulevedestä. Tulokset osoittavat, että hiekka poisti 96 % sadetapahtuman aikaisen valunnan mikromuoveista ja biohiili 93 %. Polyeteenin (PE) ja polypropeenin (PP) osuus oli 99 % kaikista mikromuovityypeistä. Mikromuovien keskiarvomassa oli 14.8 µg/l tulevassa hulevedessä, 0.2 µg/l hiekkasuodatuksen jälkeen ja 1.9 µg/l biohiilisuodatuksen jälkeen.

Kaupunkien hulevesien mikromuovien laadun ja määrän tarkemmaksi arvioimiseksi suositellaan säännöllistä seurantaa sadetapahtuman aiheuttaman valunnan kuljettamien mikromuovien poistumisesta suodatinarkkulaitteiston prosessin kautta. Tästä tutkimuksesta saadut tiedot ja tulokset muodostavat tärkeitä lähtötietoja jatkotutkimuksia varten.

Avainsanat hulevesi, kaupunkiympäristö, mikromuovi, pintavalunta, suodatus

Acknowledgements

The study was conducted in collaboration with WSP Finland Oy, the City of Helsinki (Urban Environment Devision) and Smart & Clean Stormwater Quality Management programme.

Many thanks to the City of Helsinki and Smart & Clean Stormwater Quality Management programme for funding the research project and all the equipment needed for this comprehensive study and the project supervisor Sonja-Maria Ignatius for your comments. I would also like to thank Sven Hallinin tutkimussäätiö sr for funding this thesis and Maa- ja vesitekniikan tuki ry for funding the analyses. Additionally, thanks to MIF project (Microplastics in Finnish waters-Assessing their potential threat, funded by Academy of Finland: 296169).

Many thanks to my thesis supervisors DSc Julia Talvitie and DSc Nora Sillanpää for your helpful comments and insights with this study. Special thanks to Julia for contributing to the idea of the sampling device and organizing me the premises to work in! Equally thanks to professor Harri Koivusalo for your essential commentary for the thesis.

Thank you Aalto University Department of Built Environment pilot laboratory, Aino Peltola and Marina Sushko for offering the premises and the chance to pilot my sampling device. I would also like to thank lab technician Antti Louhio for providing help and valuable knowledge with assembling the device. Also, thanks to Luode Consulting for providing the water level data.

I own my gratitude to researcher Erika Sainio from Finnish Environment Institute for helping me with the sample processing and researcher Emilia Uurasjärvi from Sib Labs (University of Eastern Finland) for training me to use the FT-IR. You are experts! Also, thanks to the research groups and personnel from both institutes.

From WSP Finland Oy, I want to thank business unit manager Olli Sorvari for your useful comments with this study. And project manager Olli Hakala, there is not enough gratitude for your help with this research, installing the sampling device and collecting the samples. Who else would enter a narrow, dark and wet sampling base with me and feel positive afterwards?

I would like to thank my family for their support during this study. My greatest gratitude goes towards my fiancée Reetta who kept me sane all these months, even when I came home after the samplings covered in who knows what. This was the last Master's thesis I wrote!

In Sipoo 27th of March 2020

Pietu Pankkonen

Table of Contents

Abbreviations and symbols

A / a		area
ABS		acrylonitrile butadiene styrene
ATR		attenuated total reflectance
BC		biochar
C	[particles/l]	concentration
EMC	[particles/l]	event mean concentration
FPA		focal plane array
FS		(filtration) sand
FT-IR		Fourier-transform infrared spectroscopy
h_f	[m]	friction loss
H_2O_2		hydrogen peroxide
MP		microplastic
MP/L		microplastic particles in litre
NaOAc		sodium acetate
PA		polyamide
PE-HD		high-density polyethylene
PE-LD		low-density polyethylene
PET		polyethylene terephthalate
PMMA		poly(methyl-methacrylate)
PP		polypropylene
PS		polystyrene
PU / PUR		polyurethane
PVC		polyvinyl chloride
PVOH		polyvinyl alcohol
pyrolysis-CG/MS		pyrolysis–gas chromatography–mass spectrometry
R_{Eff}	[%]	event mean concentration efficiency
Raw		influent stormwater
SDS		sodium dodecyl sulfate
TSS		total suspended solids
V	[l]	discharge volume
WWTP		wastewater treatment plant
$ZnCl_2$		zinc chloride

1 Introduction

1.1 Microplastics

Plastics are a wide group of organic and synthetic or semi-synthetic polymers that are used extensively from infrastructure and transportation to textiles and packaging (PlasticsEurope 2019). In 2018, plastic production was 359 million tonnes annually on a global scale (PlasticsEurope 2019). It is estimated that the production of plastic may increase up to 2 000 million tonnes annually by 2050 (UNEP 2016). Based on their distribution and production rate, the most dominant polymer types in 2018 on global scale were PP, PE-LD, PE-HD and PVC, PUR, PET and PS respectively (PlasticEurope 2019). Approximately 40 % of plastic produced is used for packaging (UNEP 2016).

The term *microplastics* (MP) was first introduced in 2004 describing microscopically visible plastic particles (Thompson et al. 2004). However, a comprehensive definition for microplastics is still under debate due to broad variety of polymers and their physicochemical properties (Hartmann et al 2019). An accurate definition for the term microplastic is important for concordant methods to research and monitor microplastics through all fields of study.

Frias & Nash (2019) defined microplastics as *"...any synthetic solid particle or polymeric matrix, with regular or irregular shape and with size ranging from 1 μm to 5 mm, of either primary or secondary manufacturing origin, which are insoluble in water*". Additionally, in their categorization framework Hartmann et al. (2019) proposed criteria, which excludes slightly modified natural polymers and includes semi-synthetic polymers and natural rubber and defines size range from 1 μm to 1 mm. Plastic particles from 1 nm to 1 μm have colloidal behavior preventing sedimentation and are defined as *nanoplastics* (Gigault et al. 2018).

Microplastics come in various shapes based on their use and end-of-cycle. Primary microplastics (intentionally added to products) are mostly smooth beads, pellets or fibers used in for example cosmetics, where secondary microplastics are non-symmetric and formed from larger plastic particles through physical, chemical and biological degradation and fragmentation (Bergmann et al. 2015, UNEP 2016, PlasticEurope 2019).

1.1.1 Fate and impacts of microplastics in aquatic environment

Microplastics as a contaminant is a novel research area but also an emerging environmental problem and the adverse effects on the environment, the human health and food safety are not yet well recognized (UNEP 2016). However, the studies indicate its possibility to bioaccumulate in food chains (e.g. Gouin et al. 2011, Browne et al. 2013, Setälä et al. 2014). Due to constantly increasing use of plastic in various applications (Rochman et al. 2013, PlasticsEurope 2019), the need for microplastic removal from the environment requires immediate actions and efficient solutions. In Finland, the need for environmental monitoring and reference measurements of microplastics was introduced by government´s analysis of assessment and research activities (Myllylä et al. 2018).

Ever since the research on marine litter begun, microplastics have been found in ecosystems all around the globe from the poles (Browne et al. 2011, Peeken et al. 2018) to groundwater systems (Panno et al. 2019). Based on a particle-tracking model with known estimates of particle data, 5.25 trillion pieces of plastic (micro- and macroplastic combined) are floating in coastal areas and open sea (UNEP 2016). As more closely described in Section 1.1.2,

microplastics end up in aquatic environments through several pathways of which many are still unknown.

The studied adverse effects towards aquatic biota include chemical absorption and adsorption of pollutants (Browne et al. 2013), ingestion of microplastic particles (Setälä et al. 2014), trophic transfer in food web (Browne et al. 2013, Wright et al. 2013, Setälä et al. 2014) and physical effects and injuries on organisms (Wright et al. 2013, Jovanovic 2017). While studies are performed on bioavailability in single species, ecosystem level effects remain unknown.

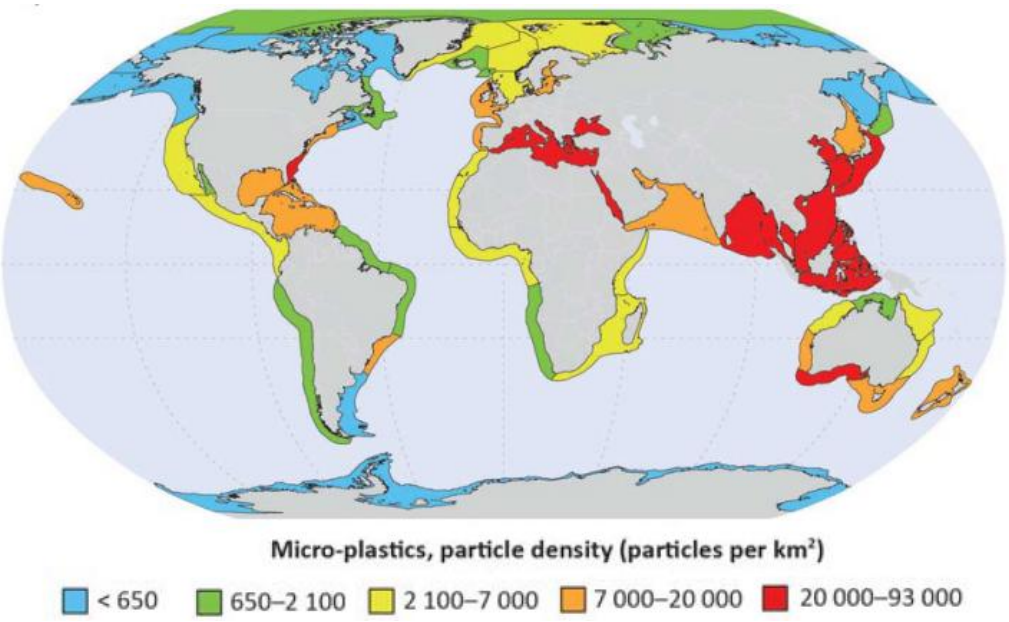


Figure 1. Relative distribution of microplastics around the globe (UNEP, 2016; modified from Lebreton et al. 2012).

1.1.2 Sources and pathways in urban environment

Finnish Environment Institute (2014) classifies urban areas in Finland as densely built and continuously developed areas with more than 15 000 residents and its adjacent surroundings. Urbanization has been recognized as a contributing factor for microplastic abundance (Horton et al. 2017). Similar results were obtained by Mani et al. (2015) concluding that microplastics are found in higher concentrations near urbanized areas where anthropogenic influence is high. Based on Dikareva & Simon (2019), the amount of microplastic particles are greater in the proximity of a known point or diffuse source. Additionally, urban stormwater runoff from diffuse sources is the main contributor to polluting urban water systems (Gong et al. 2016). Water Services Act of Finnish legislation (119/2001) describes stormwater as rain water and melt water that enters soil surface, rooftops or other surfaces in a built environment and is conveyed in a stormwater system.

In relation to diffuse sources, spatial and temporal changes are a major factor concerning the amount of microplastic particles (Horton et al. 2017, Vogelsang et al. 2018). Where spatial differences in microplastic concentrations are indicated by the activities and rate of impervious surfaces in the catchment area (Kole et al. 2017, Liu et al. 2019), the temporal differences are shown by seasonal changes or time of day (Johansson et al. 2007), such as the amount of traffic (Kole et al. 2017, Vogelsang et al. 2018).

Kim et al. (2004) studied litter pollutant loading during a rain event and noted that stormwater runoff may transport plastic debris such as microplastic of secondary origin. Liu et al. (2019) investigated microplastics from stormwater retention basins in urban and highway adjacent areas. They found that microplastics emissions from commercial and industrial areas are higher than those in residential areas or adjacent to the motorway.

Microplastics are studied to transport into aquatic and terrestrial systems via e.g. air and wind (Kole et al. 2017, Vogelsang et al. 2018), stormwater runoff (Liu et al. 2019), WWTP effluent (Carr et al. 2016, Murphy et al. 2016, Talvitie 2018b), and litter and waste (Bergmann et al. 2015, Horton et al. 2017). A more detailed structure of different pathways and end-of-chain of microplastics is described in Figure 2.

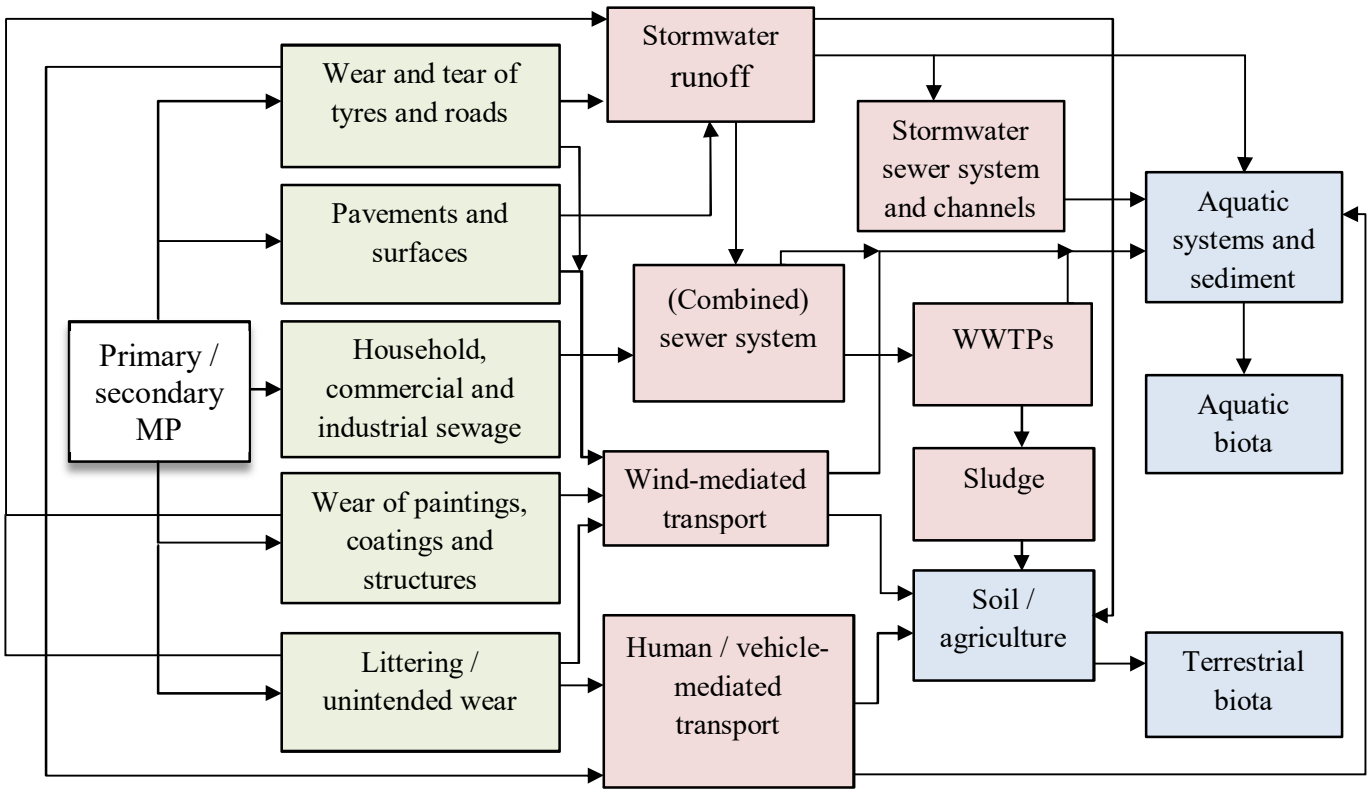


Figure 2. Possible microplastic sources and pathways (green = source, red = pathway, blue = end-of-chain) based on several studies (Dris et al. 2015, Talvitie et al. 2015, Magnusson et al. 2016, Napper et al. 2016, Kole et al. 2017, Vogelsang et al. 2018, Fahrenheld et al. 2019, Liu et al. 2019).

The knowledge about microplastic quality, quantity and transportation by urban stormwater runoff is scarce. Based on a few available peer-reviewed scientific publications, sources of microplastics can be identified in urban catchments: Sources that can be identified in a busy and highly trafficked urban areas include car tyres, road surfaces and road markings (Vogelsang et al. 2018). Tires and road markings have been evaluated in several computational estimates as the largest source of microplastics emissions in urban areas (Kole et al. 2017, Hann et al. 2018, Setälä et al. 2017). Traffic-related and other common polymer types and their sources in urban environment are described in Table 1.

Table 1. Plastic polymer types in urban environment and their sources (UNEP 2016, Vogelsang et al. 2018, Liu et al. 2019, PlasticsEurope 2019). The most abundant polymer types in urban stormwater ponds studied by Liu et al. (2019) are highlighted.

Polymer type	Abbrev.	Potential sources in urban environment
polystrene	**PS**	protective cases, insulation material
polypropylene	**PP**	containers, pipes, casings
polyester	**PES**	workwear, textiles
high-density polyethylene	**PE-HD**	pipes, baskets, crates, bottles
low-density polyethylene	**PE-LD**	bags, membranes
polyvinyl chloride	**PVC**	building materials, hoses, tubes, pipes
polyethylene terephthalate	PET	bottles, fleece material
alkyd	-	paints
polyvinyl acetate	PVA	paints, glues and adhesives
acrylic	PMMA	hard plastic windows and covers
epoxy	EP	paints, glues and coatings
natural rubber	NR	vehicle tyres
styrene butadiene rubber	SBR	vehicle tyres
polybutadiene rubber	PBR	vehicle tyres
styrene butadiene styrene	SBS	road pavements
styrene isoprene styrene	SIS	road markings
ethylene vinyl acetate	EVA	road markings
polyamide	PA	road markings

1.2 Current microplastic research methods

Considering the number of different sources and types of microplastics in the environment, use of consistent methodologies is a crucial part for comparative studies that can be replicated. Prata et al. (2019) did a systematic review of 20 studies. They concluded that there are many ways to sample, process and analyze microplastic yet lack of universal, validated protocols for every environmental matrix. Similar findings were gained by Horton et al. (2019) and Mintenig et al. (2017) stating that there is no consensus among researchers or universal protocols on how the samples are collected, processed or analyzed. In Figure 3 the most common research methods are listed where collection equals sampling, density separation and digestion equals processing, and identification equals analyzing.

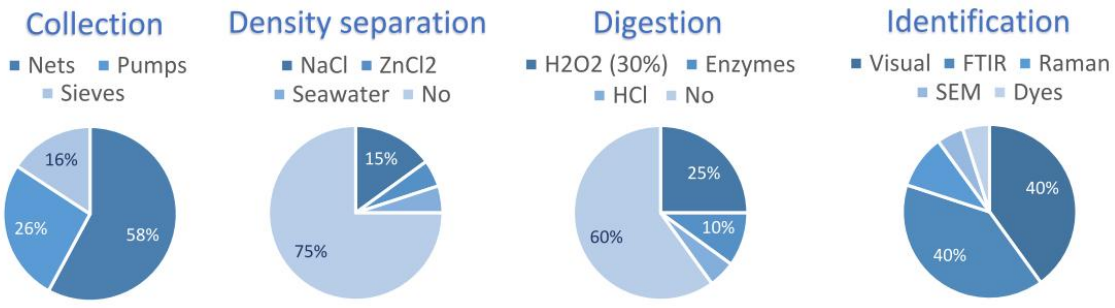


Figure 3. A summary of methods for collecting, processing and analyzing microplastics based on Prata et al. (2019).

1.2.1 Sampling

Samples are collected from, for instance, soil, sediment, sludge and water, each having different sampling methods (Prata et al. 2019). In this study, the water samples are of interest which is why reviewing the sampling methods of other environmental matrices is excluded.

All sampling methods have their own benefits and disadvantages on the usage, contamination, cost-efficiency and manual labor required for the sampling. Water samples are collected using Neuston, Manta and plankton nets, or sieving and filtrating with or without pump. In open water sampling, choosing representative location and sampling depth, as well as adequate number of samples are important factors for comprehensive research. (Prata et al. 2019).

In accordance with open water sampling in urban environment, Liu et al. (2019) collected stormwater runoff microplastic samples from stormwater retention ponds with a combination of pumping and sieving. To the author's knowledge, this has been the only peer-reviewed article of urban area stormwater runoff microplastics until date. However, in their study Liu et al. (2019) took samples from ponds where water is effortless to pump. A method to collect stormwater runoff microplastic samples from surface flow is hence needed. The need for studying separate stormwater runoff during an actual rain event is previously highlighted by Liu et al. (2019).

1.2.2 Processing

The collected sample(s) should undergo a process where excessive organic and inorganic solids are removed before analysis without damaging plastic particles. The process is crucial part of the study because solids may interfere the ability to analyze the samples properly (Löder et al. 2017). A typical method for sample process involves 1) density separation with e.g. natrium chloride or zinc and 2) digestion with enzymes, hydrochloric acid, hydrogen peroxide or a combination (Löder et al. 2017, Prata et al. 2019). During the process, the used chemicals are susceptible to degrade microplastic particles in the sample (Qiu et al. 2016, Prata et al. 2019) which is why it is important to find a standardized method for various type of sample matrices.

Löder et al. (2017) proposed a universal enzymatic protocol that is suitable for different environmental samples which will be used in this study to process the stormwater samples. In relation to stormwater processing, Liu et al. (2019) processed urban stormwater samples using a combination of (wet-)oxidation, density separation and digestion, and the remarks from that study are considered in this study as well.

1.2.3 Analyzing

After the processing (Section 1.2.2), the particles in the residue material are analyzed and identified. As described in Figure 3, the particles are identified either inspecting visually with microscope or naked eye, staining with dyes and/or through spectroscopic methods with Raman or FT-IR. Analyzing with FT-IR or Raman requires an identification programme to calculate correlations between analyzed data and known spectra of different polymer types (Primpke et al. 2017). However, many plastic polymers have copolymer composition making them difficult to identify even with spectroscopic methods (Fahrenheld et al. 2019). Furthermore, spectroscopic methods rely on scattering and absorption of light with different wave lengths (Simon et al. 2018) and since black material absorbs radiation but scatters it only a little, gaining spectra data from black tyre wear and tear is problematic with spectroscopic methods (Liu et al. 2019). Currently, tyre wear and tear microplastics have

been estimated by calculations (Kole et al. 2017, Setälä et al. 2017) and analytically quantified from sediment samples with pyrolysis-CG/MS (Unice et al. 2013).

Song et al. (2015) compared microscopic and spectroscopic methods to identify MP particles. They concluded that spectroscopic method is recommended since visual inspection with a microscope is difficult due to small particle size and prone to human error (Song et al. 2015). In another review by Qiu et al. (2016), FT-IR with a focal plane array (FPA) detector is suggested for identifying microplastics in water samples.

1.3 From combined sewer system to separate sewer system

In stormwater management, the city of Helsinki follows its own stormwater strategy program that is in compliance with the Land Use and Building Act (223/2001) and Water Services Act (119/2001; City of Helsinki 2018). The program follows a five-level list of stormwater management (in priority order): 1) To treat and manage stormwater runoff where it is formed, 2) convey stormwater runoff using retention and detention structures, 3) convey stormwater runoff in stormwater sewer system to retention and detention structures before entering receiving water body, 4) convey stormwater runoff straight in stormwater sewer system to receiving water body or, as last priority, 5) convey stormwater runoff to WWTP in combined sewer system (City of Helsinki 2018). It is also important to note that both the quality and quantity of stormwater are to be managed although there are no qualitative threshold values for stormwater pollutants.

The total sewer network length governed by Helsinki Region Environmental Services Authority (HSY) is 4900 km of which 2200 km is separated stormwater sewer system and 2700 km wastewater sewer and combined wastewater sewer (HSY 2015). The current trend in Helsinki urban areas is to separate stormwater from combined sewer system to discharge stormwater runoff to a water body instead of WWTPs (HSY 2015). This is part of the quantitative management of stormwater runoff. In urban areas where rate of impervious surfaces is high, surface flow during a rain event is high and the level of soil infiltration is low. Stormwater networks conveys this surface flow away from urban areas thus decreasing the intensity of flooding (City of Helsinki 2018). Separating sewer systems decreases the discharge to the WWTPs thus reducing the level of wastewater treatment during storms and preventing wastewater sewer overflow to the environment. The most advanced technologies in WWTPs remove up to 99.9% of the microplastic particles from the wastewater (Löder et al. 2017, Talvitie et al. 2017a). However, when stormwater is separated from the wastewater sewer system, the urban stormwater runoff is channeled through the stormwater network into the nearest water body usually without any treatment. This is increases the total TSS load (Brombach et al. 2005). Setälä et al. (2017) calculated that the total traffic related wear and tear of microplastic particles from Mechelininkatu is 4-7 tonnes annually. These microplastics among from microplastics from other sources may have a pathway to the sea through stormwater runoff via the separated stormwater network.

As a result of climate change, rainfall is predicted to increase resulting in even higher stormwater runoff from paved surfaces and rooftops directly into the waterways through stormwater sewers (City of Helsinki 2018). Intense rainfall does not necessarily indicate higher microplastic concentration in runoff but dry season before rain event and rain intensity both correlate with greater flush of pollutants (Kim et al. 2004, Lee et al. 2011) and pollutant load to the receiving water body (Gong et al. 2016). On the other hand, Tuomela (2017) studied that small and intermediate rain events contribute the most to the pollution

load within stormwater runoff. Nevertheless, this emphasizes the need for qualitative stormwater management of microplastics in stormwater sewer systems as they serve as a pathway to aquatic systems.

1.4 Current methods for stormwater filtration

The Land Use and Building Act in Finnish legislation (132/1999) states the need for stormwater management (see Section 1.2) although its basis is on the quantitative rather than qualitative management. Furthermore, management of microplastics is not currently included in Finnish legislation. However, the Act on the Organisation of River Basin Management and the Marine (1299/2004) requires developing and implementing a marine strategy. In the latest marine strategy of 2016-2021 in Finland (Ministry of the Environment 2016), reducing the amount of microlitter was recognized as a pressure point for actions. Stormwater filtration as a concept includes both qualitative and quantitative management of stormwater runoff. Qualitative management of stormwater includes, for instance, removal of stormwater pollutants and particulate matter from runoff. The quantitative management includes flood and groundwater control by e.g. retention, settling and infiltration structures. Primary operational process varies within the treatments but in this section the focus is on the filtration and sedimentation structures thus excluding other treatment methods.

Stormwater filtration structures are typically either surface filters or underground systems (Erickson et al. 2013). In densely built urban areas, underground filtration systems are often used as land surface area is a limiting factor (Erickson et al. 2013, Vogelsang et al. 2018). Filtration practices include retention of suspended solids by a physical barrier. During the filtration process, sediment is trapped to a filtration media, for instance biochar or sand. Mechanical sieving with a net is another basic filtration method and equivalent to screening used in the primary treatment in WWTPs (HSY 2017).

Grain size, filter mesh size and pore size within the filtration media are important factors considering the water flow rate through the system. (Erickson et al. 2013.) Smaller mesh or pore size captures more suspended solids but are prone to clogging and vice versa, larger mesh size need less maintenance but allow higher rate of suspended solids to pass through (Erickson et al. 2013). The disadvantage with the filtration process is the possible clogging affecting the treatment effectiveness and need of maintenance (Shammaa & Zhu 2001, Kandra et al. 2015). Sediment concentration in stormwater is studied to affect the filtration media the most by decreasing the hydraulic conductivity and treatment efficiency especially in coarse filters (Kandra et al. 2015). A settling chamber for sedimentation of suspended solids can precede filtration basin to prevent the clogging of the actual filtration system (Shammaa & Zhu 2001).

Vogelsang et al. (2018) listed several compact treatment methods in removal of total suspended solids (TSS) concluding that filtration is a possibility for removal of microplastics as well. However, while the concentration of TSS may correlate with the amount of microplastic particles since microplastics are solids, there are no actual measurements to support this claim.

1.4.1 Biochar

Biochar is a carbon-based material, that is produced in high temperature conditions from organic (animal and plant based) and non-organic materials in oxygen-limited pyrolysis (Korkealaakso et al. 2016). Biochar has similar characteristics to other studied filtration media (e.g. activated carbon, charcoal) such as carbon content and large, specific surface area which is why it has been studied for stormwater filtration (Reddy et al. 2014, Tan et al. 2015). Biochar is less carbonized than activated carbon having more oxygen and hydrogen in its chemical structure (Korkealaakso et al. 2016). The temperature of which the pyrolysis takes place affects the properties of biochar in removal of contaminants: In high temperature pyrolysis organic contaminants are absorbed to biochar and in low temperatures non-organic contaminants by electrostatic attraction (Korkealaakso et al. 2016).

Reddy et al. (2014) studied the removal efficiency of contaminants using biochar filtration. Urban stormwater runoff was flown through a column with pea gravel and biochar. The desorption results indicate removal efficiency of TSS by 86 %. Tan et al. (2015) evaluated the biochar an excellent media in removal of organic and inorganic contaminants from water through absorption mechanism. However, the stability of toxics related to the absorbed contaminants and those formed in production phase are not known (Tan et al. 2015).

1.4.2 Sand

Sand is a commonly used filtration media and can be utilized both on soil surface or in underground structures. Typically, sand filters are designed to remove TSS from stormwater runoff (Kandasamy 2008, Zarazadeh et al. 2018). In sand filtration, water flows through a bed of sand where the contaminants are accumulated to the pores of the filter structure (Erickson et al. 2013). Sand filters can remove more than 90 % of TSS from stormwater (Shammaa & Zhu 2001, Zarezadeh et al. 2018, Vogelsang 2019). Zarezadeh et al. (2018) evaluated the performance of sand filter basin on various water quality parameters from 10 rain events. The sand filter removed 93.5 % of TSS but performed poorly in removal of dissolved solids (Zarazadeh et al. 2018). Although microplastics are insoluble in water, water-soluble copolymers exist (Horton et al. 2017, Molyneux 2017) and they may leach toxic plasticiser chemicals to aquatic systems (Horton et al. 2017).

Zhang et al. (2014) studied micropollutant (excl. microplastics) removal using a combination of soil surface sand and a biofiltration using plants. The conclusion was that a well-designed sand filtration system can decrease micropollutant concentrations significantly. However, the removal efficiencies between biological and mechanical processes were not distinguished. The research method is presented in Figure 2.

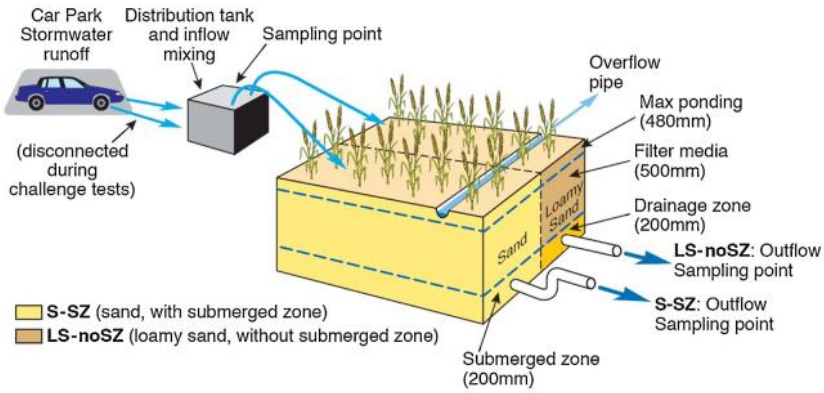


Figure 4. Stormwater runoff filtration through sand / loamy sand and sampling points in Zhang et al. (2014).

1.5 Research gap and objectives

Microplastics in urban catchments and stormwater runoff is a subject with limited knowledge. Increasing rainfall and rate of impervious surfaces lead to greater stormwater runoff and result in increased transport of contaminants. The stormwater runoff in stormwater network is a likely pathway for microplastics from land to the receiving waterbody where the ecological effects are not understood well.

The previous studies have focused mainly on open water (sea, lake, pond), sediment and wastewater microplastic quality, quantity and bioavailability. Only one peer-reviewed study (Liu et al. 2019) has been published until date regarding microplastics in urban stormwater. Additionally, the transport of microplastics from urban surfaces during rain events and the methods to filtrate microplastics from urban stormwater runoff *in-situ* have not yet been studied to the author's knowledge. In this study, a treatment method of interest was an integrated, underground and concrete-based filtration system where biochar and sand as fine filtration media were used. Studies on wastewater pre-treatment methods have showed promising results for removal of microplastic, yet studies about the treatment efficiency of microplastics in stormwater management systems have not been published. Additionally, studying microplastic polymers in stormwater runoff improves understanding of the sources and pathways of microplastics in urban environment.

While there is still lack of standard procedures to sample, process and analyze microplastics for different environmental matrices, urban stormwater runoff is a subject area with the least knowledge of methodologies. In this study, state-of-the-art methods were used to study microplastics in urban stormwater matrix. This includes designing and constructing a standardized sampling device, processing with a universal processing protocol and performing material analysis with the most novel analytical methods until date.

The main objectives of this research were:

1) to design and construct a microplastic sampling device for stormwater runoff

2) to assess microplastic quality and quantity in urban stormwater runoff and

3) to examine microplastic removal efficiencies of two comparative filtration media (biochar and sand) used in the filtration system.

2 Materials and methods

The study began by making a research plan based on previous studies, sampling methods, and limitations by the site. First a sampling device was designed and tested based on an idea of passive sampling (Talvitie 2018a). The system was tested both *ex-situ* and *in-situ* for sampling microplastics in rain-induced stormwater runoff. The sampling from a total of three rain events was carried out after separated stormwater sewer system was connected to the filtration system (Section 2.1). The samples were further processed for removal of excessive solids other than microplastics and then analyzed using spectroscopic methods. The gained spectra data went through spectra correlation for qualifying and quantifying MP particles. A detailed description of all the study phases is described in Figure 3.

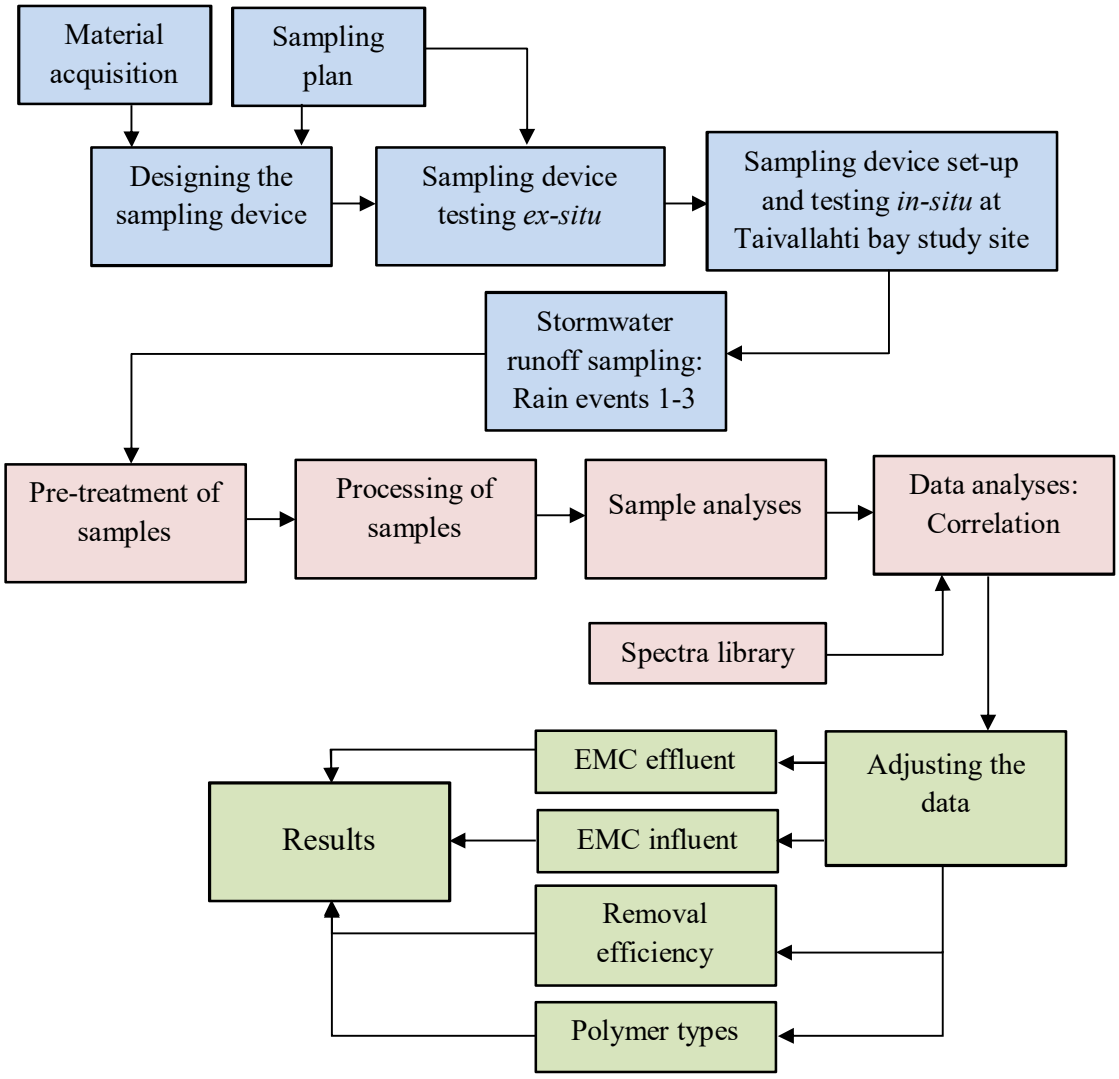


Figure 5. Flowchart representing the phases of the study (blue = testing and sampling phase, red = processes and analyses, green = data processing and results)

2.1 Description of study area

The study catchment and the filtration system are located in Töölö district in the city of Helsinki (60°10'33" N, 24°54'52" E; Figures 6 and 7). The area has a high traffic-flow with an average of 20 000–35 000 vehicles daily. Most of the traffic is in the main road of Mechelininkatu (City of Helsinki 2018). The boundaries of the catchment area are in Caloniuksenkatu (south), Sibeliuksenkatu (north), Runeberginkatu (east) and Merikannontie (west). The total imperviousness of the catchment area is presented in Table 2.

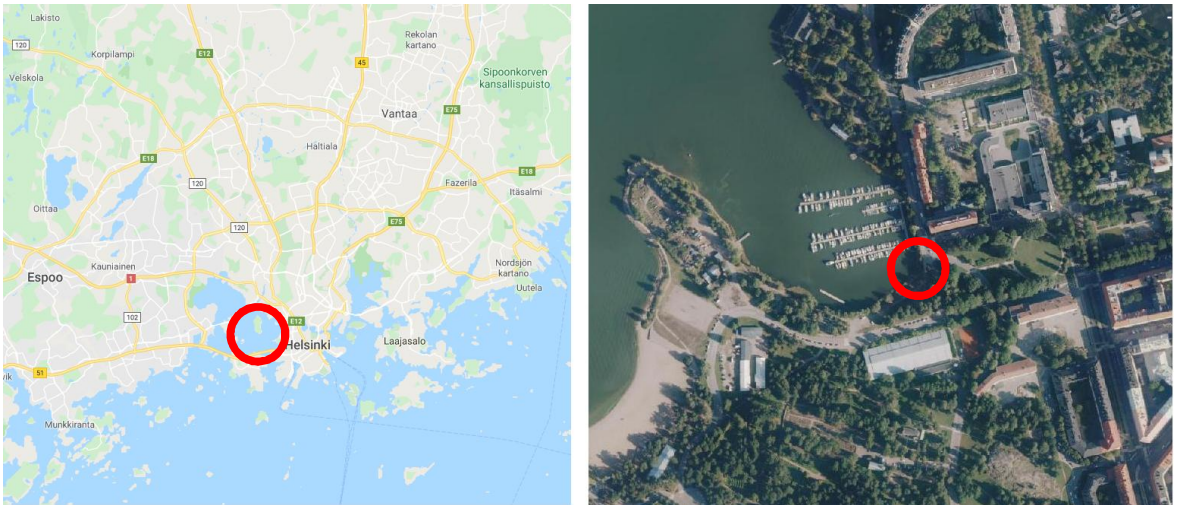


Figure 6. The location of the study site on map in regional scale (left; Google Maps 2020) and exact location within Helsinki city area (right; Helsinki Map Service 2019).

Figure 7. Receiving waterbody of Taivallahti bay and the stormwater runoff effluent discharge point (2.5.2019).

The average annual precipitation rate in the area is 655 mm and the average temperature is 5.9 °C (Finnish Meteorological Institute 2019). Figures of rain intensity (mm/h) during sampling and water level (cm) in inlet and outlet pipes in filtration system are presented in Appendix H.

Table 2. Catchment area surfaces, total coverage area and estimated runoff coefficients for surface types (Hakala 2018; Modified from HSY 2016).

Surface type	Area m^2	%	Runoff coefficient
Bare rock	949	2 %	0.55
Paved road	23495	44 %	0.80
Building	10565	20 %	0.80
Other impermeable surface	2504	5 %	0.70
Impermeable surfaces in total	37513	70 %	
Plants and planting beds	4733	9 %	0.15
Open ground	1611	3 %	0.20
Forest cover	7556	14 %	0.10
Permeable paving	1985	4 %	0.40
Permeable surfaces in total	15885	30 %	
Total / average	53398	100 %	0.60

The catchment had a combined stormwater network that was separated to stormwater and wastewater networks in spring 2019. Stormwater runoff from the area is conveyed by a separate sewer network to the seawater bay of Taivallahti (Figure 8). Previously the stormwater runoff from the catchment area was directed via combined sewer network to Viikinmäki WWTP. The combined sewer system is still in use for managing stormwater and wastewater from other catchments although the objective is to separate all the combined systems in Helsinki city area in the future (HSY 2015). The sizes of the new separated stormwater pipelines are from DN300 to DN800.

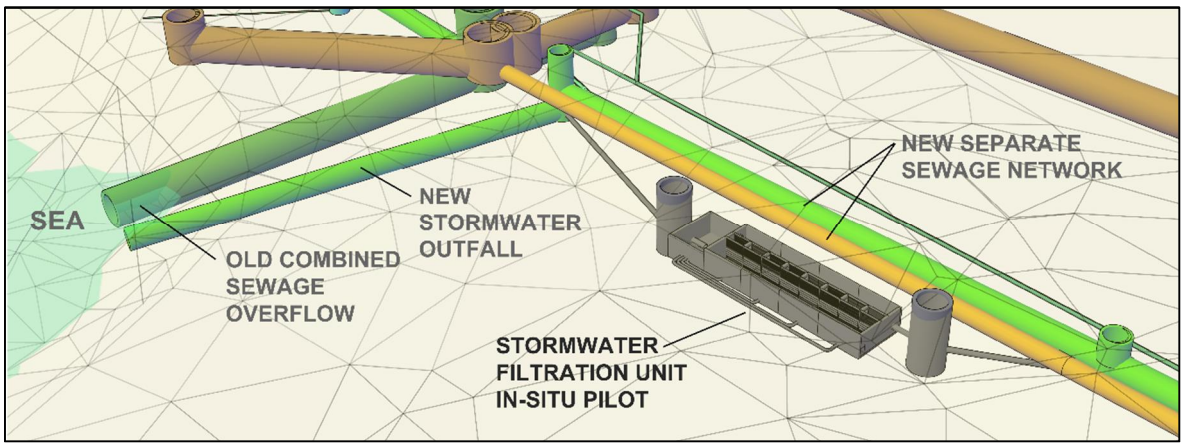


Figure 8. 3D model of the separated wastewater and stormwater sewer systems and the filtration system (stormwater filtration unit in-situ pilot) with a connection to the new stormwater sewer main line and effluent pipe to the sea (Hakala 2018).

For assessing the flow rate during a rain event, a design storm with the occurrence every third year and duration of 60 minutes was selected (Rimpiläinen 2018). With a rainfall intensity of 56 l/s/ha and average runoff coefficient of 0.60, the estimated value for stormwater runoff is 34 l/s/ha and for surface flow 180 l/s equaling to 647 m^3. Approximately 10 % of this surface flow (64 m^3) ends up in the filtration system and 90 % (583 m^3) flows straight to the sea through the stormwater sewer.

2.2 Stormwater filtration system structure

The filtration system is located in Eteläinen Hesperiankatu street, adjacent to seawater bay of Taivallahti (see Figures 6, 7 and 8). The filtration system was designed by Hakala (2018). It was built on site between spring 2018 and winter 2019 and was connected to the separated stormwater system in spring 2019 (Figure 8). The outer diameters of the filtration system are approximately 2.0 x 3.0 x 8.2 m^3 (height x width x length; Figure 9). Taivallahti filtration system also contains additional room for sampling devices in effluent side, thus total size of unit is approximately 2.0 x 3.0 x 10.0 m^3 (Figure 9).

In the filtration system, stormwater flows through three adjacent basins with different treatment practices: 1) sedimentation, 2A) screening, 2B) coarse filtration and 3) fine filtration (Table 4, Figures 9 & 10). The practice is similar to a typical sand filtration system described in Korkealaakso et al. (2016). Two comparative fine filtration media, sand and biochar were used in the filtration system. Both filtration media were water-washed prior to installation. A layer of sand was placed on top of biochar to prevent biochar floating during water flow.

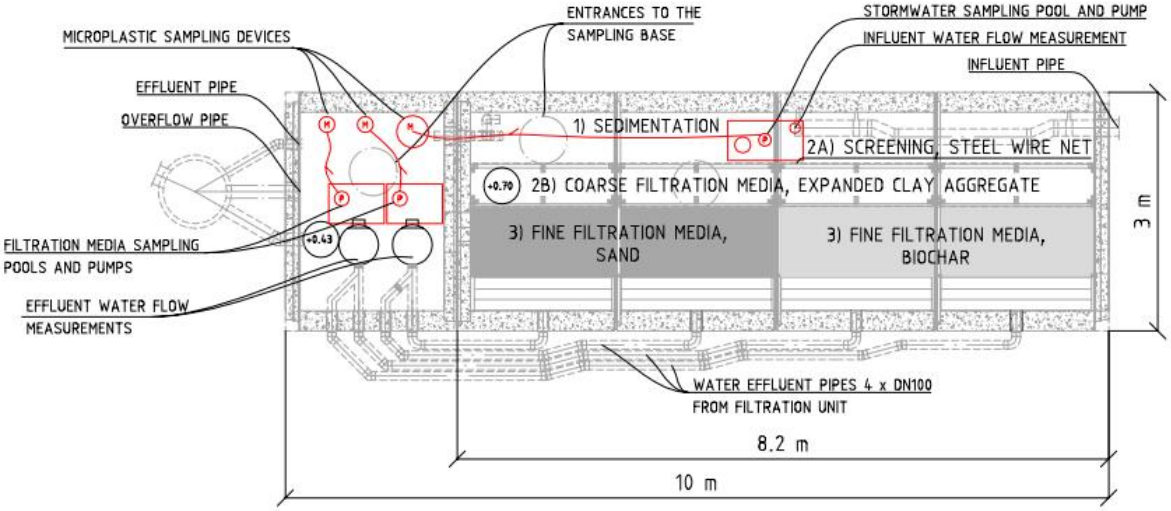


Figure 9. Taivallahti filtration system structure and location of MP sampling devices. The microplastic sampling devices (Figure 11) inside the filtration system are highlighted in red (Hakala 2018).

The filtration system was first piloted with a prototype in a laboratory to test the hydraulical properties of the structure and the filtration media (Hakala 2018). Flow rates during different discharges were also modelled and based on the results, the filtration system was optimized (Hakala 2018). Stormwater runoff flows vertically through the filtration system when the flow rates are between 0-2 m^3/h. However, during greater flow rates, stormwater can flow in up-down direction as well based on the hydraulical modelling of the filtration system. While the changes in flow directions might affect the treatment efficiency (Shammaa & Zhu 2001), the channeling of the water flow to other directions prevents clogging thus increasing lifespan of the used materials (Zarazadeh et al. 2018). Stormwater runoff flow inside the filtration system related to actual rain event is presented in Appendix H.

Table 3. Treatment methods, details of the used filtration media and structure of the Taivallahti filtration system.

Treatment step	**1**	**2A**	**2B**	**3**	**3**
Treatment type	sedimentation	screening	coarse filtration	fine filtration	fine filtration
Material	concrete basin	steel wire net	expanded clay aggregate	sand	biochar
Grain size (mm)	-	-	8-20	0.8-1.2	5-50
Manufacturer	Ruskon Betoni	Kapotek	Leca Finland Oy	Saint-Gobain Finland Oy	Carbons Finland Oy
Hydraulic conductivity (m/s)	-	-	10^{-1}	10^{-3}	$10^{-2.2}$

From each of the studied rain event, a total of three samples were collected: Influent sample from the stormwater runoff and effluent samples from both biochar and sand filtrated stormwater to assess the microplastic concentrations and quality before and after the filtration process. The initial removal of microplastics (100-1000 µm) from sample water was also tested at the piloting phase of the filtration system in the laboratory using expanded clay aggregate and sand as filtration media (Hakala 2018). The removal efficiency of microplastics was 99-100 % (Hakala 2018).

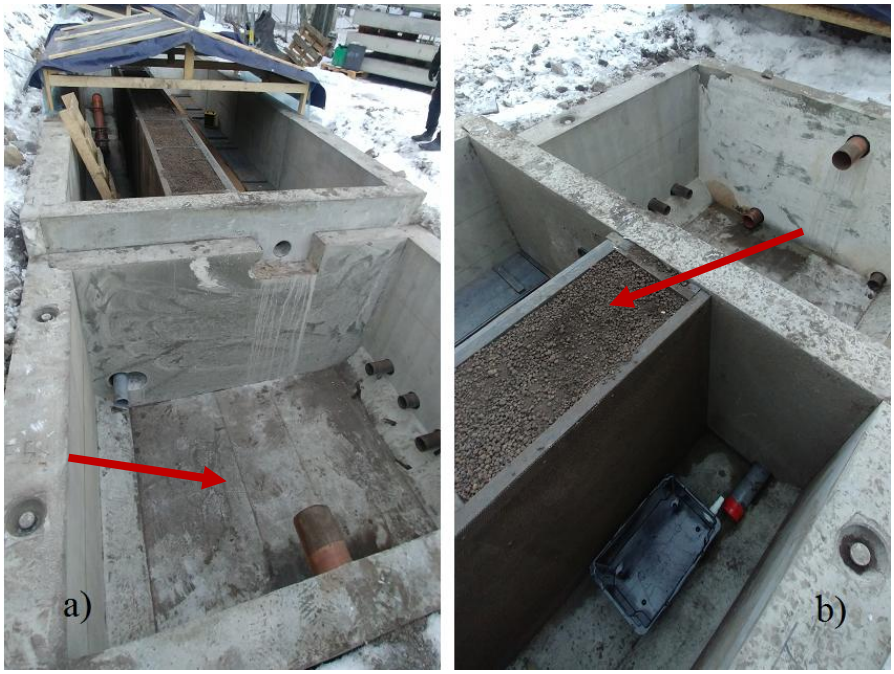


Figure 10. Construction phase of the Taivallahti filtration system. Photo shows (A) the underground sampling base at the bottom and (B) the influent unit with coarse filtration media (expanded clay aggregate).

2.3 Design and testing of a microplastic sampling device

A sampling device, based on pumping and filtration technique, was designed to collect microplastics from stormwater runoff. With the device, stormwater runoff first flows to a sampling pool with a volume of 50 litres (Figure 11, component 2). From the sampling pool, the runoff is pumped into the sieves (Figure 11, component 16) with a submersible pump (Grundfos Unilift CC5, 50 hZ; Figure 11, component 1). The flow rate varied between 1-5 m^3/h and was measured using un impeller-based flow meter (Gardena Water Smart, Figure 11, component 24).

Water was filtered through different mesh-sized sieves. The sieves used for this study were HAVER test sieves with stainless steel frame (SFS-EN 10204) with mesh sizes in the sieve column (in µm) 38, 90, 300, 1000, 4000 and 5000 respectively. The smallest mesh size (38 µm) was not used for influent stormwater based on *ex-situ* testing (Section 2.2.1). Hidalgo-Ruz et al. (2012) reviewed that the abundance of MP particles is substantially higher in 80 µm mesh than in 450 µm. In addition, Talvitie (2018) reviewed several studies where MP concentrations increase significantly when sampling size is below 80 µm.

For dimensioning the pumping, dynamic head was excluded due to minor pressure loss of 0.01 m (0.001 bar) in the system based on Darcy–Weisbach equation for head loss in the sampling device due to friction (Equation 1).

$$h_f = f \frac{L}{D} \frac{v^2}{2g} \quad (1)$$

where h_f is the head loss (m), f is the friction factor, L is the length of pipe, D is the pipe diameter, v is the velocity and g is the gravitational acceleration.

The geodetic height was used as a precondition when selecting the pumps. The height of the sampling device from the bottom of the sampling pool to the top of the guide rod was 1.5 m. The selected pumps were submersible pumps with impellers with a maximum head of 5 m and maximum flow rate of 6 m^3/h. Excluding the geodetic head loss of 0.15 bar, the maximum flow rate is thus ~4.5 m^3/h. The pumps have a level control and starts pumping when water level reaches 145 mm (Figure 11).

Due to the efficiency of the pumps and to optimize the water flow rate though the sieves, the head of the water was reduced by a throttle (Figure 11, component 8). This however led to leakage of water through the sieve edges. Therefore, the pumped water was also directed through a bypass pipe (Figure 11, component 13a) back to the sampling pool (Figure 11, component 2) where the water flow also moves the solids preventing the sedimentation or floating of the particles. Microplastic particles have the tendency to float or sink based on their density or shape (Stokes law; Kaiser et al. 2019). The purpose is to avoid the difficulties in sampling due to migration of microplastics in water column that has been noticed in other studies (Liu et al. 2019).

The flow of water through a fully open (90°) and semi-open valves was measured by flowing tap water through the entire sampling device. The effect of valve throttling on the flow rate of water was tested (Table 4).

Table 4. The empirical relation between ball valve throttle and sample water flow and velocity

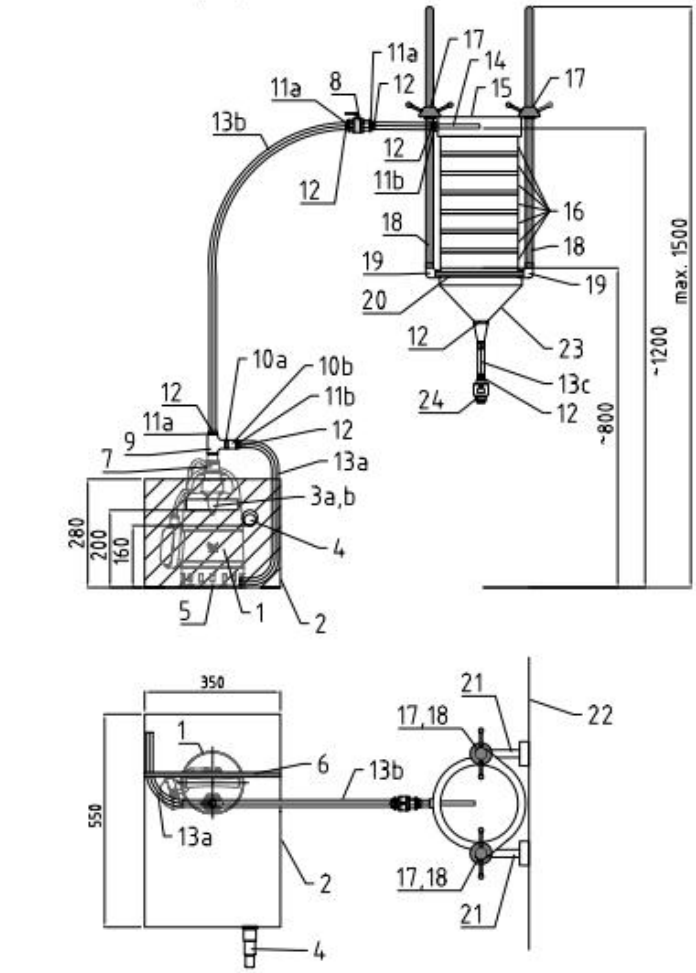
Valve handle angle in degrees	Sampling pool fill up time (s)	Sample water flow rate (l/s)	Flow rate (m^3/h)
90°	11.5	0.44	1.57
75°	11.6	0.43	1.55
60°	13.1	0.38	1.38
45°	15.2	0.33	1.18
30°	20.4	0.25	0.88
15°	28.4	0.18	0.63

With the measured flow rate between 0.18-0.44 l/s, the pump operates with a total discharge head between 3.5-4.5 m which is sufficient considering the total head loss.

The boundary conditions for the flow of sample water and for measuring the flow of water were that the sieves (Figure 11, component 16) or funnels (Figure 11, component 23) collecting the sample water should not drain the water. Drainage of water was examined by the application of Torricelli's law to the time it takes to empty the water collector (Figure 11, component 23) funnel and the sampling pool through the drain hole (Equation 2).

$$\Delta t = \frac{2A}{a\sqrt{2g}}(\sqrt{h_1} - \sqrt{h_2}) \tag{2}$$

where t is the time, A is the sampling pool area, a is the drain hole area, g is the gravitational acceleration, h_1 is the water height (start) and h_2 is the water height (end).



Components

1 Submersible pump, Grundfos Unilift CC5, 50 Hz
2 Sample pool 50 l, 550x350x280 mm, recycled plastic
3a Sample water inflow gap (behind)
3b Overflow gap (front)
4 Overflow pipe ø 30 mm / ø 40 mm
5 Drain hole ø 5 mm
6 Support bar, pump to sample pool, aluminium
7 Backflow preventer (non-return) valve
8 Ball valve 3/4" internal thread, brass
9 T-fitting 3/4" internal thread, brass
10a Compression fitting 1/2" external thread, brass
10b Muff 1/2", internal thread, brass
11a Hose nipple 3/4", external thread, brass
11b Hose nipple 1/2", external thread, brass
12 Hose clamp, inox
13a Bypass pipe, PVC hose 12/18, ToppClear, fiber braid reinforced
13b Inflow pipe, PVC hose 12/18, ToppClear, fiber braid reinforced
13c Outflow pipe, PVC hose 12/18, ToppClear, fiber braid reinforced
14 Sample water outlet pipe
15 Cover with inspection glass, 200 mm / 400 mm
16 Test sieve, HAVER 200x50/ 400x65 mm, stainless steel
17 Tension nut, metal
18 Guide rod, metal
19 Corner connector 1/2", internal thread, brass
20 Round pipe 16x1 mm, steel + round bar 12 mm, aluminium or aluminium plate 50x5 mm
21 Shelf bracket, stainless steel / aluminium
22 Wall structure, concrete
23 Water collector funnel, plastic
24 Water flow meter, Gardena

Figure 11. Sampling device component drawing

2.3.1 Testing *ex-situ*

The water permeability of the sieves was tested at a laboratory with snow melt water (Figure 12). A volume of 50 litres of snow melt water was passed through the sieves (Ø 20 cm). During the test, the lowest mesh sizes of 20 µm and 38 µm were clogged with solids clogging the column series so they were excluded from influent stormwater sampling device (Figure 13). Unlike in other studies where the filters were either changed or sampling was stopped after clogging of the filters (Talvitie et al. 2017a, Liu et al. 2019, respectively), the sampling device in this study could not clog during the sampling because the sampling should cover the entire rain event hence the sieves were not replaceable.

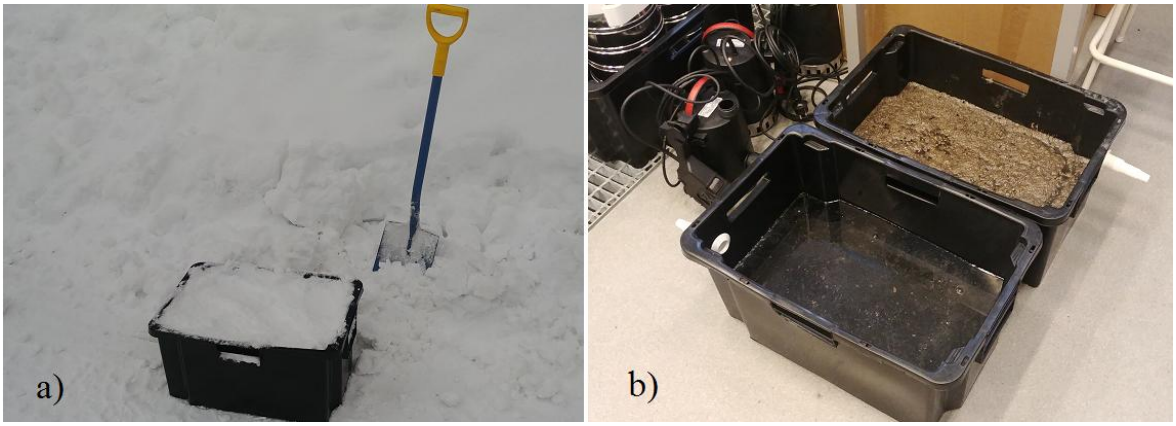


Figure 12. (A) Collecting snow for ex-situ testing in January 2019 and (B) snow melt water in sampling pools.

Figure 13. Clogged sieve due to solids (Ø 20 cm) with a mesh size of 20 µm

The transport of plastics from the sampling pool to the sieves was tested with colored beads made of polyvinyl alcohol (PVOH). A total of 80 beads were dropped into the sample water pool (Figure 14a), after which the pump operated for 90 s. The experiment was repeated twice. In the first iteration, a total of 41 beads entered the sieves and in the second iteration 38 beads (Figure 14b).

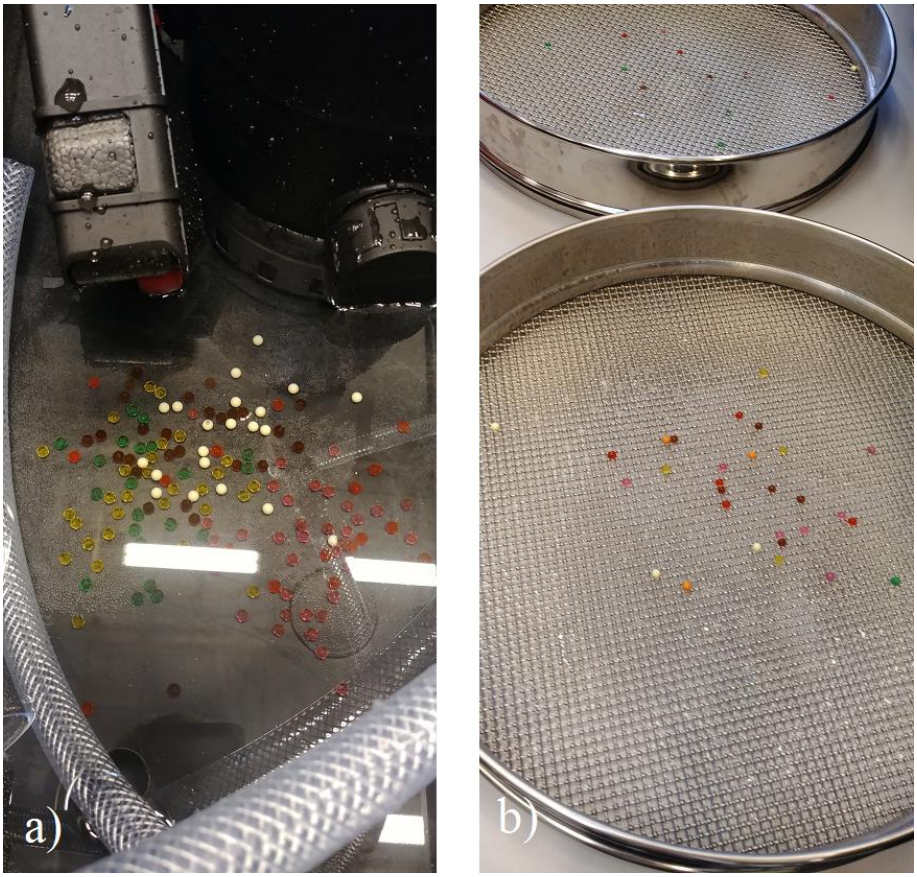


Figure 14. (A) PVOH beads in sampling pool and (B) in sieves with a mesh size of 4000 µm (upper) and 5000 µm (lower).

2.3.2 Testing *in-situ*

The sampling device was installed on study site in Taivallahti bay, Helsinki, between 7-8th of March 2019 for sampling (Figure 15). Altogether three sampling devices were placed into the filtration system. The first sampling pool (Figure 11, component n:o 2) was attached next to the influent pipe and the second and third sampling pools next to the effluent pipes in the sampling base after the filtration process (sand and biochar). The sampling pools were secured in place with ropes to prevent strong water flow or upthrust from moving the sampling pools or the pumps. The sieves were attached to the concrete wall structure of the filtration system (Figure 11, components n:o 16 and 21). After the installing of the sampling device, the filtration system basin was cleaned manually by collecting the visible litter and solids with a steel net (mesh size 1 mm) by hand to minimize contamination from the filtration system during the sampling.

The sampling device was tested *in-situ* by pumping a volume of 60 litres of biochar filtrated stormwater runoff through a sieve column. The sampling device worked flawlessly, and the sieves were not clogged. These sieves were later rinsed to beakers in a laboratory for use as recovery samples to assess microplastic sampling efficiency and loss of microplastics during the sample processing. The determination of the recovery of particles after sample processing is based on Löder et al. (2017; see Section 3.1).

Figure 15. (A) Sampling pool attached next to the stormwater influent pipe in the filtration system and (B) sieve columns attached to the concrete wall of the underground sampling base.

2.4 Sample collection during rain events

Stormwater runoff was collected from a total of three rain events between May and June 2019 in Taivallahti bay study site (Figure 16, Table 5). The sampling was started by turning on the pumps immediately after the stormwater runoff flow was visible in the filtration system chambers. The samples were composite samples. All the sieves attached to one sieve column make one independent sample.

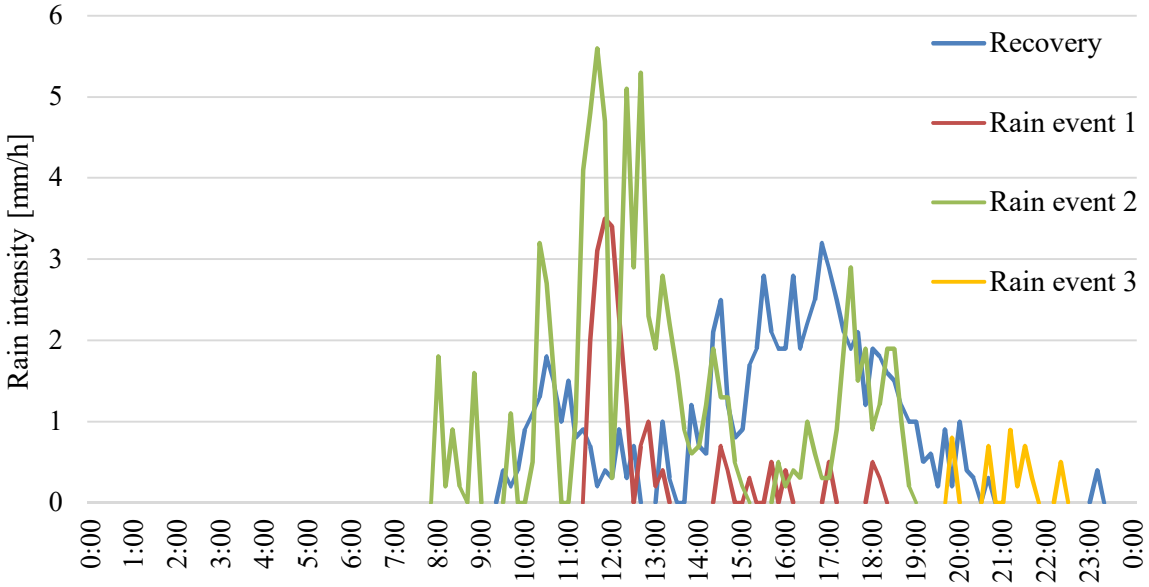


Figure 16. Rain intensity [mm/h] during sampling days (Table 5). The measuring point for the rain intensity was located in Kaisaniemi, 1 km distance from the sampling location (data from Finnish Meteorological Institute 2020).

Table 5. Sampling dates and volumes, and sample pre-treatment in the laboratory.

Rain event	Recovery	Rain event 1	Rain event 2	Rain event 3
Sampling date	2.5.2019	10.5.2019	26.5.2019	25.6.2019
Sampling started	14:30	14:55	8:00	19:00
Sampling ended	15:00	16:28	13:00	0:00
Pre-treatment	8.5.2019	15.5.2019	28.5.2019	26.6.2019
Precipitation [mm]	0.9	0.4	9.0	0.7
Influent stormwater [litres]	-	519	2880	850
Sand [litres]	-	259	1436	424
Biochar [litres]	60	470	2600	770

2.5 Sample processing

In the laboratory, the sieves with a mesh size from 38 µm to 300 µm were rinsed to separate beakers with ultrapure water in laminar cabinet. Some samples from the rain events contained high amount of solids which is why they were divided into subsamples for the processing. The subsamples were taken by shaking the sample beaker vigorously and measuring 3 x 50 mL of sample water to the filter with a glass pipette. The detailed shares of (extrapolated) subsample water volume used for processing is presented in Appendix A. In other case, the entire sample volume from the beaker was used for processing.

The samples were processed using a modified version of Löder et al. (2018) enzymatic purification protocol (Table 6) with a combination of oxidation, enzyme digestion and density separation. During each phase of the process, the (sub)samples were rinsed and filtered through a stainless-steel filter (20 µm) using a dry vacuum pump with compressor. The same filter was used for the sample during the entire process to prevent loss of particles.

Table 6. Modified sample processes used for the recovery samples and actual samples (Löder et al. 2017).

Recovery samples and 1st rain event samples

30 mL H_2O_2	24 h		40 °C
5 mL of cellulase, 20 mL of NaOAc	24 h	pH 5	
4 mL of amylase, 20 mL of NaOAc	24 h		50 °C
50 mL SDS 10%	96 h		
Density separation, $ZnCl_2$	24 h		
Filtration through silver membrane filters (5 µm)			
FTIR analysis			

2nd and 3rd rain event samples

30 mL H_2O_2	24 h		40 °C
5 mL of cellulase, 20 mL of NaOAc	24 h	pH 5	
30 mL H_2O_2	24 h		
50 mL SDS 10%	96 h		50 °C
Density separation, $ZnCl_2$	24 h		
Filtration through silver membrane filters (5 µm)			
FTIR analysis			

Amylase enzyme treatment was replaced with second hydrogen peroxide treatment for the second and the third rain event sample processes: Amylase together with 10% SDS solution formed a coagulant in the sample water clogging the filters thus complicating the filtration process (Figure 17).

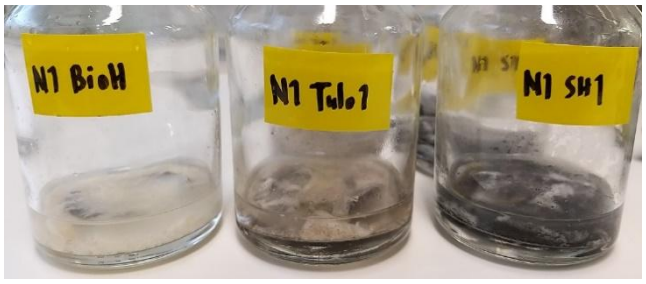


Figure 17. Coagulant on the bottom of sample glasses (Event 1).

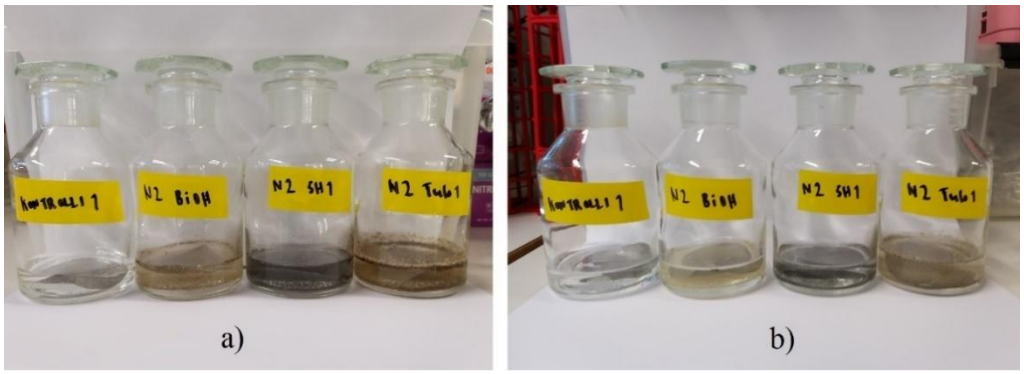


Figure 18. The 2nd rain event runoff control sample, filtrated stormwater samples and influent stormwater sample (respectively) (A) before processing and (B) after cellulase enzyme treatment.

The density separation is used to settle particles for removal of excess solids from the samples. The density separation was done with zinc chloride ($ZnCl_2$) that had a density between 1.68 g/cm^3 and 1.8 g/cm^3. Most plastics have a density between 0.8 g/cm^3 and 1.6 g/cm^3 (UNEP 2016) so they have the tendency to float in $ZnCl_2$ solution. The settled particles were removed from the samples.

Processed sample filters were stored in the same sample glasses as was used during the processing and 50 mL of ultrapure water were added to prevent the material and filter from drying.

The material in the sieves with a mesh size of 1000 µm and 4000 µm was transferred to separate Petri dishes with tweezers, and then inspected visually under a transmitted light stereomicroscope (Leica Wild M6, magnification ×10). The microplastic particles based on the author's assumption were picked with tweezers and moved to rinsed glass bottles for sample analysis.

Figure 19. (A) Influent stormwater runoff solids (1000-5000 µm) on Petri dishes and (B) a potential microplastic particle under stereomicroscope.

2.6 Recovery rate of microplastic particles

The sampling efficiency test was performed to assess the loss of microplastic particles during the sample processing. To determine the recovery rate, luminescent, yellow-green polystyrene (PS) microplastic beads (Fluoresbrite® Yellow Green Microspheres) with a size of 90 µm were added to three separate glass Petri dishes. The number of beads was counted (60, 49 and 49 respectively) under a stereomicroscope. The beads were transferred from the Petri dishes to separate glass bottles with 50 mL of biochar filtrated stormwater sample from the study site each. The recovery samples went through the same process method as actual samples. After the process, the beads were counted under using a stereomicroscope (Leica M 165 FC) with a fluorescence light source (Leica EL6000). The results are presented in Section 3.1.

2.7 Sample analyses

Even after the processing, the samples contained some solids, particularly influent stormwater and biochar samples. In these cases, the processed sample was divided to subsamples. Liu et al. (2019) presented that "…*too large sample volume on a window would impede the subsequent interpretation of the data obtained by the µFTIR imaging*". The filtered sample volumes were extrapolated to estimate the amount of stormwater runoff that was included for the analysis (Appendix C). The processed samples were further filtered to silver membrane filters (5 µm, Sterlich Co), let dry and placed on microscope slides (Thermo Scientific) for material analysis with FT-IR (Figure 20). The samples were stored in the slides on Petri dishes for further studies.

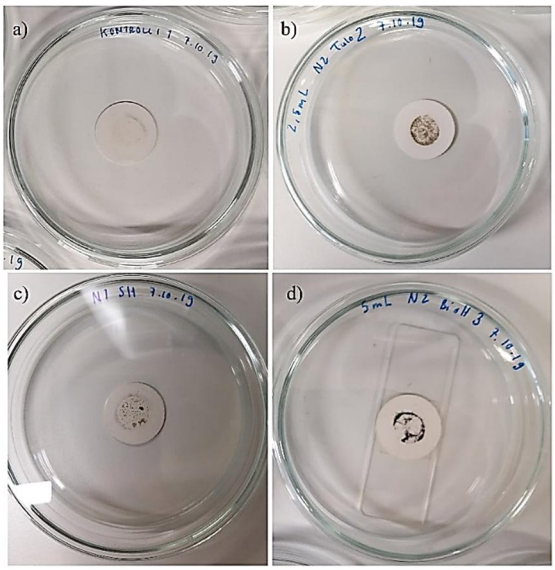


Figure 20. (A) Control, (B) influent stormwater runoff, (C) sand and (D) biochar samples in 5 µm silver membrane filters.

The analysis for the processed samples from sieves with a mesh size of 38 µm to 300 µm was conducted using FPA-based FT-IR imaging technique (Agilent Cary 670 FTIR spectrometer) coupled with Cary 620 microscope with a 15x magnification (Agilent Technologies; Figure 21). The microscope and spectroscope were connected to the computer and controlled with Resolutions Pro FTIR Software (Agilent Technologies). The FPA detector was a 128x128 Mercury Cadmium Telluride FPA detector with a 5.5 µm pixel resolution. The samples were scanned with infrared absorbance mode.

In the identification of polymers using FPA-based FT-IR, four parameters are of interest: wavenumber range, spectral resolution, the number of scans and the scanned area which all affect the quality of the gained data. Wavenumber affects the range where the polymer spectra can be identified. High spectral resolution increases the spectrum precision but is time and data consuming. The number of scans measured in the analysis affects the signal-to-noise ratio where the result is the average of the measured scans. Scanning the entire sample area prevents the bias from subsample extrapolation. (Löder et al. 2015.)

In this study, the number of scans per (sub)sample was 4 and the resolution 8 cm^{-1}. Wavelength (spectral) range of 3800-800 cm^{-1} was used which is optimal for analyzing plastic particles (Löder et al. 2015). The entire sample on the silver membrane with a measurement area of approximately 12x12 mm^2 was scanned. The total number of spectra from one scanned sample was 3.2 million. Prior to analyzing the actual sample, a background spectrum of air was measured using a gold coated mirror plate. The background spectra were automatically subtracted from scanned sample spectra.

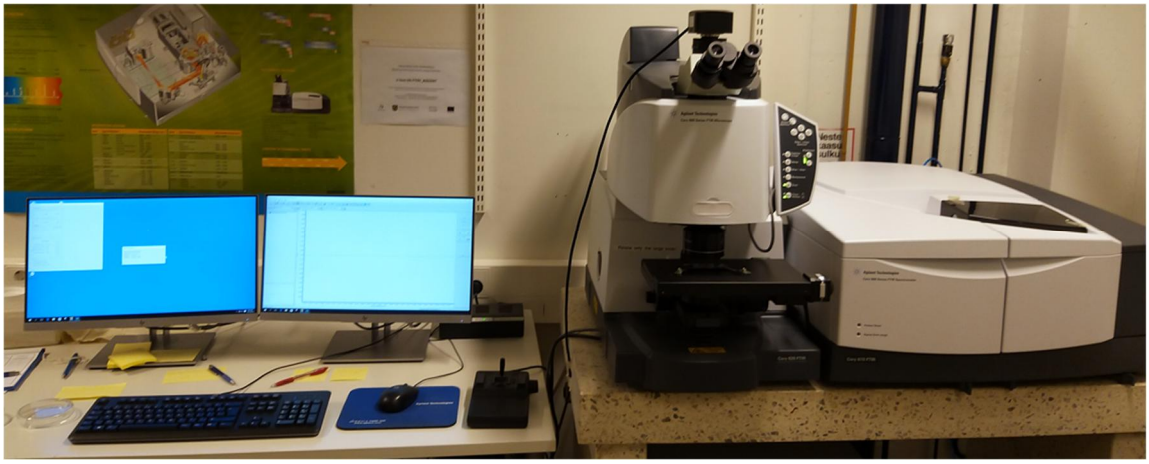


Figure 21. FT-IR spectrometer coupled with microscope (right) connected to a computer with image analysis software (left).

The picked particles from sieves with a mesh size of 1000 µm and 4000 µm were analyzed using attenuated total reflectance (ATR) along with FT-IR spectroscopy (Nicolet iS50 FTIR Spectrometer, Thermo Scientific; Figure 22). The total number of scans per particle was 32 and the resolution 4 cm^{-1}. The spectral range was 4000-400 cm^{-1}. The particles were identified using OMNIC™ Specta Software.

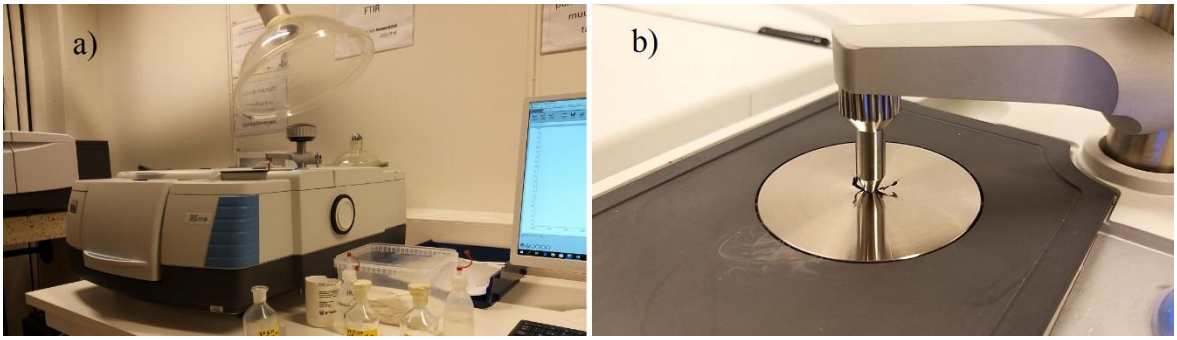


Figure 22. (A) ATR spectroscopy used for analyzing particles from 1000 µm to 5000 µm, and (B) a possible MP particle in analysis.

2.8 Data analyses

The generated spectrum data was analyzed with a microplastic identification software, siMPle (Systematic Identification of MicroPLastics in the Environment), developed by Aalborg University, Denmark and Alfred Wegener Institute, Germany (Primpke et al. 2017). The correlations between the spectra of reference plastics and samples are calculated with spectral correlation analysis to determine particle numbers, sizes, materials and mass estimations (Primpke et al. 2018, Liu et al. 2019). The software uses Pearson's correlation to compare reference and analyzed particles. In this study, the probability threshold value for identification was 0.6. A further background to microplastic particle quantification and identification using siMPle is presented by Olesen et al (2018) and Liu et al. (2019). However, as mentioned in Section 1.2.3, microplastic particles emitted from car tyres (see Table 1) cannot be analyzed due to the carbon black (Kyle et al. 2017, Liu et al. 2019).

The total amount of microplastic particles during the rain events in stormwater effluent and influent is based on event mean concentration (EMC) using Equation 3. The number of particles is multiplied by the total discharge volume.

$$EMC = \frac{\sum_{i=1}^{n} V_i C_i}{\sum_{i=1}^{n} V_i} \quad (3)$$

where V_i is the discharge amount corresponding to sample i, C_i is the pollutant concentration in sample i, i is the sample number and n is the total number of samples collected.

The removal efficiency of microplastic particles was calculated by event mean concentration efficiency (R_{Eff}; Equation 4), separately for each filtration media. The influent stormwater concentration is compared separately for both filtration media with event mean concentration (EMC) efficiency.

$$R_{Eff} = \frac{EMC_{influent} - EMC_{effluent}}{EMC_{inluent}} \times 100\ \% \quad (4)$$

where $EMC_{influent}$ is the EMC of influent stormwater and $EMC_{effluent}$ is the EMC of filtrated stormwater.

As is usually the case in assessing the performance of stormwater filtration structures, the number of rain events is the single most important factor that can be used to verify the removal efficiency (Erickson et al. 2013). The standard deviation of average removal efficiency and removal efficiency adjusted to confidence level can be used to determine the required number of rainfall events for stormwater monitoring and assessment programmes (Erickson et al. 2013). It should be noted that on time being, processing with enzymatic protocol and FT-IR analyses for stormwater microplastic samples is a time consuming which may set limit to number of rain events and, consequently, samples for studies. An individual sample may take up to three weeks to finish from sampling to data analysis results although samples can be processed simultaneously.

The microplastic particles were divided into three size classes: 90-300 µm, 300-1000 µm and 1000-5000 µm. Sizing is based on the size of the sieves used in the sampling phase of the study. Similar size classes were used by Talvitie et al. (2017b) in a wastewater study.

The mass of MP particles was calculated automatically by siMPle based on the density of known polymers and presuming an ellipsoid shape for the particle (Mintenig et al. 2017, Olesen et al. 2018).

Even though microplastic concentrations in stormwater runoff are not straightforwardly dependent on previous rain events, the data of three rain events in this study was combined in most cases. This is to address the mean values of the microplastic concentrations in stormwater runoff and highlight the removal efficiency of MP using the filtration system. However, the concentrations between the rain events may vary greatly thus resulting in high standard deviation.

2.9 Mitigation of contamination

The sampling devices were rinsed first with tap water and then three times with ultrapure water before in contact with the samples. After the sampling, the collected sieves were covered in aluminum foil and stored in plastic boxes that were rinsed with reverse osmosis water. To prevent contamination through textiles, the used workwear at the laboratory and cloths for drying rinsed equipment were made of 100% cotton. Although all the possible precautions were taken, workwear made of organic material could not be used at the sampling site due to safety requirements. Additionally, the material used in the sampling device included hoses (PVC) and recycled plastic sampling pool (PE-HD) since there were no replacing parts. These materials may affect the contamination levels in the samples.

To prevent airborne contamination, all the used equipment that was in contact with air was covered in aluminum foil prior and after handling. The processed sample filters for the analysis were covered with glass Petri dishes. Moreover, all the sample processes were done in laminar cabinets.

The solutions used during the process were filtered once through a 20 µm steel net filter to prevent solution-mediated MP contamination in the samples.

To assess contamination level during the process, three control samples were made by adding 50 mL of ultrapure water to glass bottles. These samples were treated through the same process as actual samples (Section 2.4) and material analyses were conducted (Sections 2.5 and 2.7). The results for levels of contamination are in Section 3.2.

3 Results and discussion

The results focus on microplastic concentration and characteristics in stormwater runoff during three different rain events in densely built-up urban areas and the performance of two different filtration media, sand and biochar, in removal of microplastics from rain-induced stormwater runoff.

Rain intensity and cumulative precipitation during the study period between May and June 2019 were plotted to illustrate the occurrence of dry and wet periods between sampling events (Figure 23). The data between the first and last sampling date is divided into three 18 days periods to assess the effect of precipitation and adjacent dry periods to MP concentrations (Section 3.6). The cumulative precipitation was 31.8 mm during the first period (2.5.–20.5.), 33.7 mm during the second period (21.5.–7.6.) and 4.8 mm during the third period (8.6.–25.6.; Finnish Meteorological Institute 2019).

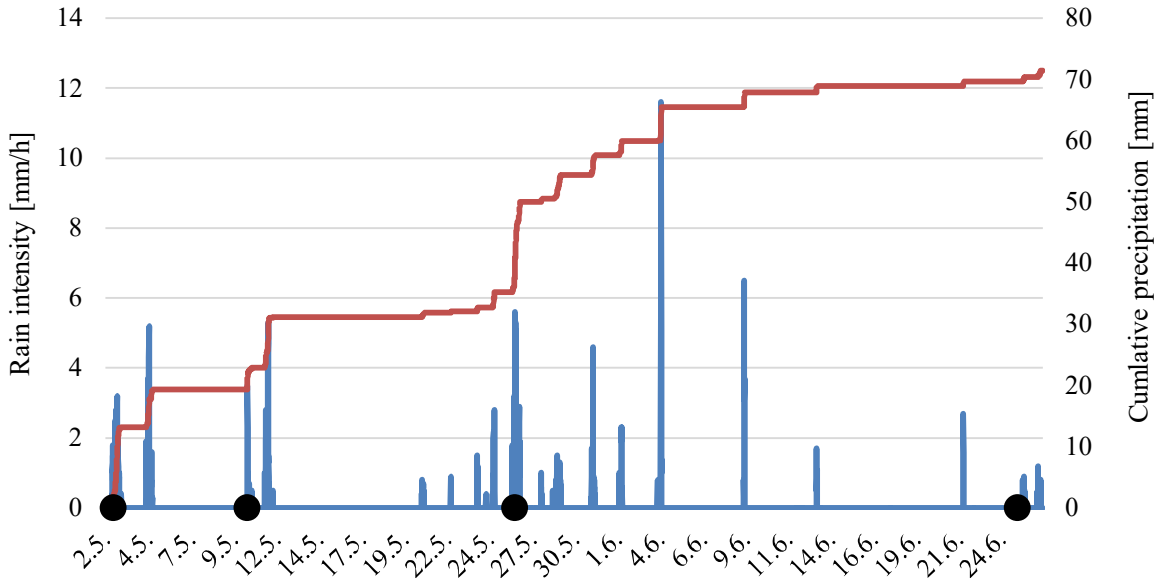


Figure 23. Rain intensity (mm/h) and cumulative precipitation (mm) during the study period. Data from Finnish Meteorological Institute (2020). The studied rain event dates (recovery & events 1-3 respectively) are highlighted with black dots.

3.1 Sample processing validation

The recovery rate of microplastics was performed to assess the loss of microplastic particles during sample processing (see Section 2.3.2). The average recovery rate for the three processed samples was 81 ± 2.2 % (Table 7) and was considered to be acceptable. In their study, Simon et al. (2018) concluded that *"...recovery rates are only indicative of the efficiency of the extraction method as the features of the MP particles used for spiking did not cover all the diversity of MP particles in the sample regarding their size, material and shape. Therefore, to avoid introducing unknown bias data is not corrected for recovery"*. For this same reason, the results are not corrected in this study either.

Table 7. Microplastic recovery rate after sample processing. 81 % of the beads were recovered and 19 % of the beads were lost during the process.

Sample	Beads added	Beads recovered	Recovery rate
1	60	48	80 %
2	49	41	84 %
3	49	39	80 %
Average ± sd			81 ± 2.2

3.2 Contamination

In the control samples, a total of 42 microplastic particles were found. The procedural control samples went through the same laboratory protocol as the actual samples. The results did not cover the field contamination from the sample collection due to difficulties in taking procedural control samples during field work thus excluding the contamination levels from the sampling device or study area. However, to reduce the risk of contaminating stormwater samples in the field, the steps described in Section 2.9 were taken. However, based on visual inspection of the images derived from the microscope, a total of 38 particles in one of the samples consist of possible only one larger particle (Figure 24). Thus, it is uncertain what is the actual contamination level of that particular sample. The other two control samples had a total of four identified microplastic particles. Due to uncertainties and moderate contamination levels in these two control samples, microplastic concentrations are not corrected for actual samples.

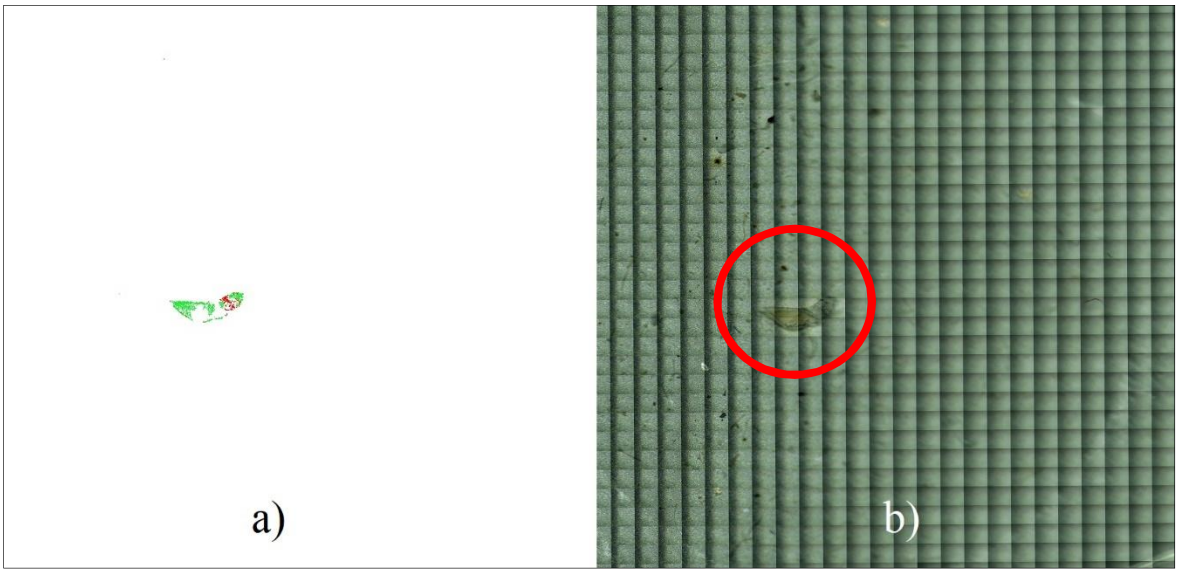


Figure 24. (A) Data analysis of the control sample with 38 identified microplastic particles and (B) mosaic image derived from FT-IR microscope. Based on the mosaic image, the data analysis may have given false positive data.

3.3 Microplastic size and mass in influent and filtrated stormwater runoff

The characteristics of microplastics in the samples was examined by both particle size and mass. The identified particles were extrapolated to the total sample volume (Appendix C) in a litre of sample water. A total of 1154 microplastic particles from three separate rain events (90-1000 µm) were analyzed, of which 148 were in sand samples, 308 in biochar samples and 698 in influent stormwater samples. The following results are based on the properties of these particles. The detailed results for the microplastics in size class ≥ 1000 µm are shown under Section 3.5 (Table 14). Because the smallest mesh size used for influent stormwater samples was 90 µm, particles smaller than 90 µm are not comparable and therefore excluded from the results. However, the analyzed samples showed that large amounts of particles smaller than 90 µm were present in influent stormwater samples, which may be due to particle adherence to other solids in the sieves due to sorption. Half of all the analyzed MP particles (including filtrated stormwater samples) were less than 90 µm in size (50.8 %). The abundance of MP particles in sieves with smaller mesh sizes is in line with the observation by Hidalgo et al. (2012) and Talvitie (2018): Microplastics are found in higher concentrations as sampling size gets smaller.

The average size of the microplastics from three rain events in influent stormwater samples was 172 µm, in sand filtrated samples 148 µm and in biochar filtrated samples 142 µm (Table 8). Larger microplastic particles were thus removed from influent stormwater.

Table 8. Measures and values of dispersion for the analyzed MP particles (90-1000 µm) based on major dimension (µm) of three rain events.

Sample	min (µm)	max (µm)	median	average	stdev
Sand	91	353	131	148	57
Biochar	90	750	123	142	67
Influent	90	1290	149	172	88

The mass estimate was based on the known polymer density and dimensions of identified polymers (Simon et al 2018). The average mass of the microplastics from three rain events in influent stormwater samples was 0.26 µg, in sand filtrated samples 0.20 µg and in biochar filtrated samples 0.19 µg (Table 9). The heaviest identified particle in biochar filtrated sample was 18.7 µg. One large identified particle can greatly increase the average mass as was the case in the study of Simon et al. (2018). The mass data of MP particles above 1000 µm was not measured due to limitations with FTIR-ATR spectroscopy which may contribute to the overall total mass values.

Table 9. Measures and values of dispersion for the analyzed MP particles (90-1000 µm) based on mass (µg) of three rain events.

Sample	min (µg)	max (µg)	median	average	stdev
Sand	0.009	3.3	0.11	0.20	0.36
Biochar	0.008	18.7	0.06	0.19	1.14
Influent	0.005	6.7	0.11	0.26	0.51

In Figure 25 the influent stormwater samples and filtrated stormwater samples are addressed in terms of size and mass cumulative frequency. A total of 99 % of all identified particles from influent stormwater, sand and biochar samples were below 400 µm in size and 0.5 µg in mass. Later peaking of size and mass frequencies in influent stormwater samples indicated similar results as in Table 11: Overall composition of the analyzed particles was larger in influent stormwater samples than in filtrated stormwater samples both in size and mass.

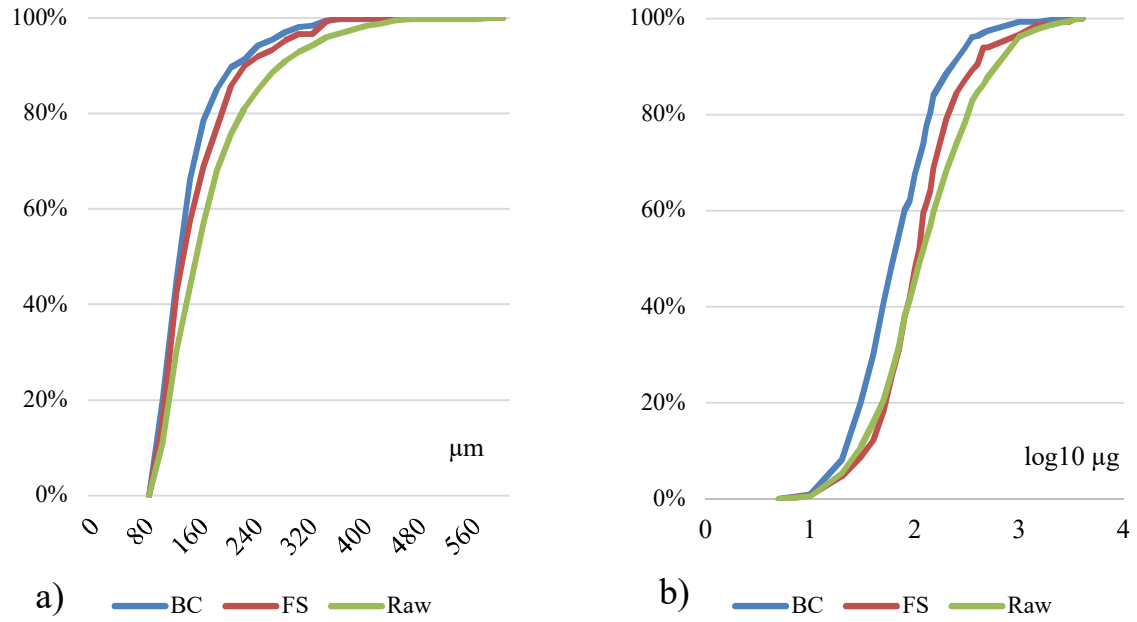


Figure 25. Relative cumulative frequency of MP particles in influent stormwater (Raw) and biochar (BC) and sand (FS) filtrated stormwater runoff by (A) major dimension and (B) mass (µg) on base 10 logarithmic scale from three rain events.

3.4 Microplastic quantity in influent and filtrated stormwater runoff

To address the quantity of MP particles, both amount and mass of particles were examined simultaneously. In this study, the average concentration of microplastics from three rain events in influent stormwater samples was between 8-66 MP/L (average 29 MP/L), 0-1.5 MP/L for sand filtrated samples and 0-2.2 MP/L for biochar filtrated samples (Figure 26). The MP concentration of influent stormwater samples in the size class 90-300 µm was 27 MP/L, in 300-1000 µm 1.7 MP/L and < 1 MP/L in size class 1000-5000 µm. This finding highlights the issue in abundance of smaller particles. Ignoring the MP particles under 90 µm decreased the total number and mass of particles in this study.

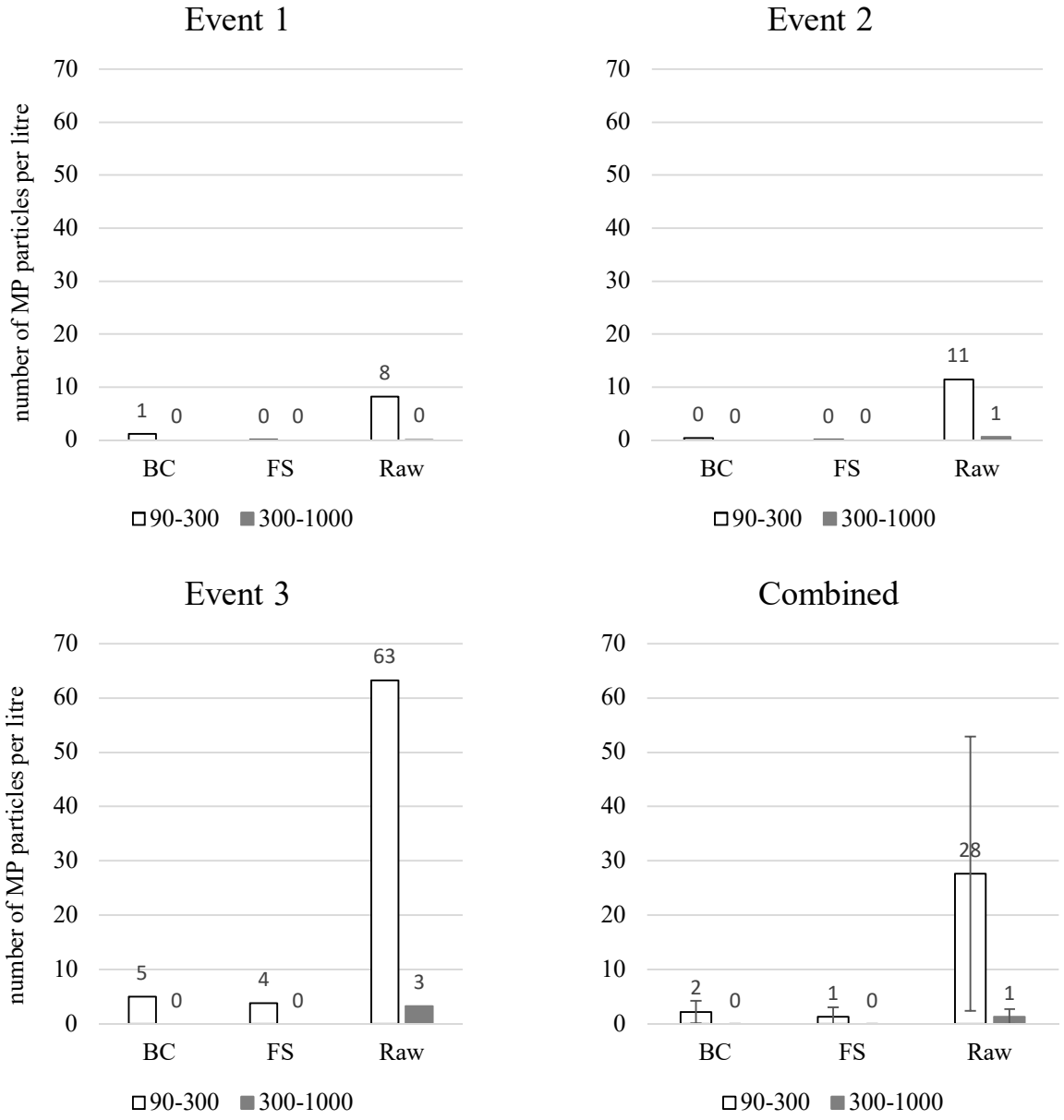


Figure 26. MP particles per litre of influent stormwater (Raw) and biochar (BC) and sand (FS) filtrated stormwater runoff in size classes 90-300 µm and 300-1000 µm separately for the three rain events and average concentrations with standard deviation (n=3).

Liu et al. (2019) analyzed MP concentrations from seven stormwater ponds and found a range between 0.49-23 MP/L with a median value of 1.4 MP/L where the highest concentrations were measured from pond with a commercial type catchment. However, direct rainwater to the ponds may dilute the MP concentrations which is why the results to this study are not straightforwardly comparable. Additionally, the sampling size was from 10 µm (Liu et al. 2019). Altogether, the concentrations of microplastic are much higher in urban stormwater runoff than in urban stormwater ponds based on this study. In other water related studies, MP particles have been found in, for instance, water streams (0.3 MP/L; Dikareva & Simon 2019), surface water (0.004-0.11 MP/L; Dris et al. 2015) and wastewater influent from studies by Murphy et al. (2016; 15.70 MP/L) and Simon et al. (2018; 5.4-10.0 MP/L). All the studied MP concentrations are lower than the results from this study despite the lower sampling size used in the studies above. However, since the microplastic size

definition varies among studies, comparison of the quantity of MP particles is challenging (Liu et al. 2019).

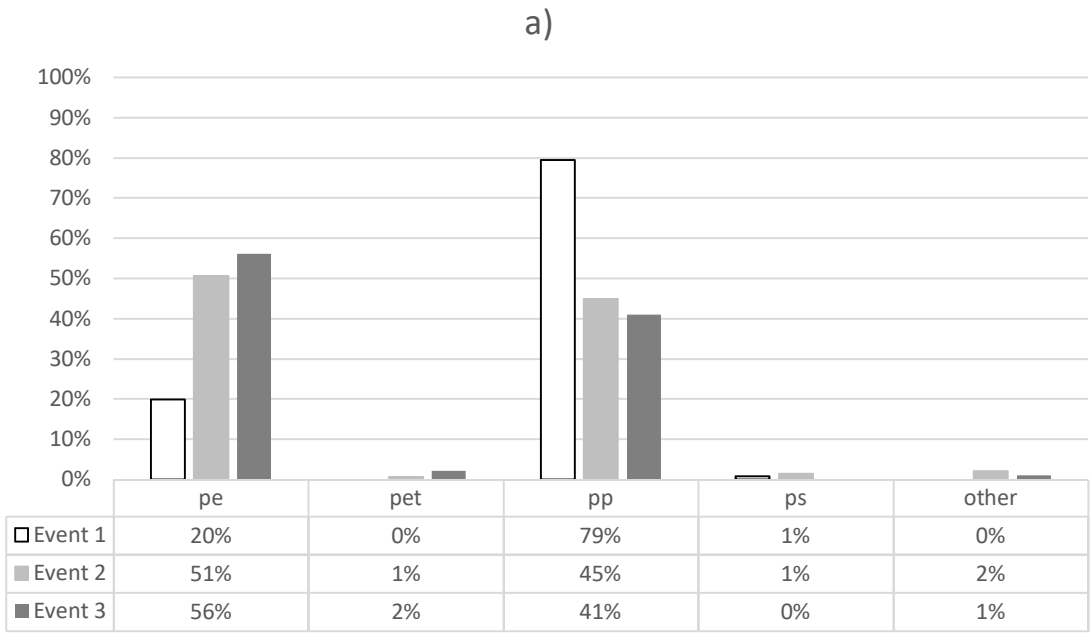
Polymer mass was 2.10-17.3 µg/l in influent stormwater samples, 0.002-0.80 µg/l in sand filtrated samples and 0.08-0.95 µg/l biochar filtrated samples. In comparison, the median microplastic mass of samples from seven studied stormwater ponds was 0.23 µg/l (Liu et al. 2019). The total mass of MP is significantly higher in this study. Nonetheless, the mass values are not fully comparable to the study by Liu et al. (2019) due to their sampling size from 10 µm.

Based on a rough estimate of surface flow (647 m^3; see Section 2.1) and the influent stormwater concentrations (8-66 MP/L), the amount of MP particles (90-5000 µm) in stormwater runoff during a rain event varies between 5.2^6 – 4.3^7 MP particles and the mass between 1.4-11.1 g. Based on the average annual precipitation rate in Helsinki (655 mm), the amount of MP particles from the catchment area stormwater runoff is 1.7^8 – 1.4^9 MP particles annually, equaling to 44-363 kg. Approximately 90 % of these particles end up in Taivallahti bay through the stormwater sewer system and 10 % goes through the treatment process of the filtration system. The particle mass could be even higher if particles 1000-5000 µm were included in the results yet the mass could not be measured using ATR-FTIR.

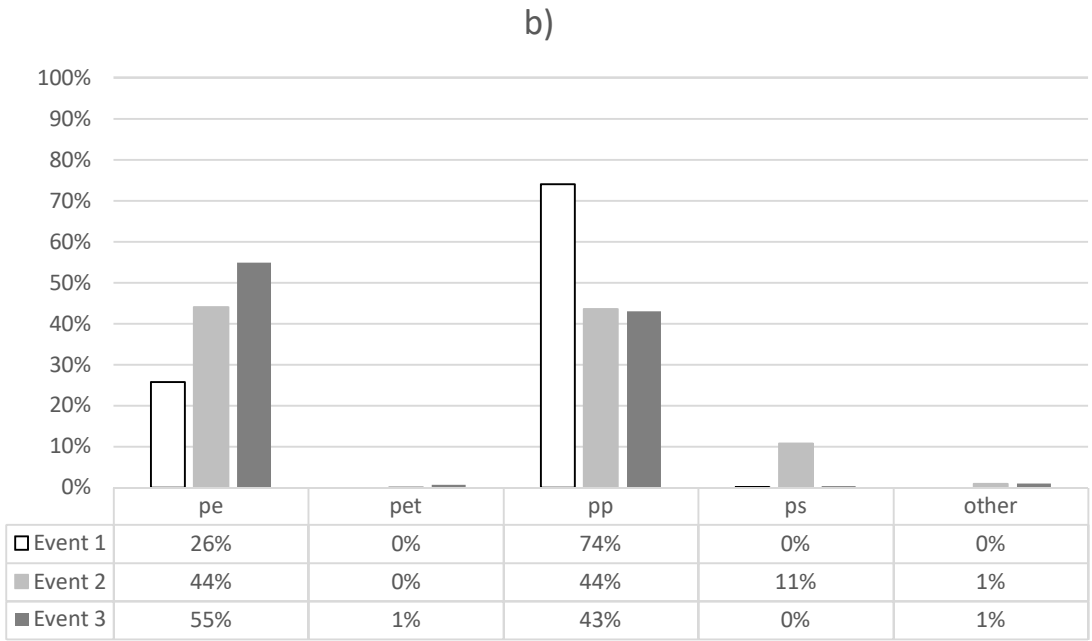
3.5 Polymer types in influent and filtrated stormwater runoff

In addition to the quantity, the quality of the microplastics was determined. The spectra data of the analyzed samples were compared to the siMPle data library (Appendix D), which showed the most common plastic types (Appendices E and F). The most common types of polymers in influent stormwater from three events were polyethylene (PE) and polypropylene (PP). These polymer types accounted for over 97% of all polymers, both of which are common and widely used plastic types (PlasticsEurope 2019; Table 1). PE (high density and low density) and PP cover half of all plastic types in Europe (PlasticEurope 2019). Typically, they are used for packaging, and containers and pipes in infrastructure (PlasticEurope 2019). The result for abundance of PP is similar to the study conducted in Denmark on stormwater ponds (Liu et al. 2019; 71.5 %), but the study also showed a significant proportion of PE, polyvinyl chloride (PVC) and polystyrene (PS; 9.1 %, 7.4 % and 5.5 % respectively).

The share of polymers by both number and mass in influent stormwater runoff varies between the rain events (Figure 27). In the first rain event, PP was the dominant polymer type (79 %) compared to PE (20 %). In the second and third rain event the difference in share of all particles was for PE (51 % and 56 % respectively) and PP (45 % and 41 % respectively). This emphasizes the issue of stormwater sampling as temporally changing activities and previous rain events may influence the polymer distribution in stormwater runoff.



	pe	pet	pp	ps	other
Event 1	20%	0%	79%	1%	0%
Event 2	51%	1%	45%	1%	2%
Event 3	56%	2%	41%	0%	1%



	pe	pet	pp	ps	other
Event 1	26%	0%	74%	0%	0%
Event 2	44%	0%	44%	11%	1%
Event 3	55%	1%	43%	0%	1%

Figure 27. Influent stormwater MP polymers (90-1000 µm) by (A) particle number and (B) mass in three rain events.

Polymers other than polyethylene or polypropylene were present in one particle or less than one particle per litre of sample water in all samples. The exact proportions of different polymers are shown in Table 13.

Table 13. Microplastic polymers from ≥ 90 µm to 1000 µm per litre of sample water. The concentrations with less than one particle per litre are shown as <1.

	Influent (MP L^{-1})	Sand (MP L^{-1})	Biochar (MP L^{-1})
PE	13	<1	1
ABS	<1	0	<1
PA	<1	<1	0
PET	<1	0	<1
PMMA	<1	<1	0
PP	15	1	1
PS	1	<1	<1
PU	<1	0	0
sum	29	1	2

All the particles above 1000 µm were found in influent stormwater samples. The particles between 1000 µm and 5000 µm were analyzed separately with FTIR-ATR. Some particles may have been missed due to human error by using naked eye in picking the possible MP particles from the sieves. The results are summarized in Table 14. The analyzed particles are shown in Appendix G.

The results for occurrence of PE are in line with the polymer results of 90-1000 µm. However, PP was not present in the identified particles larger than 1000 µm. Extrapolating the amount of PE particles in influent stormwater runoff would exceed its amount to 100 % of all polymers excluding the individual PMMA particle. To avoid this kind of generalization, the conclusion is that PE is a common polymer during rain event induced stormwater runoff in this particular case study yet there is a need for more rain event samples and data analyses to present reliable conclusions of MP particle composition over 1000 µm.

Table 14. Microplastic particles from 1000 µm to 5000 µm in influent stormwater samples, polymer type and spectrum match with software polymer library (%) analyzed with ATR.

Event n:o	Sample	Particle	Material	Match (%)
1	Influent	1	PE	80.65
1	Influent	2	PE	79.41
1	Influent	3	PE	81.24
1	Influent	4	PE	69.25
1	Influent	5	PE	74.10
1	Influent	6	PE	79.45
1	Influent	7	PE	78.87
1	Influent	8	PE	77.90
2	Influent	1	PE	70.79
2	Influent	2	PE	69.41
3	Influent	1	PMMA	78.14
3	Influent	2	Natural	53.76
3	Influent	3	PE	72.98
3	Influent	4	Natural	50.37

Regardless of the analysis results and the known polymer types in the study area, the tracking of microplastic sources is difficult due to diverse use of plastic and the many polymer types (Horton et al. 2017). In addition, they typically originate from nonpoint (diffuse) sources (Dris et al. 2015, Horton et al. 2017) and can travel long distances (Kole et al. 2017) making it complex to identify the original source.

Since FT-IR spectroscopy is not able to analyze black material, the number of plastic types in the data spectra library is limited. Therefore, tyre and traffic related rubber types are not included in the results, but only the most common known polymer types (see Table 1) resulting in loss of some quantities and qualities of microplastic particles in the results. The biochar samples contained some released carbon from the filtration system (Appendix B), which may contribute to the reliability of the data because black biochar interferes the spectroscopic method of FT-IR.

3.6 Removal efficiency of microplastics from stormwater runoff

Based on the results of three rainfall events, the average concentration of microplastics (90-5000 µm) was 1.5 MP/L in sand filtrated samples and 2.2 MP/L in the biochar filtrated samples (Table 10). As average influent stormwater concentration was 29 MP/L, the overall removal efficiency from influent stormwater became 93 % for biochar filtration and 96 % for sand filtration. Since the expanded clay aggregate and steel wire net as coarse filters preceded both fine filtration media columns in the filtration system, their importance in MP removal performance was not considered when comparing the removal efficiencies of sand and biochar.

Table 10. Average removal efficiency of stormwater runoff microplastic (90-5000 µm) with sand (FS) and biochar (BC) filtration media (average of three rain events). Before value indicates the average value of influent stormwater microplastic concentration from three rain events.

Treatment	Before (MP L^{-1})	After (MP L^{-1})	Removal efficiency
Sand	29	1.5	96 %
Biochar	29	2.2	93 %

The removal efficiencies were examined in different size classes as well. The removal efficiency using sand as filtration media was between 95-100 % depending on the size class (Table 11). The removal efficiency of biochar filtration media was between 92-100 % depending on the size class (Table 12).

Table 11. Removal efficiency of microplastic particles in sand filtrated stormwater runoff samples from three rain events in different particle size classes.

Particle size (µm)	Before (MP L^{-1})	After (MP L^{-1})	Removal efficiency
90-300	27	1.5	95 %
300-1000	1.7	<1	97 %
1000-5000	< 1	0	100 %

Table 12. Removal efficiency of microplastic particles in biochar filtrated stormwater runoff samples from three rain events in different particle size classes.

Particle size (µm)	Before (MP L^{-1})	After (MP L^{-1})	Removal efficiency
90-300	27	2.2	92 %
300-1000	1.7	<1	98 %
1000-5000	< 1	0	100 %

Since microplastics particles over 1 mm were not found in the sand or biochar samples, both filtration media removed 100 % of microplastic particles over 1 mm, regardless of the polymer type. Similar results were gained by Hakala (2018) with the filtration system pilot *ex-situ* testing as 100 % of all microplastics over 1 mm were removed from influent using sand and expanded clay aggregate as filtration media.

Considering the overall removal efficiency of 93-96 % (biochar and sand respectively) in this study, it is possible that already at the coarse filtration stage some microplastics are filtered from stormwater runoff (Kandasamy et al. 2008, Carr et al. 2016). Similar results were found by Kandra et al. (2015) who stated that coarse filters in stormwater treatment are efficient in trapping sediment particles over 1 mm in size. On the contrary, they found differences in coarse filter pore size and lack of flocculation in TSS and observed more effective transport of very fine sediment (< 75 µm) through coarse filters (Kandra et al. 2015). In our study, the difference in the removal efficiencies between the studied size classes (90-300 µm, 300-1000 µm and 1000-5000 µm) likely resulted from the pore size that enabled the mitigation of solids through the filter pores. In our study, the sand filtration media had a grain size of 0.8 to 1.2 mm, which partly explained the filtration of microplastics from stormwater to fine filtration material. On the other hand, there was only small amount of 300-1000 µm microparticle particles in sand filtrated samples (Table 11), which may be related to the small filter pore size in the filtration media and the adhesion of the microplastics to a larger solid surface (sorption), both which are found to remove solids (Shammaa & Zhu 2001). However, since the grain size of biochar filtration media in our study was 5-50 mm, the particle trapping mechanism to the filter pores was not similar to sand filtration. The mechanism may vary due to different pyrolysis methods in production of biochar and the properties it has in removal of different contaminants. If the biochar was produced in low temperature pyrolysis, the removal properties may prefer organic contaminants through absorption and in high temperature pyrolysis non-organic contaminants through electrostatic attraction (Korkealaakso et al. 2016).

The removal efficiency of MP particles in this study was compared to TSS concentrations from other studies. As discussed in Section 1.4., the removal efficiency of TSS using sand as filtration media is over 90 % (Shammaa & Zhu 2001, Zarezadeh et al. 2018, Vogelsang 2019) and 86 % using biochar as filtration media (Reddy et al. 2014). Our results are in line with the findings from these studies. In conclusion, the removal efficiency of TSS with sand and biochar filtration may be related to that of microplastic.

Talvitie et al. (2017a) compared different advanced wastewater treatment methods in removal of microplastics (sampling size from 20 µm). The primary treatment method of membrane bioreactor removed 99.9 % of MP particles (from 6.9 MP/L to 0.005 MP/L) and rapid sand filter 97 % of MP particles (from 0.7 to 0.02 MP/L) whereas the removal efficiency of disc filter was between 40-98.5 % (from 0.5-2.0 to 0.03-0.3 MP/L). Another post-treatment method, filter pile fabric, removed 93 % of MP particles from wastewater

effluent (Mintenig et al. 2017). Simon et al. (2018) found 98 % MP removal efficiency in an average of ten WWTPs effluent discharge (Simon et al. 2018; sampling size 10-500 µm). The results from these studies for MP removal efficiency in WWTPs indicate findings similar to this study.

Concentrations for the sand and biochar samples and their variations with respect to the influent stormwater concentrations were low between rain events. It indicated that both filtration media had a relatively consistent ability to filter microplastics from stormwater runoff inside the filtration system. However, in the third rain event samples, there was 4.9 MP/L in biochar filtrated samples and 3.7 MP/L in sand filtrated samples in comparison to < 1 MP/L in the first and the second rain event samples. This indicated that high amount of MP particles in influent stormwater runoff affected the removal efficiency of the filtration system. Filtration media in general needs maintenance to prevent clogging and keeping good hydraulic capacity and hydraulic conductivity of the filters (Kandra et al. 2015). The possibly clogged filtration media in the filtration system may change the flow directions which decreases the treatment efficiency (Shammaa & Zhu 2001).

Based on a SWMM modelling study of influence of rainfall characteristics, the total TSS load is the highest after a 10-day dry period compared to a short dry period of 3 days (Gong et al. 2016). Similar results were found by Kim et al. (2004) and Lee et al. (2011) suggesting that a long dry period may indicate accumulation of solids in the catchment area. As Figure 23 indicates, there was a long dry period (cumulative precipitation 4.8 mm) three weeks before the third rain event. The preceding dry period together with the small rain event partly contributed to the high MP concentration compared to the first and second rain event (Tuomela 2017). Even though microplastic concentrations peaked after a dry period (based on the studies with TSS) other factors such as wind or washing of street may affect the total MP load during a rain event in the catchment area (Unice et al. 2013, Vogelsang et al. 2018).

According to this study, in quantitative measurements sand was a more effective filtration media for removing microplastics from stormwater runoff than biochar. However, it should be noted that the removal efficiency depends on several factors, including the intensity of the rainfall event and the dry season preceding it, as well as structural and functional changes in the catchment area and maintenance demand of the filters. With more data from rain events, the microplastic concentrations can be modelled to assess total load in the catchment area based on the modeling results from TSS concentrations (Tuomela 2017).

4 Conclusions and recommendations for future research

There has been a major knowledge gap on urban areas stormwater microplastic load and the methods to study it. This study provides novel information on the microplastic removal efficiency using a filtration system developed for filtration of stormwater runoff. Simultaneously, results were obtained on the sampling, processing and analyzing results for stormwater runoff microplastics and the quantity and quality of stormwater runoff microplastics in the urban area related to actual rainfall event.

The first objective was to design and implement a sampling method for stormwater runoff microplastics. The designed and tested sampling device worked well under the studied conditions. To ease the work load during the pre-processing phase, number of sieves can be reduced. Furthermore, the submersible pump used in this study can be replaced with a vacuum pump for sampling above ground level. However, the total amount of MP particles may increase substantially as smaller particles are included in the data analysis. Therefore, time-weighted grab sampling in smaller volumes is suggested for sampling influent stormwater runoff using sieves with mesh size below 90 µm. With these modifications, the designed sampling device is applicable for stormwater runoff microplastic sampling in future studies as well.

The universal enzymatic purification protocol for sample processing was modified during the study. However, the processing was not able to fully remove all the solids including the biochar in the samples which may have interfered the FT-IR analysis. This remark should be considered for analyzing samples with biochar in later studies. Additionally, using more subsamples for sample processing and sample analysis could decrease the margin of error in extrapolating to the total sample volume yet the consumed time and data are still limiting factors in FT-IR and data analysis as number of samples increases.

The second objective was to examine the quality and quantity of microplastics in urban stormwater runoff during a rain event. A total of three rain events were studied. The MP concentration (90-5000 µm) in influent stormwater runoff samples was between 8-66 MP/L and the average concentration was 29 MP/L. The average MP concentrations (90-5000 µm) were 1.5 MP/L for sand filtrated samples and 2.2 MP/L for biochar filtrated samples. The average size and mass (respectively) were 172 µm and 0.26 µg for influent stormwater runoff samples, 148 µm and 0.20 µg for sand filtrated samples and 142 µm and 0.19 µg for biochar filtrated samples. However, only particles between 90-1000 µm were included in this result. Furthermore, a total of 99 % of all identified particles were below 400 µm in size and 0.5 µg in mass. In urban areas, the quality of stormwater can vary based on, for example, the dry period preceding the rainfall event, the surface types of the catchment or the activities in the study area. Therefore, even local and temporal variations in microplastic concentrations in stormwater can occur. Similar remark was obtained from this study as there was high standard deviation in influent stormwater runoff microplastic quantities from three rain events.

Based on the current land use in the catchment, the calculated runoff coefficient for the catchment area was calculated to be 0.60. Based on this coefficient value and the annual precipitation rate of 655 mm in Helsinki, a total of amount of 1.7^8-1.4^9 MP particles equaling to 44-363 kg end up in the separated stormwater network in the catchment area annually. The changes in land use can shift the surface flow volume thus contributing to microplastic load from separated stormwater network to the sea.

The most common polymer types from this study were PE and PP that are both commonly used plastic types in various uses. The proportion of these polymers was over 97 % of all analyzed microplastic polymers. Other identified polymer types included PS, PET, PA, PMMA, PA and ABS yet the concentrations were one or less than one particle in litre of stormwater runoff. Furthermore, the tracking of the source of these polymers is difficult due varying use in urban areas. Nonetheless, stormwater runoff can be identified as a pathway for microplastics. Based on other studies, traffic-related polymers are the major source of microplastics in urban areas and since they were not analyzed, it may affect the total quality and quantity of microplastics from the study area. Some samples from this study will be later analyzed using another novel technique, pyrolysis-GC/MS, which gives data from tyre rubber and other black polymers that FT-IR are unable to analyze.

The third objective was to assess the removal efficiency of microplastics of two comparative fine filtration media used in the filtration system. The polymer masses indicated that biochar filtrated samples had smallest MP particles in weight in average yet the size distribution between the filtration media was not significant. Sand as a filter material was slightly more efficient alternative than biochar for removal of microplastics regarding particle number. However, both materials removed significantly microplastics from stormwater runoff during rain events: sand filtration from 95 % to 100 % and biochar from 92 % to 100 % (90-1000 µm and > 1000 µm respectively). The results from this study are promising for the selection of fine filtration media for the filtration system.

In conclusion from this study, microplastic are present in urban area stormwater runoff in significant amounts. With proper maintenance the filtration system is an effective structure for filtrating microplastics from stormwater runoff. However, assessment of the filtration performance in removal of microplastics over a longer time period requires more rain events and stormwater runoff to measure and analyze. Furthermore, studying microplastic load in snow and snow meltwater runoff is another interesting view on urban stormwater microplastics and would highlight the removal performance of the filtration system in cold climate conditions.

5 References

Act on the Organisation of River Basin Management and the Marine (1299/2004). Available in Finnish: URL[https://www.finlex.fi/fi/laki/kaannokset/2004/en20041299_20141263.pdf]

Bergmann M., Gutow L. & Klages M. 2015. Marine Anthropogenic litter. Springer Open, 447 p.

Brombach H., Weiss G. & Fuchs S. 2005. A new database on urban runoff pollution: comparison of separate and combined sewer systems. Water Science and Technology 51/2, p. 119–128.

Browne M., Crump P., Niven S., Teuten E., Tonkin A. & Galloway T. 2011. Accumulation of microplastic on shorelines woldwide: Sources and sinks. Environ. Sci. Technol. 45, p. 9175–9179.

Browne M., Niven S., Galloway T., Rowland S., & Thompson R. 2013. Microplastic moves pollutants and additives to worms, reducing functions linked to health and biodiversity. Current Biology 23, p. 2388-2392.

Carr S., Liu J. & Tesoro A. 2016. Transport and fate of microplastic particles in wastewater treatment plants. Water Research 91, p. 174-182.

City of Helsinki 2018. Storm Water Management Program. City of Helsinki, publications of the Urban Environment 2018/3.

Cole M., Webb H., Lindeque P., Fileman, E., Halsband C. & Galloway T. 2015. Isolation of microplastics in biota-rich seawater samples and marine organisms. Sci. Rep. 4, p. 4528-4535.

Dikareva N. & Simon K. 2019. Microplastic pollution in streams spanning an urbanisation gradient. Environmental Pollution 250, p. 292-299.

Dris R., Gasperi J., Rocher V., Saad M., Renault N. & Tassin B. 2015: Microplastic contamination in an urban area: a case study in Greater Paris. Enviromental Chemistry 12, p. 592-599.

Erickson A., Weiss P. & Gulliver J. 2013: Optimizing stormwater treatment practices: A handbook of assessment and maintenance. Springer Open, 337 p. ISBN 978-1-4614-4623-1

Fahrenheld N., Arbuckle K., Beni N. & Bartelt-Hunt S. 2019. Source tracking microplastics in the freshwater environment. Trends in Analytical Chemistry 112, p. 248-254.

Fassman E. & Blackbourn S. 2010. Urban runoff mitigation by a permeable pavement system over impermeable system. Journal of Hydrological Engineering, p. 475-485.

Finnish Environment Institute 2014. Urban-rural classification. URL [https://www.ymparisto.fi/en-US/Living_environment_and_planning/Community_structure/Information_about_the_community_structure/Urbanrural_classification]. Accessed 10.11.2019, published 18.3.2014 at 10:11, updated 1.10.2019 at 12:51.

Finnish Meteorological Institute 2019. Climate: Annual statistics.
URL [https://www.ilmatieteenlaitos.fi/vuositilastot]. Accessed 23.2.2020, updated 24.7.2019.

Finnish Meteorological Institute 2020. FMI Open Data.
URL [https://www.ilmatieteenlaitos.fi/havaintojen-lataus/]. Accessed 30.6.2019.

Frias J. & Nash R. 2019. Microplastics: Finding a consensus on the definition. Marine Pollution Bulletin 138, p. 145-147.

Gigault J., ter Halle A., Baudrimont M., Pascal P., Gauffre F., Phi T., Hadri H., Grassl B. & Reynaud S. 2018. Current opinion: What is a nanoplastic? Environmental Pollution 235, p. 1030-1034.

Gong Y., Liang X., Li X., Li J., Fang X. & Song R. 2016. Influence of rainfall characteristics on total suspended solids in urban runoff: A case study in Beijing, China. Water 8, p. 278-300.

Gouin T., Roche N., Lohmann R. & Hodges G. 2011. A thermodynamic approach for assessing the environmental exposure to chemical absorbed to microplastic. Environmental Science & Technology 45, p. 1466-1472.

Hakala O. 2018 Hydraulic tests of a novel stormwater filtration solution: Taivallahti waterfront master plan as a case study. Aalto University, Department of Architecture, Landscape Architecture. Master's Thesis. 92 p. Available in Finnish.

Hann S., Sherrington C., Jamieson O., Hickman M., Kershaw P., Bapasola A. & Cole G. 2018. Investigating options for reducing releases in the aquatic environment of microplastics emitted by (but not intentionally added in) products: Final Report. Report for DG Environment of the European Commission.

Hartmann N., Hüffer T., Thompson R., Hassellöv M., Verschoor A., Daugaard A., Rist S., Karlsson T., Brennholt N., Cole M., Herrling M., Hess M., Ivleva N., Lusher A. & Wagner M. 2019. Are we speaking the same language? Recommendations for a definition and categorization framework for plastic debris. Environ. Sci. Technol, p. 1039-1047.

Helsinki Map Service 2019. URL [https://kartta.hel.fi/]. Accessed 23.2.2020

Hidalgo-Ruz V., Gutow L., Thompson R. & Thiel M. 2012. Microplastic in marine environment: A review of the methods used for identification and quantification. Environ. Sci. Technol. 46, p. 3060−3075.

Horton A., Walton A., Spurgeon D., Lahive E. & Svendsen C. 2017. Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities. Science of the Total Environment 586, p. 127-141.

HSY 2015. Water networks. URL [https://www.hsy.fi/en/residents/water/water-networks/Pages/default.aspx]. Accessed 26.9.2019, last modified 26.10.2015 at 14:16.

HSY 2016. Helsingin kaupunkimittauspalvelut, alueen kunnat ja HSY, 2016. Seutukartta-aineistoa, Open data, 1.1.2018. Accessed 1.11.2019. Available in Finnish.

Johansson C., Norman M. & Gidhagen L. 2007. Spatial & temporal variations of PM10 and particle number concentrations in urban air. Environ. Monit. Assess. 127, p. 477-487.

Jovanonic B. 2017. Ingestion of microplastics by fish and its potential consequences from a physical perspective. Integrated Environmental Assessment and Management 13, p. 510-515.

Ju Young L., Hyoungjun K., Youngjin K. & Moo Young H. 2011. Characteristics of the event mean concentration (EMC) from rainfall runoff on an urban highway. Environmental Pollution 159, p. 884-888.

Kaiser D., Estelmann A., Kowalski N., Glockzin M. & Waniek J. 2019. Sinking velocity of sub-millimeter microplastic. Marine Pollution Bulletin 139, p. 214-220.

Kandasamy J., Beecham S. & Dunphy A. 2008. Stormwater sand filters in water-sensitive urban design. Proceedings of the Institution of Civil Engineers, Water Management 161, p. 55–64.

Kandra H., McCarthy D. & Deletic A. 2015. Assessment of the impact of stormwater characteristics on clogging in stormwater filters. Water Resource Management, 29, p. 1031–1048.

Kim L., Kayhanian M. & Stenstrom M. 2004. Event mean concentration and loading of litter from highways during storms. Science of the Total Environment 330, p. 101-113.

Kole P., Löhr A., Van Belleghem F. & Ragas A. 2017. Wear and tear of tyres: A stealthy source of microplastics in the environment. Int. J. Environ. Res. Public Health 2017, 14, p. 1265-1296.

Korkealaakso J., Kuosa H., Kling T., Loimula K., Wahlreos O., Holopainen S., Inkilainen S., Krebs G. 2016. Urban needs and best practices for enhanced stormwater management and quality - State-of-the-Art. VTT Technical Research Centre of Finland Ltd, University of Helsinki and Aalto University, 111 p.

Land Use and Building Act (132/1999). Available in Finnish:
URL [https://www.finlex.fi/fi/laki/kaannokset/1999/en19990132.pdf]

Lebreton L., Greer S. & Borrero J. 2012. Numerical modelling of floating debris in the world's oceans. Marine Pollution Bulletin 64, p. 653-661.

Liu F., Olesen K., Borregaard A. & Vollertsen J. 2019. Microplastics in urban and highway stormwater retention ponds. Science of the Total Environment, 671, p. 992–1000.

Löder M., Kuzcera M., Mintenig S., Lorenz C. & Gerdts G. 2015. Focal plane array detector-based micro-Fourier-transform infrared imaging for the analysis of microplastics in environmental samples. Environ. Chem. 12, p. 563–581.

Löder M., Imhof H., Ladehoff M., Löschel L., Lorenz C., Mintenig S., Piehl S., Primpke S., Schrank I., Laforsch C. & Gerdts G. 2017. Enzymatic purification of microplastics in environmental samples. Environ. Sci. Technol. 51.

Magnusson K., Eliasson K., Fråne A., Haikonen K., Hultén J., Olshammar M., Stadmark J. & Voisin A. 2016. Swedish sources and pathways for microplastics to the marine environment. IVL Swedish Environmental Research Institute. IVL report C 183.

Mani T., Hauk A., Walter U. & Holm-Burkhardt P. 2015. Microplastics profile along the Rhine River. Nature. Scientific Reports 5, 17988.

Ministry of the Environment 2016. Programme of measures for the development and implementation of the marine strategy in Finland 2016–2021. Reports of the Ministry of the Environment 5/2016, 200 p.

Mintenig S., Int-Veen I., Löder M.., Primpke S. & Gerdts G. 2017. Identification of microplastic in effluents of waste water treatment plants using focal plane array-based micro-Fourier–transform infrared imaging. Water Research 108, p. 365-372.

Molyneux P. 2017. Water-soluble synthetic polymers - Volume I: Properties and behavior. CRC Press, 1 edition, 237 p.

Murphy F., Ewins C., Carbonnier F. & Quinn B. 2016. Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment. Environ. Sci. Technol. 50, p. 5800-5808.

Myllylä Y., Kaivo-oja J. & Inkeröinen J. 2018. Foresight of reference laboratory operations in the environmental field, Research report. Prime Minister´s Office. Publications of the Government´s analysis, assessment and research activities 61/2018, 67 p. Available in Finnish.

Naeimi G. & Safavi H. 2019. Integrated stormwater and groundwater management in urban areas, a case study. International Journal of Civil Engineering, 17, p. 1281–1294.

Napper I. & Thompson R. 2016. Release of synthetic microplastic plastic fibres from domestic washing machines: Effects of fabric type and washing conditions. Marine Pollution Bulletin, 112, p. 39–45.

Nuelle M., Dekidd J., Remy D. & Fries E. 2014. A new analytical approach for monitoring microplastics in sediments. Environ. Pollut. 184, p. 161-169.

Olesen K., van Alst N., Simon M., Vianello A., Liu F. & Vollertsen J. 2018. Analysis of microplastics using FTIR imaging. Application note, Environmental. Agilent Tecnologies Inc. 2018, 6 p.

Panno S., Kelly W., Scott J., Zheng W., McNeish R., Holm N., Hoellein T. & Baranski E. 2019. Microplastic contamination in karst groundwater systems. National Ground Water Association, p. 1-8.

Peeken I., Primpke S., Beyer B., Gütermann J., Katlein C., Krumpen T., Bergmann M., Hehemann L. & Gerdts G. 2018. Arctic sea ice is an important temporal sink and means of transport for microplastic. Nature Communications 9:1505, p. 1-12.

PlasticsEurope 2019. Plastics-the Facts 2019: An analysis of European plastics production, demand and waste data.
URL [https://www.plasticseurope.org/application/files/9715/7129/9584/FINAL_web_version_Plastics_the_facts2019_14102019.pdf]. Accessed 15.11.2019.

Prata J., Costa J., Duarte A. & Rocha-Santos T. 2019. Methods for sampling and detection of microplastics in water and sediment: A critical review. Trend in Analytical Chemistry 110, p. 150-159.

Primpke S., Lorenz C., Rascher-Friesenhausen R. & Gerdts G. 2017. An automated approach for microplastics analysis using focal plane array (FPA) FTIR microscopy and image analysis. Analylytical Methods 9, p. 1499-1511.

Qiu Q., Tan Z., Wang J., Peng J. Li M. & Zhan Z. 2016. Extraction, enumeration and identification methods for monitoring microplastics in the environment. Estuarine, Coastal and Shelf Science 176, p. 102-109.

Reddy K., Asce F., Xie T. & Dastgheibi S. 2014. Evaluation of Biochar as a Potential Filtration media for the Removal of Mixed Contaminants from Urban Storm Water Runoff. Journal of Environmental Engineering 140.

Rimpiläinen L. 2017. Selection of radar based design storms. Aalto University, Department of Built Environment, Water and Environmental Engineering. Master's Thesis. 49 p. Available in Finnish.

Rochman C. & Browne M. 2013. Classify plastic waste as hazardous. Comment, Nature 494, 169-171.

Setälä O., Fleming-Lehtinen V. & Lehtiniemi M. 2014. Ingestion and transfer of microplastics in the planktonic food web. Environmental Pollution 185, p. 77-83.

Setälä O., Fjäder P., Hakala O., Kautto P., Lehtiniemi M., Raitanen E., Sillanpää M., Talvitie J. & Äystö L. 2017. Microplastics-a growing environmental risk. SYKE Policy Brief. Views on Environmental Policy, 21.3.2017.

SFS-EN 10204. 2004. Metallic products. Helsinki: Finnish Standards Association SFS, 12 p.

Shammaa Y. & Zhu D. 2001. Techniques for controlling total suspended solids in stormwater runoff. Canadian Water Resources Journal 26/3, p. 359-275.

Simon M., van Alst N. & Vollertsen J. 2018. Quantification of microplastic mass and removal efficiencies at wastewater treatment plants applying Focal Plane Array (FPA)-based Fourier Transform Infrared (FT-IR) imaging. Water Research 142, p.1-9.

Song Y.K., Hong S.H., Jang M., Han G.M., Rani M., Lee J. & Shim W.J. 2015. A comparison of microscopic and spectroscopic identification methods for analysis of microplastics in environmental samples. Marine Pollution Bulletin 93, p. 202-209.

Talvitie J., Heinonen M., Pääkkönen J-P., Vahtera E., Mikola A., Setälä O. & Vahala R. 2015. Do wastewater treatment plants act as a potential point source of microplastics? Preliminary study in the coastal Gulf of Finland, Baltic Sea. Water Science & Technology 72, p. 1495-1504.

Talvitie J., Mikola A., Koistinen A. & Setälä O. 2017a. Solutions to microplastic pollution – Removal of microplastics from wastewater effluent with advanced wastewater treatment technologies. Water Research 123, p. 401-407

Talvitie J., Mikola A., Setälä O., Heinonen M. & Koistinen A. 2017b. How well is microlitter purified from wastewater? - A detailed study on the stepwise removal of microlitter in a tertiary level wastewater treatment plant. Water Research 109, p. 164-172.

Talvitie 2018a. Doctor of Science. Finnish Environment Institute. Personal communication, August 2018.

Talvitie J. 2018b. Wastewater treatment plants as pathways of microlitter to the aquatic environment. Aalto University, Department of Built Environment, Water and Environmental Engineering. Doctoral Thesis. 106 p.

Tan X., Liu Y., Zeng G., Wang X., Hu X., Gu Y. & Yang Z. 2015. Application of biochar for the removal of pollutants from aqueous solutions. Chemosphere 125, p. 70-85.

Thompson R., Olsen Y., Mitchell R., Davis A., Rowland S., John A., McGonigle D. & Russell A. 2004. Lost at Sea: Where Is All the Plastic? Science 304.

Tuomela C. 2017. Modelling Source Area Contributions of Stormwater Pollutants for Stormwater Quality Management. Aalto University, Department of Built Environment, Water and Environmental Engineering. Master's Thesis. 39 p.

UNEP 2016. Marine plastic debris & microplastics – Global lessons and research to inspire action and guide policy change. United Nations Environment Programme, Nairobi.

Unice K., Kreider M. & Panko J. 2015. Comparison of tire and road wear particle concentrations in sediment for watersheds in France, Japan, and the United States by quantitative pyrolysis GC/MS analysis. Environ. Sci. Technol. 47, p. 8138−8147.

Vogelsang C., Lusher A., Dadkhah M., Sundvor I., Umar M., Ranneklev S., Eisvoll D. & Meland S. 2018. Microplastics in road dust-characteristics, pathways and measures. Norwegian Institute for Water Research. 171 p.

Water Services Act (119/2001). Available in Finnish:
URL [https://www.finlex.fi/fi/laki/kaannokset/2001/en20010119_20150979.pdf]

Wright S., Thompson R. & Galloway T. 2013. The physical impacts of microplastics on marine organisms: A review. Environmental Pollution 178, p. 483-492.

Zarezadeh V., Lung T., Dorman. T. Shipley H. & Giacomoni M 2018. Assessing the performance of sand filter basins in treating urban stormwater runoff. Environ Monit Assess 190, p. 697-711.

Appendices

Appendix A. (Sub)sample volumes and share of total volume used in the processing.

Appendix B. Biochar under microscope.

Appendix C. (Sub)sample volumes and share of total volume after (sub)sample filtration for the analysis

Appendix D. Reference polymers and the corresponding wavenumbers.

Appendix E. Colour-coded polymers in polymer library.

Appendix F. 30x30 optical image mosaic and derived image of analyzed MP particles.

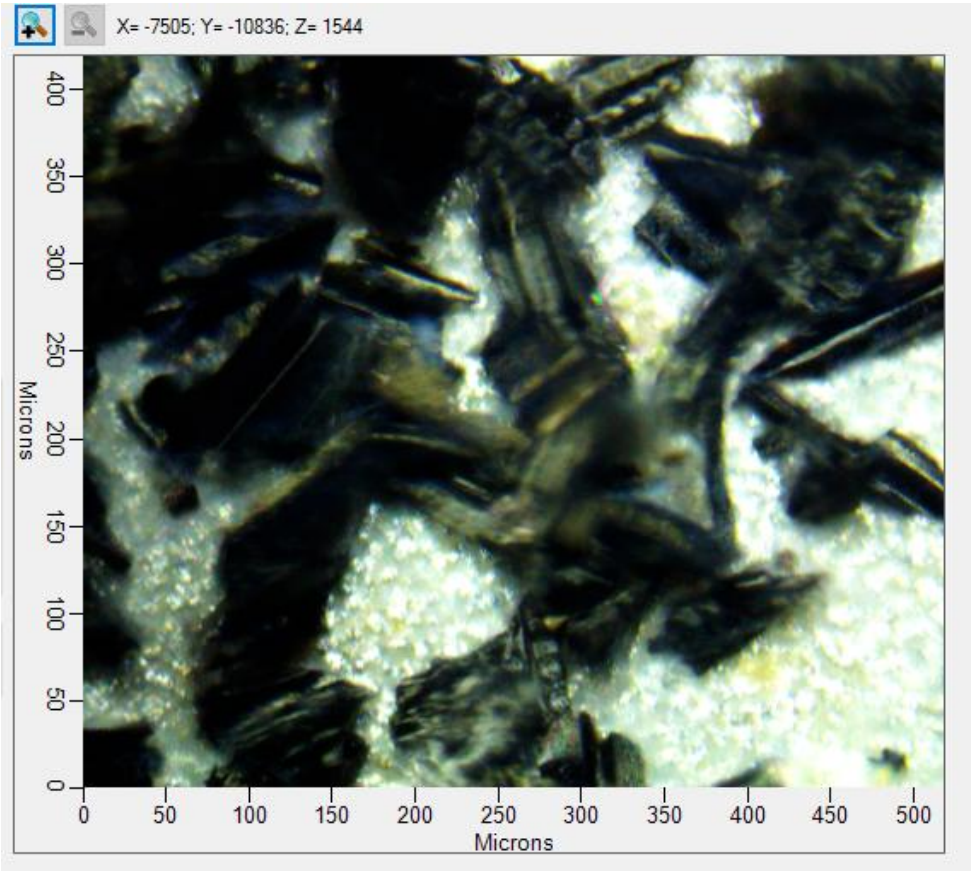
Appendix G. MP particles from 1000 µm and 4000 µm sieves of influent stormwater.

Appendix H. Rain intensity and water level at filtration system stormwater runoff inlet pipe and effluent discharge points during sampling days.

Appendix A. (Extrapolated) subsample volumes and share of total volume used in the processing. The volume (in litres) indicates the amount of sample water used for the (sub)sample.

	Event 1		Event 2		Event 3	
Sample	Litres	Share	Litres	Share	Litres	Share
Raw 1	78	15 %	490	17 %	102	12 %
Raw 2	78	15 %	490	17 %	102	12 %
Raw 3	78	15 %	490	17 %	102	12 %
FS 1	259	100 %	1436	100 %	34	8 %
FS 2	-	-	-	-	34	8 %
FS 3	-	-	-	-	34	8 %
BC 1	89	19 %	390	15 %	162	21 %
BC 2	89	19 %	390	15 %	162	21 %
BC 3	89	19 %	390	15 %	162	21 %

Appendix B. Biochar under Cary 620 microscope (Agilent Technologies).



Appendix C. (Extrapolated) volumes and share of total volume after (sub)sample filtration for the analysis. The (sub)sample volumes are combined (in comparison to Appendix A).

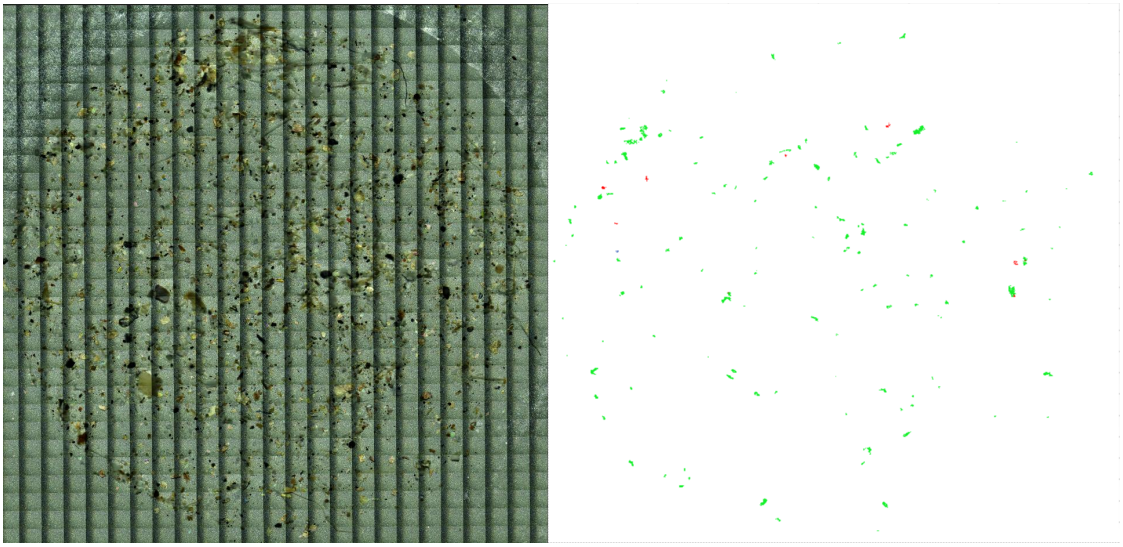
	Event 1		Event 2		Event 3	
Sample	Litres	Share	Litres	Share	Litres	Share
Raw	25	5 %	12	2%	17	2 %
FS	259	100 %	1436	100 %	101	24 %
BC	28	6%	151	6 %	166	22 %

Appendix D. Reference polymers and the corresponding wavenumbers analyzed with siMPle.

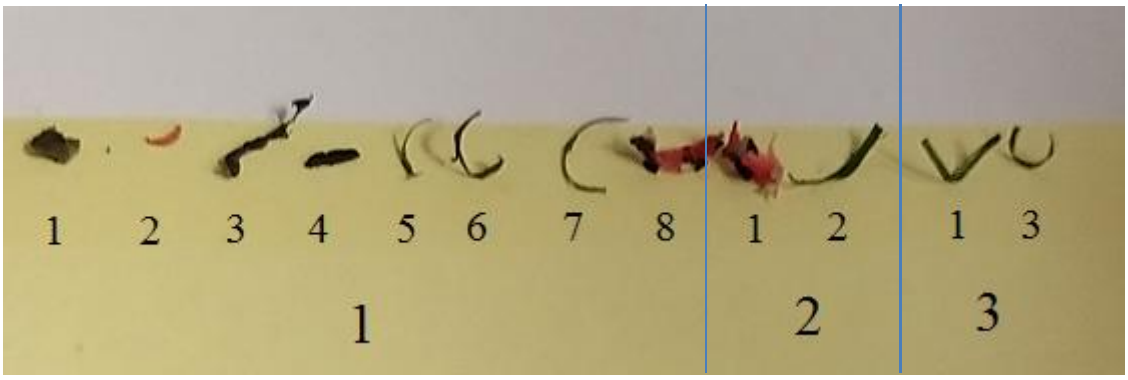
MaterialGroup 1	Wavenumber 1	**MaterialGroup 2**	Wavenumber 2
PA	PA 66 2	**Cellulose**	Cotton 1
PA	PA 66 3	**Cellulose**	Cotton 3
PA	PA 66 5	**Cellulose**	Cotton 10
Protein	Wool 3	**PU**	PU 3
Protein	Wool 5	**PU**	PU 5
Protein	Wool 8	**PU**	PU 10
PET	PET 1	**PVC**	PVC-U 1
PET	PET 7	**PVC**	PVC-U 4
PET	PET 8	**PVC**	PVC-U 6
PE	HDPE 2	**PP**	PP-R 1
PE	HDPE 4	**PP**	PP-R 3
PE	HDPE 6	**PP**	PP-R 4
PS	PS 3	**PP**	PP Ox 5
PS	PS 7	**PMMA**	PMMA 2
PS	PS 10	**PMMA**	PMMA 6
ABS	ABS 1	**PMMA**	PMMA 9
ABS	ABS 3	**Protein**	Silk 2
ABS	ABS 8	**Protein**	Silk 7
Protein	Skin 1	**Protein**	Silk 10
Protein	Skin 3	**PAN**	Polyacryl fiber
Protein	Skin 9		

Appendix E. Colour-coded polymers in polymer library.

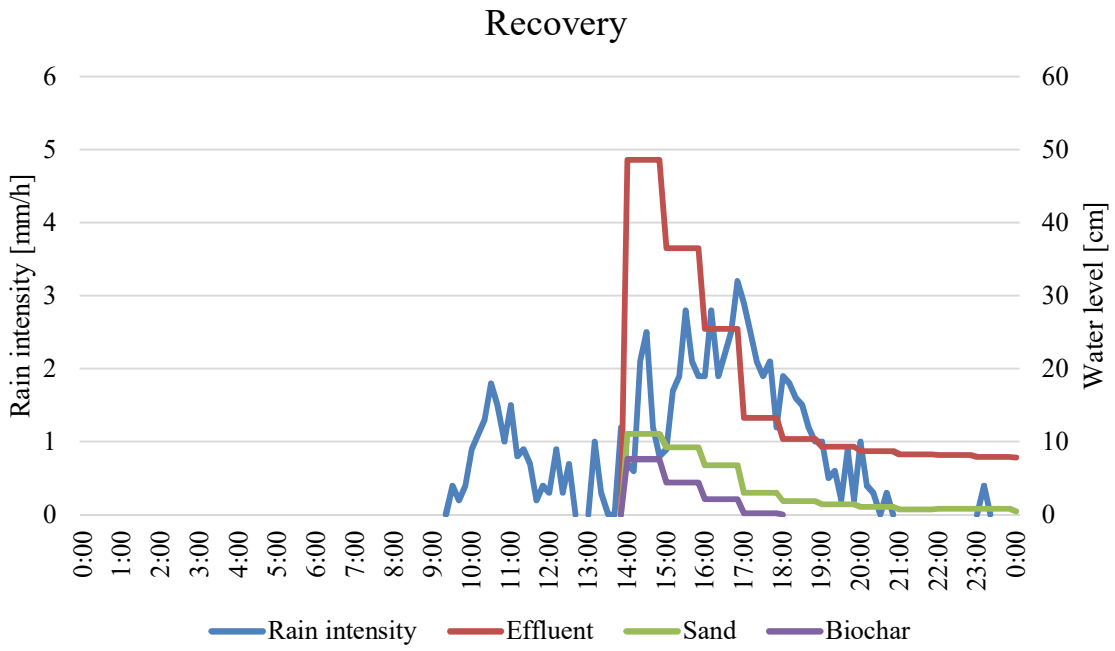
Appendix F. Left: 30x30 optical image mosaic. Right: image analysis software (siMPle) derived image of analyzed MP particles.

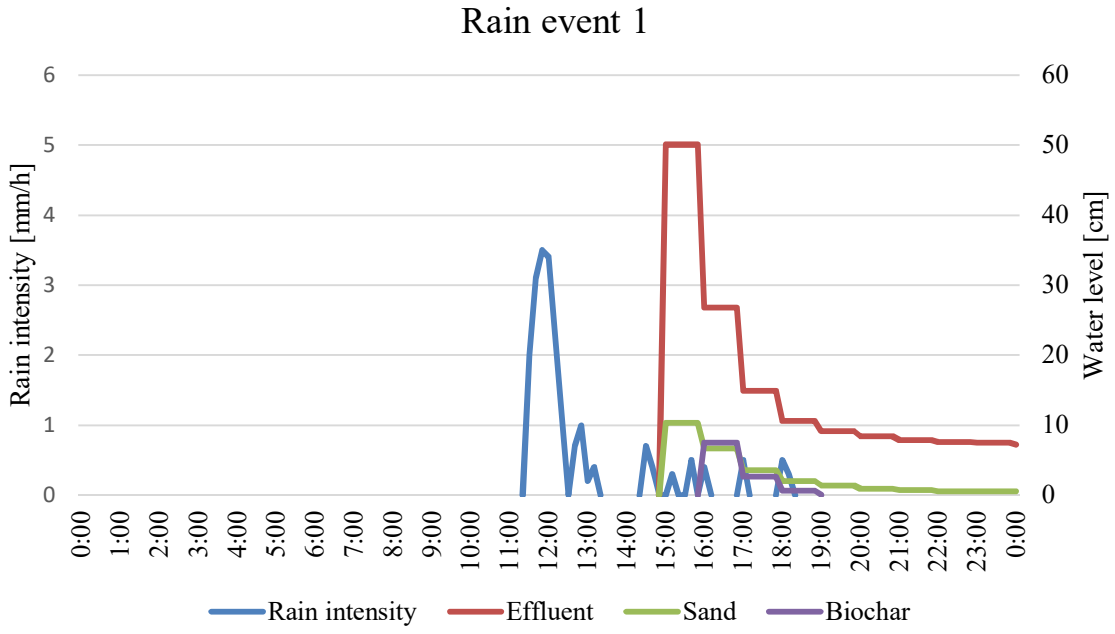


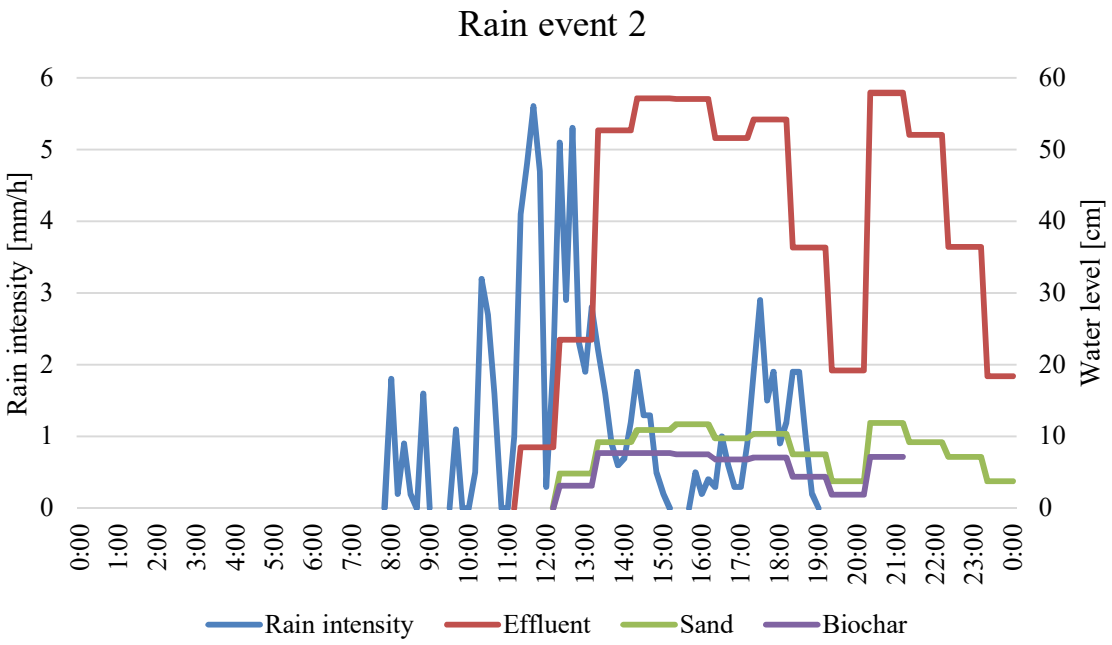
Appendix G. MP particles from 1000 µm and 4000 µm sieves of influent stormwater. Vertical lines divide the rain events 1-3.



Appendix H. Rain intensity and water level at filtration system stormwater runoff inlet pipe and effluent discharge point during sampling days (rain intensity [mm/h], water level [cm]). No water level data available for rain event 3.






Rain event 2
Rain intensity [mm/h]
Water level [cm]
0
1
2
3
4
5
6
0
10
20
30
40
50
60
0:00
1:00
2:00
3:00
4:00
5:00
6:00
7:00
8:00
9:00
10:00
11:00
12:00
13:00
14:00
15:00
16:00
17:00
18:00
19:00
20:00
21:00
22:00
23:00
0:00
Rain intensity
Effluent
Sand
Biochar