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Occurrence and Fate of Emerging micropollutants in Stormwater Retention Ponds

pharmaceuticals and microplastics

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OCCURRENCE AND FATE OF EMERGING MICROPOLLUTANTS IN STORMWATER RETENTION PONDS

PHARMACEUTICALS AND MICROPLASTICS

BY FAN LIU

DISSERTATION SUBMITTED 2019



AALBORG UNIVERSITY DENMARK

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Dissertation submitted in September 2019

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LIST OF SCIENTIFIC PAPERS

- I. *Liu, F.*, Nielsen, A.H., Vollertsen J. Sorption and degradation potential of pharmaceuticals in sediments from a stormwater retention pond. *Water* 2019 (a), 11, 526. doi:10.3390/w11030526
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- III. *Liu, F.*, Vianello, A., Vollertsen, J. Retention of microplastics in sediments of urban and highway stormwater retention ponds (*Submitted to Environmental Pollution*)
- IV. Liu, F., Nord, N.B., Bester, K., Vollertsen, J. How well can microplastics be removed from the treated wastewater? A pilot study of biofilters polishing treatment plant effluents (Manuscript. The title is tentative)

OTHER SCIENTIFIC PAPERS AND REPORTS

- I. Vingwe, E., *Liu, F.*, Remmen, A. An investigation of plastic waste in Aalborg municipality what can be learned from the bottom of a waste bin? (*Submitted to Waste Management*)
- II. Olesen, K.B., Alst, N.V., Simon, M., Vianello, A., *Liu, F.*, Vollertsen, J. Analysis of microplastics using FTIR imaging -- Identifying and quantifying microplastics in wastewater, sediment and fauna. Application Note, Environmental, Agilent Technologies, pp. 6

ENGLISH SUMMARY

Urbanization and global climate change have fundamentally affected the urban water cycle over the past decades. The subsequent more extensive urban surface runoff is exceeding the conveyance capacity of the earlier built drainage systems with increasing frequency. To ease this hydraulic transportation pressure during wet weather, a large amount of untreated wastewater mixed with stormwater is discharged into the receiving environment via combined sewer overflows. In addition, sewer misconnections, pipeline leakages, and illicit connections are further intensifying the pollution load from sewer systems to the environment in dry weather.

Stormwater retention ponds, one of most common structural best management practises (BMPs), are widely applied by the urban drainage system. The implementation was partly aimed to reduce the hydraulic loading, and partly to control the storm-induced pollution to the receiving environment. But till date, the performance of such pond with respect to pollution treatment is still mainly studied for 'traditional' pollutants like metals and nutrients. Even with the great concern of emerging micropollutants, little is known about their occurrence and fate in such pond systems.

To fill the knowledge gap on the treatment performance of stormwater retention ponds with respect to emerging micropollutants, this PhD study chose pharmaceuticals and microplastics to present the group of soluble and particulate emerging micropollutants, and investigated their fate in stormwater retention ponds. Furthermore, an alternative treatment to the stormwater retention pond, or a further stormwater polishing tool — a biofilter, was also evaluated for the retainment of microplastics.

The fate of selected pharmaceuticals in the sediment-water system of stormwater ponds was found to be governed by a combined process of sorption and degradation. Despite that these two processes showed preferred oxygen and pH condition specific for the different compounds, the overall removal was significant. Sulfamethoxazole, naproxen, fenofibrate, and furosemide were removed by 99.6%, 98.6%, 96.8%, and 76%, respectively. Carbamazepine gained relatively less retainment (64%), but compared to a conventional sewage treatment, this removal efficiency was still promising.

The fate of microplastics in the studied stormwater retention ponds was more complex, and their occurrence and distribution between the water column and sediment phase from the same pond were governed by different factors. While land use in the catchment of the ponds had significant impact on the polymer distribution, particle size, and mass in the water phase, a similar dependency could not be found for their sediments. The microplastic accumulation in pond sediments was positively associated with the hydraulic loading of the pond, and to a lesser degree with the sediment organic matter content. Another observation was that ponds serving a highway catchment had the least microplastic pollution, while studied ponds serving industrial or commercial land use had the most. It should be note that the applied microplastic detection method (μ FTIR imaging) in this PhD study was not able to quantify car tyre wear, a plastic debris

which accounts for an important portion in the entire plastic pollution, particularly in urban and highway areas. This leaves the microplastic mass balance in urban and highway areas unclosed. Nevertheless, this PhD study points in the direction that a retaining efficiency of roughly 66% by the stormwater retention pond can be expected.

The studied biofilter lowered the microplastic concentration in the wastewater effluent (79-89%) with which it was loaded, with a tendency to retain larger and heavier particles. However, the microplastic retainment was not enhanced by the multi-layer design of the filter, since most of the removal happened in the top layer.

Overall, this PhD study contributed to the knowledge on the occurrence and fate of two groups of emerging micropollutants: pharmaceuticals and microplastics in stormwater retention ponds. The findings of the present study, particularly in respect of microplastics, provided some very first detailed results on the occurrence and distribution of the investigated environmental issue in stormwater-related environments. The results can further be applied to support the design of treatment solutions for urban and highway stormwater.

DANSK RESUME

Urbanisering og globale klimaforandringer har drastisk påvirket den urbane vandcyklus igennem de sidste årtier. Den medfølgende stigning i overfladeafstrømning overstiger transportkapaciteten af de eksisterende afløbssystemer med øget frekvens. For at lette den hydrauliske belastning under en regnhændelse, bliver store mængder af urenset spildevand blandet med regnvand udledt til en recipient gennem overløbsbygværker. Fejlkoblinger i afløbssystemet, brud på rør og ulovlige tilkoblinger øger yderligere forureningsbelastningen fra kloaksystemet til nærmiljøet under tørvejr.

Regnvandsbassiner, en af de mest almindelige driftspraksisser, er meget benyttet i urbane afløbssystemer. Implementeringen er delvist rettet mod at minimere den hydrauliske belastning og delvist mod at kontrollere regnvejrsbetinget forurening til recipient. Indtil nu er rensevirkningen af regnvandsbassinerne primært blevet undersøgt i forhold til 'traditionelle' foreningskilder så som metaller og næringsstoffer. På trods af den voksende bekymring omkring mikroforurenere, vides meget lidt omkring deres forekomster og hvad der sker med dem i regnvandsbassiner.

For at udbygge den eksisterende viden omkring rensevirkningen af regnvandsbassiner i forholdt til den voksende fremkomst af mikroforurenere, er der i dette Ph.d.-studium valgt at fokusere på medicinrester og mikroplastik til at repræsentere opløst og partikulær mikroforurening, og undersøge deres skæbne i tilbageholdelsesbassiner. Herudover er en alternativ rensemetode i stedet for regnvandsbassinerne eller i kombination hermed – et biofilter, blevet evalueret i forhold til tilbageholdelsen af mikroplastik.

De udvalgte medicinresters skæbne i sediment-vandsystemet i regnvandsbassiner var styret af en kombineret proces af sorption og nedbrydning. På trods af at disse to processer viste specifikke fortrukne ilt- og pH-betingelser for de forskellige stoffer, var den generelle fjernelse signifikant. Sulfamethoxazole, naproxen, fenofibrate og furosemide blev fjernet med hhv. 99,6%, 98,6%, 96,8% og 76%. Carbamazepine's fjernelsesgrad var relativt lavere (64%), men sammenlignet med traditionel spildevandsrensning var effektiviteten stadig lovende.

Skæbnen for mikroplastik i regnvandsbassiner var mere kompleks og deres fremkomst, samt fordeling mellem vandsøjle og sediment, fra samme bassin var styret af forskellige faktorer. Arealanvendelse i oplandet havde signifikant påvirkning på polymerfordelingen, partikelstørrelsen og massen i vandsøjlen, hvorimod der ikke kunne findes en lignende sammenhæng for sedimentet. Mikroplastikakkumuleringen i sedimentet var positivt forbundet med den hydrauliske belastning af regnvandsbassinet og i en mindre grad også sedimentets organiske indhold. Det blev også observeret at bassiner med afstrømning primært fra motorvej havde mindst mikroplastik forurening, hvorimod bassiner ved arealer anvendt til industri og erhvervs havde størst forekomst af mikroplastik. Det skal bemærkes at den anvendte mikroplastikdetektionsmetode (µFTIR imaging) til dette Ph.d.-studium, ikke kunne detektere gummi f.eks. fra slid på bildæk, en plastik rest som udgør en væsentlig del af den totale plastikforurening, specielt på motorveje og i urbane sområder. Dette efterlader mikroplastikmassebalancen for bebyggede områder og omkring motorvejene åben. Alligevel peger dette Ph.d.-studium i retning af at en tilbageholdelsesgrad på omkring 66% kan forventes for regnvandsbassiner.

Det undersøgte biofilter mindskede mikroplastikkoncentrationen i renset spildevand (79-89%) med en tendens til at tilbageholde større og tungere partikler. Tilbageholdelsesgraden blev ikke øget ved et design af filteret med flere lag, da størstedelen af fjernelsen skete i det øverste lag.

Alt i alt har dette Ph.d.-studium tilført viden omkring forekomsten og skæbnen af to grupper af voksende mikroforurenere: medicinrester og mikroplastik i regnvandsbassiner. Resultaterne fra dette studium, specielt i forhold til mikroplastik, er nogle af de første detaljerede resultater omkring forekomst og fordeling af de undersøgte miljøforureninger i regnvandsbassiner. Ydermere kan resultaterne anvendes til designoptimering af renseteknologier til regnvand fra motorveje og urbane områder.

中文摘要

城市化和全球气候变化在过去几十年来已经从根本上改变了城市水循环。随之而来的大量城市地表径流正在以不断增长的频率超出早期修建的排水系统的运载能力。为了缓解这种水利运输负荷,大量未经处理的污水在降雨时通过与雨水混合的方式直接被排入环境。此外,下水管道连接错误,管道泄漏和非法连接在非降雨时进一步加剧了下水管道对环境的污染负荷。

雨水滞留池, 作为一种最常见的最佳管理实践(BMPs)之一, 已被广泛应用在城市排水系统。该实施一部分是为了减少已有排水管网的水力负荷,一部分是控制以雨水为介质的环境污染。但目前为止,雨水滞留池在污染控制的性能仍只保留在以"传统污染物"为研究对象,如重金属和一些营养物。即便新型微污染物已成为人们的着重关注对象,但它们在此类池塘系统中的出现,迁移和转化还知之甚少。

为了填补有关雨水滞留池对新型微污染物处理性能的知识,本博士选择药物和微塑料来 分别代表可溶性和颗粒状新型微污染物,并研究它们在雨水滞留池中的迁移和转化。此 外,一种可替代雨水滞留池的雨水处理工具 — 生物过滤器,在为塑料滞留方面也给予 了评估。

研究结果表示,选定药物在雨水滞留池中的迁移受吸附和降解共同控制。尽管不同化合物对这两种过程中的含氧条件和 pH 值表现出不同的偏好,但总体去除率是比较高的。磺胺甲基异恶唑,萘普生,非诺贝特和呋塞米的去除率分别为 99.6%,98.6%,96.8%, 76%。 卡马西平的去除率相对较低(64%),但是与常规污水处理相比,这种去除效率仍然很可观。

微塑料在其中的迁移和转换相对来说较为复杂。在同一滞留池中,水相和沉积相中微塑料的出现,浓度和分布受不同因素控制。尽管滞留池集水区的土地使用类型对水相中的聚合物分布,颗粒大小和质量有显著影响,但在沉积相中却没有发现类似的依赖性。确切来说,沉积相中微塑料的积累与滞留池的水力负荷正相关,而与沉积物的有机质含量关系较小。总体来说,微公路积水区服务的滞留池微塑料污染最低,而为工业或商业用地服务的污染最高。值得注意的是,本博士研究所采用的微塑料检测方法(微傅里叶变换红外成像 — μFTIR imaging)无法量化汽车轮胎磨损。而这种塑料类型在整个塑料污染中占有中有地位,特别是城市和公路地区。这使得城市与公路领域的微塑料质量平衡无法实现。但该博士研究指出,雨水滞留池对微塑料的滞留效率可估计微 66%。

所研究的生物过滤器降低了废水中微塑料浓度(79-89%),并且更倾向于滞留大直径、 大质量的颗粒。但是,由于大部分的去除效果都发生在顶层,因为过滤器的多层设计并 没有显著提高微塑料的滞留能力。

总体而言,这项博士研究为两种具有代表性的新型微污染物:药物和微塑料在雨水滞留 池中的发生和转换提供了有力知识。本研究的成果,特别在微塑料方面,提供了其在雨 水相关环境中的出现和分布的非常详细的初步结果。其结果可进一步用于支持城市和公路雨水处理方案的设计。

PREFACE

This thesis has been submitted for assessment in partial fulfilment of the PhD degree. As part of the assessment, co-author statements have been made available to the assessment committee and are also available at the Faculty.

This PhD was granted by Chinese Scholarship Council, and was carried out at Aalborg University, Department of Civil Engineering, Division of Water and Environment, in the period from September 2015 to September 2019. The PhD included a cooperation with Arhus University, Department of Environmental Science. The joint study resulted in a manuscript (**Paper IV**), which is ready to submit for publication.

This thesis is based on two published scientific papers (**Paper I, II**), and two scientific manuscripts (**Paper III, IV**). Contents of the papers are briefly discussed in the extended summary of the thesis. Additional details are given in the papers and manuscripts.

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Doing a PhD is though challenging, but not that much when you have the right team, plus the best supervisor on the whole planet. My secret completing the PhD: don't be stressed about the stress, because it's simply just a "must-have" in this process. Face it, deal with it, play with it, and enjoy it.

Deep gratitude first and foremost goes to my supervisor, Professor Jes Vollertsen (usually he does not like to be called so formally). Working with him is always full of fun, optimism, energy, inspirations, caring, and of course, teasing. His magic is, while giving you lots of freedom, he always finds the right moment and perfect way to be there for you. Try not just being good, but also nice and fun. This probably is the most valuable thing I learned from him (my PhD is of course valuable as well). The four years here are among my most precious, and will be forever remembered.

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CHAPTER 1. INTRODUCTION

Urbanization, a complex process aimed to transform the natural landscape into urban and industrial ones (Antrop, 2000), has been one of the fundamental characteristics of civilization. From the late 19th century, urbanization had exponential growth (Antrop, 2004). By 2050, 70% of the world's population is expected to live in urban areas (United Nations Population Division, 2008), which requires continuous land developing and converting.

A wide range of environmental challenges has been brought up along with the urbanization, since the change of the natural landscape has direct impacts on the biochemical, physical, and hydrological systems (Jacobson, 2011). Among such, land imperviousness is one of the most significant changes resulting from the urbanization (Fletcher et al., 2013). The impervious cover fundamentally changes the hydrological cycle by attenuating the surface water, or groundwater infiltration (Figure. 1-1) (Schueler, 1994), leading to larger and more intense urban surface runoff, which subsequently requires larger conveyance system dimensions and more stormwater storage volume (Figure. 1-2) (Hvitved-Jacobsen et al., 2010; Jacobson, 2011; Saraswat et al., 2016).



Figure 1-1. Influence of the urbanization on the water cycle

Along with the city expansion, drainage systems were also developed to manage the interaction between human activity and the natural water cycle (Butler and Davies, 2004). Historically speaking, most of the cities in the early urbanization applied combined sewer system, where stormwater and wastewater are drained in the same pipe (Burian and Edwards, 2002). Combined sewer systems are still widely in use in many of the world's cities, such as London, Paris, Copenhagen, New York, Maine, Philadelphia, and many other urbanized areas all over the world (Gasperi et al., 2010). However, during a heavy rainfall, these earlier built sewer systems cannot meet the transportation needs required by the large stormwater volume accumulated in a short time. Hence to release the hydraulic loads and prevent downstream flooding, an overflow (combined sewer overflow – CSO) occurs, resulting in a mixture of untreated wastewater and stormwater being discharged into the receiving environment (Launay et al., 2016). The ongoing changes in the world's climate are intensifying this problem in many cities, making the drainage systems exceed their design capacity more often.



Figure 1-2. Hydrograph comparison before and after urbanization

Many modern cities have begun to install separated sewer systems to avoid CSOs by draining the stormwater separately from the wastewater. However, this approach does not solve all the stormwater-related pollution. Contaminations have been evidenced in urban and highway stormwater runoff (SWR) since the early 1990s as a result of anthropogenic activities (Pitt et al., 1995). The occurrence of such storm-induced contaminations covers a wide range of both dissolved and particulate pollutants including pesticides, polynuclear aromatic hydrocarbons (PAHs), biocides, heavy metals, etc (Pitt et al., 1995). In addition hereto, misconnections, that is cross-connections between the stormwater and wastewater pipes, as well as leakage between pipes do also contribute to the pollution discharge to the environment (Revitt and Ellis, 2016; Beckers et al., 2018). For substances which are efficiently retained in wastewater treatment plants, such as microplastics, this can lead to the misconnected wastewater being a, if not the, major source of such pollutants in the receiving environment (Bollmann et al., 2019).

1.1. WET WEAHTER POLLUTANT DISCHARGES

Wet weather pollutant discharges occur from separate as well as combined systems. For combined systems, the pollutants reach the aquatic environment via CSOs, a source which has been of particular concern and investigated since the 1970s (Suárez and Puertas, 2005; Gasperi et al., 2010). The origin of pollutants in CSOs are the urban surface runoff connected to the sewers and wastewater from households and industries, which are mixed into the combined flow. For separate systems, the pollutants originate from the urban surfaces, but also from misconnected wastewater entering storm sewers (Hoes et al., 2009). It has been evidenced that wet-weather discharges are one of the major causes of the long-term persistence of low-quality receiving waters (Hvitved-Jacobsen et al., 2010; Gasperi et al., 2012). The potential effects of wet weather discharges are listed in Table 1-1.

Type of pollutant	CSO	SWR
Sediments	Deposition in flowing water, close to the inlet in stagnant waters	Deposition in flowing water, close to the inlet in stagnant waters

Biodegradable organic matter	Reduction in dissolved oxygen (DO); Excessive microbial growthMinor importance	
Nutrients, N and P	Eutrophication	Eutrophication
Heavy metals	Acute and accumulative toxic effects both in the water phase and sediments	Acute and accumulative toxic effects both in the water phase and sediments
Pathogenic microorganisms	Effects of pathogenic bacteria, viruses, and protozoa Minor importance	
Gross solids	Aesthetic deterioration	Minor importance
Organic Acute and accumulative toxic effects both in the water phase and sediments		Acute and accumulative toxic effects both in the water phase and sediments

Table 1-1. Potential effects of wet weather discharges (reprinted from Hvitved-Jacobsen et al., 2010)

1.2. DRY WEATHER POLLUTANT DISCHARGES

Separate sewers with misconnected wastewater will discharge wastewaters during dry weather. These dry-weather discharges can furthermore come from illegal dumping of wastewater or from wastewater sewer leakages (Walker et al., 1999; Yi et al., 2017), resulting a higher pollution concentration than that of wet weather because of the lack of dilution (Schiff and Tiefenthaler, 2003; Weston et al., 2009; Yin et al., 2017). In many cases, dry weather discharges have significant influence on the annual pollution load from a separate sewer (Deffontis et al., 2013).

In conclusion, both the wet and dry weather pollution discharges are somewhat related to the wastewater, either with dilution via CSOs or without dilution, but with a smaller discharge volume, via misconnected or illegally connected wastewater. Compared to the traditional macro-pollutants (nutrients, organic matter, total suspended solids, etc), organic micropollutants are of particular concern, because the fate of these compounds in the environment is highly dependent on their properties like hydrophobicity, solubility and volatilization (Vezzaro et al., 2011). And even a trace amount of exposure is able to cause long-term toxicity to biota including human. Eriksson et al. (2005) reported that stormwater runoff could contain at least 656 organic micropollutants, typically including pharmaceuticals, personal care products, biocides, pesticides, artificial sweeteners, and iodinated X-ray contrast agents, PAHs, etc. (Launay et al., 2016; Al Aukidy and Verlicchi, 2017; Becouze-Lareure et al., 2019).

1.2.1. SOLUBLE EMERGING POLLUTANT – PHARMACEUTICALS

The pharmaceutically active compounds (PhACs), is a group of substances that includes antibiotics, hormones, beta-blockers, lipid regulators, painkillers, etc. This group of compounds is of increasing concern when discharged to the environment, and for example the European commission has recently defined a strategic approach to manage this issue (European Commission, 2019). It is estimated that 3000 types of pharmaceutical ingredients are used in Europe (Ternes and Joss, 2006). The induction of PhACs into the environment is mainly via human metabolism (Al Aukidy et al., 2012). In fact, only part (generally 55-80%) of the compounds can be metabolized by the human body. Both the metabolized and unmetabolized compounds will be discharged through the urine, or partially the faces, and end up in the wastewater (Jjemba, 2006; Lienert et al., 2007), most of which will be treated at a wastewater treatment plant (WWTP).

Unfortunately, traditional WWTPs are not sufficient to remove all the received PhACs (Boyd et al., 2003; Roberts et al., 2016; Li et al., 2016; Tran et al., 2018). A 2-years sampling campaign monitoring the fate of 43 pharmaceutical compounds in three conventional WWTPs in Spain revealed that most of the substances were not completely eliminated (Jelic et al., 2011).

Thus, the occurrence of PhACs, both the parent compounds and the metabolized forms have been widely detected in surface waters (Spongberg et al., 2011; Wang et al., 2019; Galindo-Miranda et al., 2019). Because these emerging pollutants cause a wide range of physicochemical and biological impacts, posing risks to the aquatic fauna, their presence in the water bodies cannot be ignored (Okuda et al., 2009; Jelic et al., 2011; Tran et al., 2018).

1.2.2. PARTICULATE EMERGING POLLUTANT - MICROPLASTICS

Millions of tons of plastics are produced every year (PlasticsEurope, 2017), and plastic debris has become a top emerging environmental issue (Sutherland et al., 2010)(Eerkes-Medrano et al., 2015). Currently, an estimation of 4.8-12.7 million metric tons of plastic is entering the sea every year (Jambeck et al., 2015). Microplastics (MPs) often defined as < 5 mm in diameter (Thompson et al., 2009), has been of particular concern, and on the scientific, political, and public agenda. The occurrence of MPs has been thoroughly documented in the marine environment, including its wildlife such as deep-sea organisms (Taylor et al., 2016) and zooplankton (Cole et al., 2013). Some recent studies even found its presence in indoor air (Vianello et al., 2019), snow from the Alps to the Arctic (Bergmann et al., 2019), and remote mountains and islands (Ríos et al., 2018; Allen et al., 2019).

MPs can be grouped into two catalogues: primary MPs and secondary MPs. The former are the ones intentionally manufactured into this size, to facilitate the effectiveness of abrasion and cleaning. Typical examples are the microbeads and micro-pellets added in personal care products (Gatidou et al., 2019). Secondary MPs are formed from the breakdown and fragmentation of large plastic debris (Panel and Chain, 2016). Compared with macroplastics, MPs have a higher surface-volume ratio (Strungaru et al., 2019). This is particularly important when assessing the toxicity of MPs to aquatic organism since the higher ratio not only holds more sorption sites to attract

organic micropollutants (Frias et al., 2010), but also has the tendency to release more additives in the environment. These additives, made to enhance the polymer properties and prolong the usage life, including plasticizers, antioxidants, heat stabilizers, and slip agents, are able to migrate from the polymer and enter the biota, water environment, soil, and potentially even the food chain (Samsonek and Puype, 2013; Koelmans et al., 2014; Puype et al., 2015; Hahladakis et al., 2018).

Both freshwater and terrestrial environments are subjected to MP pollution (Horton et al., 2017). Wastewater discharges have been identified as a significant point source in these environmental compartments. This is partly due to the incomplete MP removal in most of the conventional WWTPs (Carr et al., 2016; Simon et al., 2018; Magni et al., 2019), and partly due to the raw wastewater discharge through CSOs and misconnected wastewater (Bollmann et al., 2019).

1.3. STORMWATER MANAGEMENT AND TREATMENT

To control and mitigate the environmental impacts from CSOs and SWR, best management practices (BMPs), also known as sustainable urban drainage systems (SUDs), have been widely implemented. BMPs can be divided into non-structural and structural approaches. The former is a group of joint actives by authorities and public, including regulations, rules, and educations. The latter is an engineering approach, aimed to mimic the natural ecological systems (Hvitved-Jacobsen et al., 2010). This group of solutions include constructed wetlands, wet ponds, sand filters, infiltration basins, and swales, etc. But in practice, the specific approach is strongly dependent on the local conditions.

1.3.1. STORMWATER RETENTION PONDS

Stormwater retention ponds is one of the most commonly used structural BMPs. Retention ponds, also known as wet ponds, are often designed with a twofold purpose: Reduction of the downstream hydraulic loading and pollutant retainment to the receiving environment. Such pond has a permanent water volume to support the treatment processes in the pond, over-layered by a storage volume to provide water storage capacity during heavy rainfall or snow melting events (Figure. 1-3). Typically, these ponds are designed to allow for an average residence time of the received water of days to weeks. In addition, the outlet flow during and after rain events is often restricted to avoid erosion in the receiving environment (Pitt et al., 1995). During this water-holding time, various natural processes can occur both in the water phase and sediments, which cause a reduction of the stormwater pollutants in a so-called "natural" way. Relevant processes are for instance, sorption, hydrolysis, photodegradation, and sedimentation (Istenič et al., 2011; Istenič et al., 2012; Minelgaite et al., 2017).



Figure 1-3. Schematic of a stormwater retention pond receiving stormwater discharges from urban and highway area

In practice, retention ponds are applied to treat runoff from catchments with combined sewer systems as well as separated sewer systems (Figure. 1-4). In a combined sewer system, CSOs are drained into the retention pond before discharging to the receiving environment; while in a separated system, only the stormwater is lead to the pond. The CSOs and SWR are collected and temporally stored in the ponds. By doing so, the transportation pressure of the current drainage networks is eased, and the receiving environment is also protected from degrading by discharges of high flow and concentrated pollutions.



Figure 1-4. Outline of the application of pond systems in a combined sewer system and a separated sewer system

With the increasing focus on environmental impacts from storm-induced discharges, as well as the realisation of problems related to emerging pollutants in these discharges, the knowledge on the treatment performance of stormwater ponds with respect to these pollutants should also be filled and updated. Although this evaluation has started in the 1990s, until now the focus largely has remained on the removal of 'traditional' pollutants such as heavy metals, nutrients, and PAHs (Hvitved-Jacobsen et al., 1994; Istenič et al., 2011; Wium-Andersen et al., 2011; Istenič et al.,

2012; Minelgaite et al., 2017). With respect to emerging micropollutants such as PhACs, there are some studies on constructed wetlands, as it has been argued that these systems are well-suited for removal hereof due to their low water depth (0.1–0.3m) and denser vegetation (Dordio et al., 2010; Matamoros and Salvadó, 2012; Zhang et al., 2012; Hijosa-Valsero et al., 2016; ávila et al., 2013). Little is, however, known about the occurrence and fate of the emerging micropollutants in wet retention ponds even though these are amongst the most common BMPs used for management of urban runoff. These systems, and how they retain emerging pollutants like PhACs and microplastics, are hence the focus of the present PhD study.

CHAPTER 2. STUDY AIM AND OBJECTIVES

Stormwater retention ponds receive emerging organic micropollutants both in dry and wet weather. These micropollutants are present in both soluble and particulate forms. But their occurrence and fate after entering the pond are mostly unknown. It is hence the aim of this PhD study, to investigate the occurrence and fate of selected soluble and particulate emerging micropollutants in stormwater retention ponds.

To address this aim, the study was divided into several research questions, and each was answered to complete a particular objective.

Research question 1: what is the fate of soluble emerging micropollutants in stormwater retention ponds?

To answer this, pharmaceuticals, a group of compounds covering various chemical properties, was selected to represent soluble emerging micropollutants. The fate of the pharmaceuticals was investigated in a microcosm study.

Research question 2: what is the fate of particulate emerging micropollutants in stormwater retention ponds?

To answer this, microplastics (MPs), an emerging particulate micropollutant of great environmental concern, was selected. The occurrence and fate of the MPs were studied both in the water phase and the sediment phase of stormwater retention ponds.

Research question 3: How efficient are biofilters to further polish stormwater or treated wastewater?

Biofilers can be used as an alternative to stormwater retention ponds, or to further polish urban polluted waters discharged from e.g. ponds or treatment plants. To answer question #3, a biofilter intended to simulate CSOs treatment was studied for its retainment of microplastics.

CHAPTER 3. METHODOLOGY

The PhD study was carried out through 3 primary sub-topics:

- Investigation of the fate of pharmaceuticals in stormwater retention ponds
- Investigation of the fate of MPs in stormwater retention ponds
- Investigation of the performance of a biofilter in polishing and further removing MPs

The first research focus was addressed in a lab-scale study, using microcosms holding both pond water and sediments to mimic a real pond system. The second was addressed by taking large field samples, coupled with method development in MPs sampling, sample extraction, and sample analysis. The third research focus was addressed with a study carried out on a pilot-scale biofilter setup.

3.1. THE FATE OF PHARMACEUTICALS IN STORMWATER RETENTION PONDS

Five PhACs, covering five common therapeutic categories, were selected as the study compounds (Table 3-1). The fate of the selected compounds was investigated with a focus on the role of sorption and degradation in stormwater pond sediments. This was achieved by studying

a) <u>The sorption potential of the selected compounds to sediments from a stormwater</u> retention pond under various environmentally realistic pH conditions

It is well known that the sorption ability of an organic compound is strongly affected by the pH of the matrix. Hence this experiment was designed to study the effect of 4 environmentally realistic pH values (pH=5, 6, 7, 8) on the sorption potential of the 5 compounds to the pond sediments. A batch equilibrium method was used as the experimental approach to study

b) The degradation potential of the selected compounds by the pond sediments under various oxygen regimes

The degradation of organic compounds in stormwater pond sediments is mainly associated with the activity of microorganism, where the available oxygen is a major governing factor. Hence this experiment was carried out under three controlled oxygen condition in microcosms (aerobic, anaerobic, and undisturbed conditions. The latter constituted an intermediate state between the two former states).

c) <u>The overall removal efficiency of the selected compounds by sediments from the</u> <u>stormwater retention pond</u>

Whether by sorption or degradation, a chemical compound will be somewhat trapped by the pond system instead of being discharged directly into the receiving environment. Hence, the combination of sorption and degradation were considered as overall removal processes. This was assessed for each of the selected compounds under the three oxygen conditions (Table 3-1).

Name	Structure	Physical and chemical characteristics	Therapeutic category
Naproxen (NAP)	H ₃ CO	MW: 230.3 log Kow: 3.18 pKa: 4.15	Anti-inflammatory
Carbamazepine (CAR)		MW: 236.3 log Kow: 2.45 pKa: 13.9	Antiepileptic agent
Sulfamethoxazole (SUL)	H ₂ N H ₂ N	MW: 253.3 log Kow: 0.89 pKa: 1.6, 5.7	Antibiotic
Furosemide (FUR)		MW: 330.7 log Kow: 2.03 pKa: 3.9	Diuretic
Fenofibrate (FEN)	CI CI CI CI CH ₅ CI CI CI CH ₅ CI CI CH ₅	MW: 360.8 log Kow: 5.19 pKa: –	Lipid regulator

Table 3-1. Physicochemical properties and therapeutic category of the selected PhACs compounds.

Further details about the sampling, experiment setup, and analytical methods are presented in **Paper-I**.

3.2. THE FATE OF MICROPLASTICS IN STORMWATER RETENTION PONDS

The fate of MPs in the stormwater retention ponds was assessed by looking at the MP occurrence and distribution both in the water phase and the sediment phase. Hence this research topic was divided into two work packages:

a) Microplastics in the water phase of stormwater retention ponds

The occurrence of MPs in stormwater is hypothesized to be associated with the land use in the corresponding catchment. To verify this hypothesis, seven retention ponds receiving stormwater runoff from different catchment types (residential, industrial, commercial and highway land use) were selected for this study (Figure. 3-1).

A uniform method for sampling, sample processing, and sample analysis was applied to the seven ponds. In short, around a cubic meter of pond water was filtered on-site onto 10 μ m steel filters. The deposits on the filters were analysed for microplastics by extracting and concentrating the MPs applying a combination of oxidation with hydrogen peroxide, degradation applying enzymes, and density separation to remove inorganic particles. The extracted particles were analysed applying μ FTIR imaging and an automated MP analysis software – MPhunter – which was developed along with this study. Further details can be reviewed in **Paper-II**.

b) Microplastics in the sediments of stormwater retention ponds

Aside from the land use in the catchment, the amounts of MPs accumulated in the pond sediments was also hypothesized to relate to the hydraulic loading of the pond, as well as the sediment characteristics. Hence to verify this hypothesis, sediment samples from the same seven stormwater retention ponds were collected, processed, and analysed with a uniform method. In short, three litres of sediments were obtained from each stormwater pond. The sediments were pre-oxidized and a representative sub-sample was density separated. The extracted particle concentrate was further purified by a hydrogen peroxide oxidation and density separation. Finally, the extracted particles were analysed by μ FTIR imaging and the data analysed by the automatic MP analysis tool, MPhunter.

The correlation between the MP abundance and the pond hydraulic loading, the sediment organic matter content, and the land use in catchment were assessed. Further details are presented in **Paper-III.**



Figure 3-1. Locations of the seven stormwater retention ponds in Denmark

3.3. BIOFILTERS FOR FURTHER POLISHING THE WATER

A pilot-scale biofilter setup was established by Aarhus University in the context of an ongoing research project. It was located in Avedøre wastewater treatment plant (WWTP) in Hvidovre,

Denmark, with the purpose to test the performance in further removing PhACs and MPs from treated wastewater, simulated stormwater discharges and simulated CSO discharges. The present PhD study does, however, only address the retainment of MPs, not PhACs. One of the reasons for using WWTP effluents instead of real stormwater or discharges from a real CSO for this experiment was that the flow of stormwater as well as CSO discharges depend on precipitation, and flow to the filter is not continuous, which would have complicated the operation of the pilot setup significantly. While treated wastewater is not identical to stormwater runoff or CSO discharges, and it also matters for a filter performance whether it is continuously or intermittently loaded, it was believed to be sufficient close to allow testing the concept of such filter for the mentioned purposes. Considering the incomplete MP removal by WWTPs, to some extent, the wastewater effluents were believed to have MP concentration levels similar to stormwater.



Figure 3-2. Overview of the pilot-scale biofilter. The effluent water from the wastewater treatment plant flows in from the top (inlet), and out at the bottom (outlet)

The filter was sampled for MPs at the inlet and the 4 levels (Figure. 3-2), where level 4 represents the outlet. The water was filtered on-site applying an approach similar to the stormwater pond investigations described in **Paper-II**, and also purified, concentrated, and analysed in a similar way.

The assessment of the biofilter setup included the MP removal efficiency quantified both by particle mass and particle number, as well as the mass, size, and polymer composition of the particles retained by the filters. Further details can be found in **Paper-IV**.

CHAPTER 4. RESEARCH OUTCOMES

The research outcomes of the PhD study resulted in four scientific papers, aimed to address the three main research topics:

- The fate of pharmaceuticals in stormwater retention ponds
- The fate of MPs in stormwater retention ponds
- The performance of a biofilter in further removing the selected emerging micropollutants.

4.1. PHARMACEUTICALS

The microcosms study (**Paper-I**) on the sorption and degradation of the five selected PhACs (naproxen, carbamazepine, sulfamethoxazole, furosemide, and fenofibrate) by stormwater pond sediments showed that the degradation potential of the chemical compound was somewhat affected by the oxygen condition in the sediment-water system. The system was able to reduce most of the sulfamethoxazole, naproxen, and fenofibrate (99.6%, 98.6%, 96.8%, respectively) by degradation. Carbamazepine and furosemide were more persistent towards the degradation. However, as these substances to some degree sorbed to the sediments, it was found that a stormwater pond would still be able to reduce the environmental impacts, as the sorption would lead to a decreased mobility in the water phase and hence at least to an equalization in peak concentrations were somewhat pH-dependent. Overall, it was found that these two compounds were retained (sorbed) by the system by 64% and 76%, respectively.

Comparing these values to what has been reported for sewage treatment plants, this efficiency was actually quite significant as WWTPs generally only eliminate carbamazepine by less than 10% (Ternes, 1998)(Heberer, 2002)(Clara et al., 2004)(Clara et al., 2005)(Focazio et al., 2008). Although some advanced techniques have been evaluated to further polish the water from this persistent compound, for instance biofilm reactors and soil column systems (Escolà Casas and Bester, 2015)(Zhang et al., 2015)(Tang et al., 2017)(Zhang et al., 2019), also these systems do not show significant effect on this compound. Hence it seems that stormwater retention ponds can play a role in mitigating some of the PhACs received from the urban drainage system.

4.2. MICROPLASTICS IN THE WATER OF STORMWATER RETENTION PONDS

Microplastics (MPs) were chosen as the representative of particulate emerging micropollutants in urban stormwater. At the same time, the study included in this PhD thesis (**Paper-II**) is the very first of its kind as no previous study has addressed stormwater retention ponds, and very few have addressed other aspects of MPs in stormwater. It was found that the stormwater of the ponds on average held 1409 item m⁻³, corresponding to 231 μ g m⁻³. This was slightly lower than what has been previously reported for treated wastewater (Simon et al., 2018; Ljung et al., 2018), but higher than what was found for the effluent for the Avedøre WWTP where the pilot biofilter discussed in **Paper-IV** was located. In the latter study, the MP concentrations were 917 item m⁻³,

corresponding to 24.8 μ g m⁻³. It is often difficult to compare results regarding the abundance of microplastics, however these four studies were performed with rather comparable methods, putting confidence into the observation that stormwater from retention ponds contain microplastics at concentration levels quite comparable to treated wastewater. It should, however, in this context be mentioned that none of those studies encompass care tyre debris as this material cannot be quantified by the applied method (μ FTIR imaging).

The study on MPs in the water phase of stormwater retention ponds (**Paper-II**) further revealed that the most common MPs were of PVC (polyvinylchloride), PS (polystyrene), PP (polypropylene), PE (polyethylene), and polyester. A quite large number of other polymers was also identified, but at much lower concentration levels. It was also found that there was quite some variability in MP concentrations in the waters of the ponds. This variability could to some degree be related to land use in the pond catchment. Land use was found to have significant impacts on the MP abundance, polymer distribution, particle size, and particle mass. For example were the MPs from ponds serving residential areas and a highway significantly larger in size than those serving industrial / commercial catchments. Another finding was that some polymer types tended to be present as larger particles than others. Here especially particles of PVC and to some degree also of PS were larger than MPs of other polymers.

4.3. MICROPLASTICS IN THE SEDIMENTS OF STORMWATER RETENTION PONDS

The relation between MP occurrence and the land use of the stormwater pond catchments was though limited to the water phase. When addressing the MP accumulation in their sediments, no such correlation could be identified (**Paper-III**). The only seeming agreement that could be found was that the highway pond had the lowest concentrations of MPs in both its water and sediments (**Paper-II** and **III**). For the sediments, there was, on the other hand, an association with the hydraulic loading of the pond, and to a lesser degree also with the sediment organic matter content. The higher the hydraulic loading, the higher the concentration of MPs in the pond sediments.

The sediments of the ponds had accumulated substantial amounts of MP, with an average sediment concentration amounting to 17490 item kg⁻¹ corresponding to 3085 μ g kg⁻¹. Giving a rough estimation of 1.24 t m⁻³ being the average dry sediment bulk density (Verstraeten and Poesen, 2001), when comparing stormwater from the ponds with their sediments, the concentrations in the sediments were more than 4 orders of magnitude higher on a volume to volume basis.

The dominating polymer in the sediments was PP. It accounted for about half of all the plastics found in the sediments. PS, PE, and polyester accounted for less than 10% each, while PVC accounted for about 5%. In other words, the polymer composition of the water phase, where PVC was the dominating polymer, was not reflected in the sediments. A likely explanation here for is that the sediments reflect a long-term accumulation of MPs from the catchments, while the water phase is a snapshot.
PP and PE, which together made up nearly 70% of all the MP mass in the sediments, have a density below that of water. Nevertheless, they were accumulated in the sediments and did not float on the pond surface. In general, when looking at the polymer distribution between the water phase and the sediment phase, it was clear that particle density was not the only factor determining the final fate of MPs in the stormwater retention ponds. It seemed that a combination of various environmental and anthropogenic factors was likely to be the cause. Possible explanations could be related to the MPs being ballasted by biofilm growth, flocculation with heavier particles, ingestion and subsequent excretion by fish or invertebrates, or simply the intensive mixing that occurs in the ponds during inflow of stormwater or during strong winds.

4.4. TRYING TO CLOSE THE MASS BALANCE FOR MICROPLASTICS IN STORMWATER

Assuming that the average sediment build-up rate in the pond was 2 kg m⁻² y⁻¹ of dry sediments (Szmytkiewicz and Zalewska, 2014), the annual MP accumulation in sediments ranged from 0.23 – 57 mg m⁻² y⁻¹. In terms of MP number, the range of accumulation was $3.0 \times 10^3 - 2.6 \times 10^5$ item m⁻² y⁻¹ (**Paper-III**). This indicates that the seven selected ponds retain 2 - 374 g, or $1.9 \times 10^7 - 1.7 \times 10^9$ items of MP each year. Normalizing to the impervious catchment area, this corresponds to 0.16 - 5.35 g ha⁻¹ y⁻¹, or $2.1 \times 10^6 - 2.9 \times 10^7$ item ha⁻¹ y⁻¹. In Denmark, the total impervious area served by separate sewer systems is 45561 ha (Skovmark et al., 2018). Assuming that all this area was served by stormwater retention ponds of good design (which it is not) and that the average accumulation of MP determined in this study is representative, a total of 83 kg of MP could be retained per year (5.4×10^{11} item per year). The average MP concentration in the water phase of the ponds was 231 µg m⁻³, or 1409 items m⁻³ (**Paper-II**). Assuming an annual runoff of 4000 m³ ha⁻¹ y⁻¹ as typical for the Jutland Peninsular of Denmark (Thorndahl et al., 2006), this means 42 kg of MPs are discharged with Danish stormwater every year if all were treated with such pond system. Compared to the 83 kg accumulated in the sediments, a treatment efficiency of 66% can be roughly expected.

Simon et al. (2018) estimated the total discharge from Danish wastewater treatment plants to be nearly 3,000 kg of MPs per year, and the discharge from stormwater, being it treated or untreated, is hence small compared to what enters the receiving environment by treated wastewater. However, it must be kept in mind that the present study does not cover MPs from tyre wear, which has been estimated to account for over half of all directly discharged MPs in Denmark (Lassen et al., 2015). It is furthermore reasonable to believe, that concentrations of tyre wear particles is higher in runoff from urban and highway surfaces than it is in municipal wastewater. The urban and highway MP mass balance is hence not yet closed, and caution is in place when comparing the importance of wet weather and dry weather discharges.

4.5. FURTHER POLISHING OF TREATED WATERS

Compared to a traditional WWTP, where the MPs are typically removed by some 90-99% (Simon et al., 2018)(Talvitie et al., 2017)(Magni et al., 2019)(Sun et al., 2019), the treatment efficient of the stormwater retention ponds was lower. Hence a further polishing could be argued for, and

tested in the present study on the form of a pilot-scale biofilter for polishing of treated water (**Paper-IV**). While the filter was not loaded with stormwater or CSO water treated in a pond, it is still believed that the knowledge gained on how such filter retains MPs will be valid also for these systems.

The biofilter (**Paper-IV**) was able to further reduce the MPs from treated water by 79-89%, with most of the retention happening in the top layer of the filter. The lower layers seemed not to contribute much to the particle retainment. Nevertheless, the particle sizes were lowest at the outlet, indicating that the lower filter levels still contributed somewhat to retaining particles. After the final filtration layer, no particles > 100 μ g were detected. Such behaviour of particles when filtered through a porous media is not unexpected (Faber et al., 2016), and it seems likely that the general knowledge on how porous media retain particles will be a good starting point to understand how MPs are retained in porous media filters.

The overall result of the biofilter study suggested that, although the biofilter could lower the MPs from wastewater effluent, a high removal was not guaranteed. This is most likely because the pores in the chosen filter material, stonewool, were too large to efficiently retain the very fine MP particles.

CHAPTER 5. CONCLUSIONS

The PhD study was divided into three main research questions, and the conclusion was drawn for each of the questions:

Research question 1: what is the fate of soluble emerging micropollutants in stormwater retention ponds?

In a stormwater retention pond, the fate of the selected PhACs, which represent a group of soluble emerging micropollutants, was determined by a combination of the potential to be degraded by and adsorbed to the pond sediments. Although some chemical compounds had certain preferences on the oxygen and pH condition towards degradation and sorption, the overall removal was significant for most of the compounds. Carbamazepine, as a rather persistent compound among the selected PhACs, still achieved a considerably higher removal efficiency than what has been reported for most sewage treatment plants.

In practice, the actual removal efficiency of a compound will depend on the design and operation of the pond, but nevertheless, it can be concluded that stormwater retention ponds can play a role in mitigating stormwater induced PhACs, hence to eliminate, or at least lower, the discharge of PhACs to the receiving environment.

Research question 2: what is the fate of particulate emerging micropollutants in stormwater retention ponds?

The distribution and fate of MP, an emerging particulate micropollutant, is complex and depends on a combination of environmental and anthropogenic factors. The MP concentration in the water phase of the seven studied stormwater retention ponds depended on the land use in the catchment. However, this was not so for the MP accumulated in pond sediments. Here there was an association with the pond hydraulic loading, and to some degree also the sediment organic matter content. The reason why the MPs in the water phase and sediment phase of the same stormwater retention pond were influenced by different factors was unclear, but could partly be related to the fact that the MPs in sediments represent a long term accumulation over several years, while the ones in the water phase represent a short term MP concentration in the runoff.

Research question 3: How efficienty is a biofilter to further polish stormwater or treated wastewater?

The investigated biofilter was able to lower the MP concentration in wastewater effluent, with a preference for retaining larger and heavier particles. Although wastewater was used in this pilot study, similar results should be expected if it had been stormwater, since the MP concentration in wastewater effluent is close to the level of that in stormwater runoff. In other words, biofilters

can be applied to treat or further polish the stormwater before it is discharged to the receiving environment.

5.1. MAIN CONTRIBUTIONS TO THE SCIENCE

Stormwater retention ponds have been studied in quite some detail, however, when it comes to emerging micropollutants, the information becomes scarce. It was the main objective of this PhD to contribute to filling this research gab by addressing selected dissolved and particulate micropollutants, which had hitherto received little scientific attention in these systems.

Very little has been published on the fate of organic dissolved micropollutants in stormwater retention ponds, and when it comes to the fate of pharmaceuticals in such systems, **Paper-I** represents – to the best knowledge of the thesis author – a very first.

The same goes for microplastics in stormwater ponds. Very little is known on microplastics in urban stormwater in general, and **Paper-II** was the very first published detailed study here on (to the best knowledge of the thesis author). Furthermore, very few studies have applied μ FTIR imaging in freshwater systems. This method allows particle recognition down to the low micrometer range, and hence lowers the detection limit significantly compared to more manual recognition methods.

The study on microplastics in the sediments of stormwater retention ponds (**Paper-III**) is also a first with respect to such systems. It is furthermore one of the first studies applying μ FTIR imaging on aquatic sediments, and hence contributes substantial to the analytical techniques for this kind of matrix.

Finally, only few studies have till date been published on polishing treated water using various types of filters. While **Paper-IV** hence is not a first in this respect, it still yields new and valuable information on this type of treatment system.

LITERATURE LIST

- Al Aukidy, M., Verlicchi, P., 2017. Contributions of combined sewer overflows and treated effluents to the bacterial load released into a coastal area. Sci. Total Environ. 607–608, 483–496. https://doi.org/10.1016/j.scitotenv.2017.07.050
- Al Aukidy, M., Verlicchi, P., Jelic, A., Petrovic, M., Barcelò, D., 2012. Monitoring release of pharmaceutical compounds: Occurrence and environmental risk assessment of two WWTP effluents and their receiving bodies in the Po Valley, Italy. Sci. Total Environ. 438, 15–25. https://doi.org/10.1016/j.scitotenv.2012.08.061
- Allen, S., Allen, D., Phoenix, V.R., Le Roux, G., Durántez Jiménez, P., Simonneau, A., Binet, S., Galop, D., 2019. Atmospheric transport and deposition of microplastics in a remote mountain catchment. Nat. Geosci. 12, 339–344. https://doi.org/10.1038/s41561-019-0335-5
- Antrop, M., 2004. Landscape change and the urbanization process in Europe. Landsc. Urban Plan. 67, 9–26. https://doi.org/10.1016/S0169-2046(03)00026-4
- Antrop, M., 2000. Changing patterns in the urbanized countryside of Western Europe. Landsc. Ecol. 15, 257–270. https://doi.org/10.1023/A:1008151109252
- ávila, C., Reyes, C., Bayona, J.M., García, J., 2013. Emerging organic contaminant removal depending on primary treatment and operational strategy in horizontal subsurface flow constructed wetlands: Influence of redox. Water Res. 47, 315–325. https://doi.org/10.1016/j.watres.2012.10.005
- Beckers, L.M., Busch, W., Krauss, M., Schulze, T., Brack, W., 2018. Characterization and risk assessment of seasonal and weather dynamics in organic pollutant mixtures from discharge of a separate sewer system. Water Res. 135, 122–133. https://doi.org/10.1016/j.watres.2018.02.002
- Becouze-Lareure, C., Dembélé, A., Coquery, M., Cren-Olivé, C., Bertrand-Krajewski, J.L., 2019. Assessment of 34 dissolved and particulate organic and metallic micropollutants discharged at the outlet of two contrasted urban catchments. Sci. Total Environ. 651, 1810–1818. https://doi.org/10.1016/j.scitotenv.2018.10.042
- Bergmann, M., Mützel, S., Primpke, S., Tekman, M.B., Trachsel, J., Gerdts, G., 2019. White and wonderful? Microplastics prevail in snow from the Alps to the Arctic. Sci. Adv. 5, eaax1157. https://doi.org/10.1126/sciadv.aax1157
- Bollmann, U.E., Simon, M., Vollertsen, J., Bester, K., 2019. Assessment of input of organic micropollutants and microplastics into the Baltic Sea by urban waters. Mar. Pollut. Bull. 148, 149–155. https://doi.org/10.1016/j.marpolbul.2019.07.014
- Boyd, G.R., Reemtsma, H., Grimm, D.A., Mitra, S., 2003. Pharmaceuticals and personal care products (PPCPs) in surface and treated waters of Louisiana, USA and Ontario, Canada. Sci. Total Environ. 311, 135–149. https://doi.org/10.1016/S0048-9697(03)00138-4
- Burian, S.J., Edwards, F.G., 2002. Historical Perspectives of Urban Drainage. Steven J. Burian and Findlay G. Edwards, in: Computer. pp. 1–16.
- Butler, D., Davies, J.W., 2004. Urbna Drainage.
- Carr, S.A., Liu, J., Tesoro, A.G., 2016. Transport and fate of microplastic particles in wastewater treatment plants. Water Res. 91, 174–182. https://doi.org/10.1016/j.watres.2016.01.002
- Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N., Kroiss, H., 2005. Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. Water Res. 39, 4797–4807.

https://doi.org/10.1016/j.watres.2005.09.015

- Clara, M., Strenn, B., Kreuzinger, N., 2004. Carbamazepine as a possible anthropogenic marker in the aquatic environment: Investigations on the behaviour of Carbamazepine in wastewater treatment and during groundwater infiltration. Water Res. 38, 947–954. https://doi.org/10.1016/j.watres.2003.10.058
- Cole, M., Lindeque, P., Fileman, E., Halsband, C., Goodhead, R., Moger, J., Galloway, T.S., 2013. Microplastic ingestion by zooplankton. Environ. Sci. Technol. 47, 6646–6655. https://doi.org/10.1021/es400663f
- Deffontis, S., Breton, A., Vialle, C., Montréjaud-Vignoles, M., Vignoles, C., Sablayrolles, C., 2013. Impact of dry weather discharges on annual pollution from a separate storm sewer in Toulouse, France. Sci. Total Environ. 452–453, 394–403. https://doi.org/10.1016/j.scitotenv.2013.03.014
- Dordio, A., Carvalho, A.J.P., Teixeira, D.M., Dias, C.B., Pinto, A.P., 2010. Removal of pharmaceuticals in microcosm constructed wetlands using Typha spp. and LECA. Bioresour. Technol. 101, 886–892. https://doi.org/10.1016/j.biortech.2009.091
- Eerkes-Medrano, D., Thompson, R.C., Aldridge, D.C., 2015. Microplastics in freshwater systems: A review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. Water Res. https://doi.org/10.1016/j.watres.2015.02.012
- Eriksson, E., Baun, A., Mikkelsen, P.S., Ledin, A., 2005. Chemical hazard identification and assessment tool for evaluation of stormwater priority pollutants. Water Sci. Technol. 51, 47–55.
- Escolà Casas, M., Bester, K., 2015. Can those organic micro-pollutants that are recalcitrant in activated sludge treatment be removed from wastewater by biofilm reactors (slow sand filters)? Sci. Total Environ. 506–507, 315–322. https://doi.org/10.1016/j.scitotenv.2014.10.113
- European Commission, 2019. European union strategic approach to pharmacauticals in the environment. Brussels.
- Faber, S., Al-Maktoumi, A., Kacimov, A., Al-Busaidi, H., Al-Ismaily, S., Al-Belushi, M., 2016. Migration and deposition of fine particles in a porous filter and alluvial deposit: laboratory experiments. Arab. J. Geosci. 9. https://doi.org/10.1007/s12517-016-2309-x
- Fletcher, T.D., Andrieu, H., Hamel, P., 2013. Understanding, management and modelling of urban hydrology and its consequences for receiving waters: A state of the art. Adv. Water Resour. 51, 261– 279. https://doi.org/10.1016/j.advwatres.2012.09.001
- Focazio, M.J., Kolpin, D.W., Barnes, K.K., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Barber, L.B., Thurman, M.E., 2008. A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States — II) Untreated drinking water sources. Sci. Total Environ. 402, 201–216. https://doi.org/10.1016/j.scitotenv.2008.02.021
- Frias, J.P.G.L., Sobral, P., Ferreira, A.M., 2010. Organic pollutants in microplastics from two beaches of the Portuguese coast. Mar. Pollut. Bull. 60, 1988–1992. https://doi.org/10.1016/j.marpolbul.2010.07.030
- Galindo-Miranda, J.M., Guízar-González, C., Becerril-Bravo, E.J., Moeller-Chávez, G., León-Becerril, E., Vallejo-Rodríguez, R., 2019. Occurrence of emerging contaminants in environmental surface waters and their analytical methodology – a review. Water Supply. https://doi.org/10.2166/ws.2019.087
- Gasperi, J., Gromaire, M.C., Kafi, M., Moilleron, R., Chebbo, G., 2010. Contributions of wastewater, runoff and sewer deposit erosion to wet weather pollutant loads in combined sewer systems. Water Res. 44, 5875–5886. https://doi.org/10.1016/j.watres.2010.07.008

- Gasperi, J., Zgheib, S., Cladière, M., Rocher, V., Moilleron, R., Chebbo, G., 2012. Priority pollutants in urban stormwater: Part 2 Case of combined sewers. Water Res. 46, 6693–6703. https://doi.org/10.1016/j.watres.2011.09.041
- Gatidou, G., Arvaniti, O.S., Stasinakis, A.S., 2019. Review on the occurrence and fate of microplastics in Sewage Treatment Plants. J. Hazard. Mater. 367, 504–512. https://doi.org/10.1016/j.jhazmat.2018.12.081
- Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E., Purnell, P., 2018. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. J. Hazard. Mater. https://doi.org/10.1016/j.jhazmat.2017.10.014
- Heberer, T., 2002. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data. Toxicol. Lett. 131, 5–17. https://doi.org/10.1016/S0378-4274(02)00041-3
- Hijosa-Valsero, M., Reyes-Contreras, C., Domínguez, C., Bécares, E., Bayona, J.M., 2016. Behaviour of pharmaceuticals and personal care products in constructed wetland compartments: Influent, effluent, pore water, substrate and plant roots. Chemosphere 145, 508–517. https://doi.org/10.1016/j.chemosphere.2015.11.090
- Hoes, O.A.C., Schilperoort, R.P.S., Luxemburg, W.M.J., Clemens, F.H.L.R., van de Giesen, N.C., 2009. Locating illicit connections in storm water sewers using fiber-optic distributed temperature sensing. Water Res. 43, 5187–5197. https://doi.org/10.1016/j.watres.2009.08.020
- Horton, A.A., Walton, A., Spurgeon, D.J., Lahive, E., Svendsen, C., 2017. Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities. Sci. Total Environ. https://doi.org/10.1016/j.scitotenv.2017.01.190
- Hvitved-Jacobsen, T., Johansen, N.B., Yousef, Y.A., 1994. Treatment systems for urban and highway runoff in Denmark. Sci. Total Environ. 146–147, 499–506. https://doi.org/10.1016/0048-9697(94)90275-5
- Hvitved-Jacobsen, T., Vollertsen, J., Nielsen, A.H., 2010. Urban and Highway Stormwater Pollution: Concepts and Engineering. CRC Press, Taylor & Francis Group.
- Istenič, D., Arias, C.A., Matamoros, V., Vollertsen, J., Brix, H., 2011. Elimination and accumulation of polycyclic aromatic hydrocarbons in urban stormwater wet detention ponds. Water Sci. Technol. 64.4, 818–825. https://doi.org/zorac.aub.aau.dk/10.2166/wst.2011.525
- Istenič, D., Arias, C.A., Vollertsen, J., Nielsen, A.H., Wium-Andersen, T., Hvitved-Jacobsen, T., Brix, H., 2012. Improved urban stormwater treatment and pollutant removal pathways in amended wet detention ponds. J. Environ. Sci. Heal. Part A 47, 1466–1477. https://doi.org/10.1080/10934529.2012.673306
- Jacobson, C.R., 2011. Identification and quantification of the hydrological impacts of imperviousness in urban catchments: A review. J. Environ. Manage. https://doi.org/10.1016/j.jenvman.2011.01.018
- Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. Science (80-.). 347, 768–771. https://doi.org/https://doi.org/10.1126/science.1260352
- Jelic, A., Gros, M., Ginebreda, A., Cespedes-Sánchez, R., Ventura, F., Petrovic, M., Barcelo, D., 2011. Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. Water Res. 45, 1165–1176. https://doi.org/10.1016/j.watres.2010.11.010

Jjemba, P.K., 2006. Excretion and ecotoxicity of pharmaceutical and personal care products in the

environment, in: Ecotoxicology and Environmental Safety. pp. 113–130. https://doi.org/10.1016/j.ecoenv.2004.11.011

- Koelmans, A.A., Gouin, T., Thompson, R., 2014. Plastics in the marine environment. Environ. Toxicol. Chem. 33. https://doi.org/10.1002/etc.2426
- Lassen, C., Hansen, S.F., Magnusson, K., Hartmann, N.B., Rehne Jensen, P., Nielsen, T.G., Brinch, A., 2015. Microplastics Occurrence, effects and sources of releases, Danish Environmental Protection Agency.
- Launay, Marie A, Dittmer, U., Steinmetz, H., 2016. Organic micropollutants discharged by combined sewer overflows-Characterisation of pollutant sources and stormwater-related processes. Water Res. 104, 82–92. https://doi.org/10.1016/j.watres.2016.07.068
- Launay, Marie A., Dittmer, U., Steinmetz, H., 2016. Organic micropollutants discharged by combined sewer overflows – Characterisation of pollutant sources and stormwater-related processes. Water Res. 104, 82–92. https://doi.org/10.1016/j.watres.2016.07.068
- Li, Z., Sobek, A., Radke, M., 2016. Fate of Pharmaceuticals and Their Transformation Products in Four Small European Rivers Receiving Treated Wastewater. Environ. Sci. Technol. 50, 5614–5621. https://doi.org/10.1021/acs.est.5b06327
- Lienert, J., Bürki, T., Escher, B.I., 2007. Reducing micropollutants with source control: Substance flow analysis of 212 pharmaceuticals in faeces and urine, in: Water Science and Technology. pp. 87–96. https://doi.org/10.2166/wst.2007.560
- Ljung, E., Borg-Olesen, K., Andersson, P.-G., Fältström, E., Vollertsen, J., Wittgren, H.B., Hagman, M., 2018. Microplastics in the water and nutrient-cycle (Mikroplaster i kretsloppet), Svenskt Vatten Utveckling.
- Magni, S., Binelli, A., Pittura, L., Avio, C.G., Della Torre, C., Parenti, C.C., Gorbi, S., Regoli, F., 2019. The fate of microplastics in an Italian Wastewater Treatment Plant. Sci. Total Environ. 652, 602–610. https://doi.org/10.1016/j.scitotenv.2018.10.269
- Matamoros, V., Salvadó, V., 2012. Evaluation of the seasonal performance of a water reclamation pondconstructed wetland system for removing emerging contaminants. Chemosphere 86, 111–117. https://doi.org/10.1016/j.chemosphere.2011.09.020
- Minelgaite, G., Nielsen, A.H., Pedersen, M.L., Vollertsen, J., 2017. Photodegradation of three stormwater biocides. Urban Water J. 14, 53–60. https://doi.org/10.1080/1573062X.2015.1076489
- Okuda, T., Yamashita, N., Tanaka, H., Matsukawa, H., Tanabe, K., 2009. Development of extraction method of pharmaceuticals and their occurrences found in Japanese wastewater treatment plants. Environ. Int. 35, 815–20. https://doi.org/10.1016/j.envint.2009.01.006
- Panel, E., Chain, F., 2016. Presence of microplastics and nanoplastics in food, with particular focus on seafood. EFSA J. 14. https://doi.org/10.2903/j.efsa.2016.4501
- Pitt, R., Field, R., Lalor, M., Brown, M., 1995. Urban Stromwater Toxic Pollutants: Assessment, Sources, and Treatability. Water Environ. Res. 67, 953–955. https://doi.org/10.2175/106143096x127965

PlasticsEurope, 2017. Plastics-the Facts 2017. Brussels.

Puype, F., Samsonek, J., Knoop, J., Egelkraut-Holtus, M., Ortlieb, M., 2015. Evidence of waste electrical and electronic equipment (WEEE) relevant substances in polymeric food-contact articles sold on the European market. Food Addit. Contam. - Part A Chem. Anal. Control. Expo. Risk Assess. 32, 410– 426. https://doi.org/10.1080/19440049.2015.1009499

- Revitt, D.M., Ellis, J.B., 2016. Urban surface water pollution problems arising from misconnections. Sci. Total Environ. 551–552, 163–174. https://doi.org/10.1016/j.scitotenv.2016.01.198
- Ríos, N., Frias, J.P.G.L., Rodríguez, Y., Carriço, R., Garcia, S.M., Juliano, M., Pham, C.K., 2018. Spatiotemporal variability of beached macro-litter on remote islands of the North Atlantic. Mar. Pollut. Bull. 133, 304–311. https://doi.org/10.1016/j.marpolbul.2018.05.038
- Roberts, J., Kumar, A., Du, J., Hepplewhite, C., Ellis, D.J., Christy, A.G., Beavis, S.G., 2016. Pharmaceuticals and personal care products (PPCPs) in Australia's largest inland sewage treatment plant, and its contribution to a major Australian river during high and low flow. Sci. Total Environ. 541, 1625–1637. https://doi.org/10.1016/j.scitotenv.2015.03.145
- Samsonek, J., Puype, F., 2013. Occurrence of brominated flame retardants in black thermo cups and selected kitchen utensils purchased on the European market. Food Addit. Contam. - Part A Chem. Anal. Control. Expo. Risk Assess. 30, 1976–1986. https://doi.org/10.1080/19440049.2013.829246
- Saraswat, C., Kumar, P., Mishra, B.K., 2016. Assessment of stormwater runoff management practices and governance under climate change and urbanization: An analysis of Bangkok, Hanoi and Tokyo. Environ. Sci. Policy 64, 101–117. https://doi.org/10.1016/j.envsci.2016.06.018
- Schiff, K., Tiefenthaler, L., 2003. Contributions of Organophosphorus Pesticides From Residential Land Uses During Dry and Wet Weather.
- Schueler, T.R., 1994. The importance of imperviousness. Watershed Prot. Tech. 1, 100–111.
- Simon, M., Van Alst, N., Vollertsen, J., 2018. Quantification of microplastic mass and removal rates at wastewater treatment plants applying Focal Plane Array (FPA)-based Fourier Transform Infrared (FT-IR) imaging. Water Res. 142, 1–9. https://doi.org/10.1016/j.watres.2018.05.019
- Skovmark, B., Nielsen, L., Gade Holm, A., 2018. Punktkilder 2016 (point sources 2016). The Danish Environmental Protection Agency.
- Spongberg, A.L., Witter, J.D., Acuña, J., Vargas, J., Murillo, M., Umaña, G., Gómez, E., Perez, G., 2011. Reconnaissance of selected PPCP compounds in Costa Rican surface waters. Water Res. 45, 6709– 6717. https://doi.org/10.1016/j.watres.2011.10.004
- Strungaru, S.A., Jijie, R., Nicoara, M., Plavan, G., Faggio, C., 2019. Micro- (nano) plastics in freshwater ecosystems: Abundance, toxicological impact and quantification methodology. TrAC - Trends Anal. Chem. 110, 116–128. https://doi.org/10.1016/j.trac.2018.10.025
- Suárez, J., Puertas, J., 2005. Determination of COD, BOD, and suspended solids loads during combined sewer overflow (CSO) events in some combined catchments in Spain. Ecol. Eng. 24, 199–217. https://doi.org/10.1016/j.ecoleng.2004.11.005
- Sun, J., Dai, X., Wang, Q., van Loosdrecht, M.C.M., Ni, B.J., 2019. Microplastics in wastewater treatment plants: Detection, occurrence and removal. Water Res. https://doi.org/10.1016/j.watres.2018.12.050
- Sutherland, W.J., Clout, M., Côté, I.M., Daszak, P., Depledge, M.H., Fellman, L., Fleishman, E., Garthwaite, R., Gibbons, D.W., De Lurio, J., Impey, A.J., Lickorish, F., Lindenmayer, D., Madgwick, J., Margerison, C., Maynard, T., Peck, L.S., Pretty, J., Prior, S., Redford, K.H., Scharlemann, J.P.W., Spalding, M., Watkinson, A.R., 2010. A horizon scan of global conservation issues for 2010. Trends Ecol. Evol. https://doi.org/10.1016/j.tree.2009.10.003
- Szmytkiewicz, A., Zalewska, T., 2014. Sediment deposition and accumulation rates determined by sediment trap and 210Pb isotope methods in the outer puck bay (Baltic Sea). Oceanologia 56, 85–106. https://doi.org/10.5697/oc.56-1.085

- Talvitie, J., Mikola, A., Setälä, O., Heinonen, M., Koistinen, A., 2017. How well is microlitter purified from wastewater? A detailed study on the stepwise removal of microlitter in a tertiary level wastewater treatment plant. Water Res. 109, 164–172. https://doi.org/10.1016/j.watres.2016.11.046
- Tang, K., Ooi, G.T.H., Litty, K., Sundmark, K., Kaarsholm, K.M.S., Sund, C., Kragelund, C., Christensson, M., Bester, K., Andersen, H.R., 2017. Removal of pharmaceuticals in conventionally treated wastewater by a polishing moving bed biofilm reactor (MBBR) with intermittent feeding. Bioresour. Technol. 236, 77–86. https://doi.org/10.1016/j.biortech.2017.03.159
- Taylor, M.L., Gwinnett, C., Robinson, L.F., Woodall, L.C., 2016. Plastic microfibre ingestion by deep-sea organisms. Sci. Rep. 6. https://doi.org/10.1038/srep33997
- Ternes, T., Joss, A., 2006. Human pharmaceuticals, hormones and fragrances: The micropollutant challenge for urban water management. Water 21 31, 53–54.
- Ternes, T.A., 1998. Occurrence of drugs in German sewage treatment plants and rivers. Water Res. 32, 3245–3260. https://doi.org/10.1016/S0043-1354(98)00099-2
- Thompson, R.C., Moore, C.J., Saal, F.S.V., Swan, S.H., 2009. Plastics, the environment and human health: Current consensus and future trends. Philos. Trans. R. Soc. B Biol. Sci. https://doi.org/10.1098/rstb.2009.0053
- Thorndahl, S., Johansen, C., Schaarup-Jensen, K., 2006. Assessment of runoff contributing catchment areas in rainfall runoff modelling. Water Sci. Technol. 54, 49–56. https://doi.org/10.2166/wst.2006.621
- Tran, N.H., Reinhard, M., Gin, K.Y.H., 2018. Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review. Water Res. https://doi.org/10.1016/j.watres.2017.12.029
- United Nations Population Division, 2008. UNITED NATIONS EXPERT GROUP MEETING ON POPULATION DISTRIBUTION, URBANIZATION, INTERNAL MIGRATION AND DEVELOPMENT. New York.
- Verstraeten, G., Poesen, J., 2001. Variability of dry sediment bulk density between and within retention ponds and its impact on the calculation of sediment yields. Earth Surf. Process. Landforms 26, 375– 394. https://doi.org/10.1002/esp.186
- Vezzaro, L., Eriksson, E., Ledin, A., Mikkelsen, P.S., 2011. Modelling the fate of organic micropollutants in stormwater ponds. Sci. Total Environ. 409, 2597–2606. https://doi.org/10.1016/j.scitotenv.2011.02.046
- Vianello, A., Jensen, R.L., Liu, L., Vollertsen, J., 2019. Simulating human exposure to indoor airborne microplastics using a Breathing Thermal Manikin. Sci. Rep. 9, 8670. https://doi.org/10.1038/s41598-019-45054-w
- Walker, W.J., McNutt, R.P., Maslanka, C.A.K., 1999. The potential contribution of urban runoff to surface sediments of the Passaic River: Sources and chemical characteristics. Chemosphere 38, 363–377. https://doi.org/10.1016/S0045-6535(98)00186-6
- Wang, Y., Liu, Y., Lu, S., Liu, X., Meng, Y., Zhang, G., Zhang, Y., Wang, W., Guo, X., 2019. Occurrence and ecological risk of pharmaceutical and personal care products in surface water of the Dongting Lake, China-during rainstorm period. Environ. Sci. Pollut. Res. 1–12. https://doi.org/10.1007/s11356-019-06047-4
- Weston, D.P., Holmes, R.W., Lydy, M.J., 2009. Residential runoff as a source of pyrethroid pesticides to urban creeks. Environ. Pollut. 157, 287–294. https://doi.org/10.1016/j.envpol.2008.06.037

- Wium-Andersen, T., Nielsen, A.H., Hvitved-Jakobsen, T., Vollertsen, J., 2011. Heavy metals, PAHs and toxicity in stormwater wet detention ponds. Water Sci. Technol. 64, 503–511. https://doi.org/10.2166/wst.2011.075
- Yi, X., Tran, N.H., Yin, T., He, Y., Gin, K.Y.H., 2017. Removal of selected PPCPs, EDCs, and antibiotic resistance genes in landfill leachate by a full-scale constructed wetlands system. Water Res. 121, 46– 60. https://doi.org/10.1016/j.watres.2017.05.008
- Yin, H., Lu, Y., Xu, Z., Li, H., Schwegler, B.R., 2017. Characteristics of the overflow pollution of storm drains with inappropriate sewage entry. Environ. Sci. Pollut. Res. 24, 4902–4915. https://doi.org/10.1007/s11356-016-8145-4
- Zhang, D.Q., Hua, T., Gersberg, R.M., Zhu, J., Ng, W.J., Tan, S.K., 2012. Fate of diclofenac in wetland mesocosms planted with Scirpus validus. Ecol. Eng. 49, 59–64. https://doi.org/10.1016/j.ecoleng.2012.08.018
- Zhang, L., Carvalho, P.N., Bollmann, U.E., EI-taliawy, H., Brix, H., Bester, K., 2019. Enhanced removal of pharmaceuticals in a biofilter: Effects of manipulating co-degradation by carbon feeding. Chemosphere 236, 124303. https://doi.org/10.1016/j.chemosphere.2019.07.034
- Zhang, Y., Zhu, H., Szewzyk, U., Geissen, S.U., 2015. Removal of pharmaceuticals in aerated biofilters with manganese feeding. Water Res. 72, 218–26. https://doi.org/10.1016/j.watres.2015.0

Paper-I

Sorption and Degradation Potential of Pharmaceuticals in Sediments from a Stormwater Retention Pond





MDPI

Sorption and Degradation Potential of Pharmaceuticals in Sediments from a Stormwater Retention Pond

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Abstract: Stormwater retention ponds commonly receive some wastewater through misconnections, sewer leaks, and sewer overloads, all of which leads to unintended loads of organic micropollutants, including pharmaceuticals. This study explores the role of pond sediment in removing pharmaceuticals (naproxen, carbamazepine, sulfamethoxazole, furosemide, and fenofibrate). It quantifies their sorption potential to the sediments and how it depends on pH. Then it addresses the degradability of the pharmaceuticals in microcosms holding sediment beds and pond water. The sediment-water partitioning coefficient of fenofibrate varied little with pH and was the highest (average log Kd: 4.42 L kg⁻¹). Sulfamethoxazole had the lowest (average log Kd: 0.80 L kg⁻¹), varying unsystematically with pH. The coefficients of naproxen, furosemide and carbamazepine were in between. The degradation by the sediments was most pronounced for sulfamethoxazole, followed by naproxen, fenofibrate, furosemide, and carbamazepine. The first three were all removed from the water phase with half-life of 2-8 days. Over the 38 days the experiment lasted, they were all degraded to near completion. The latter two were more resistant, with half-lives between 1 and 2 months. Overall, the study indicated that stormwater retention ponds have the potential to remove some but not all pharmaceuticals contained in wastewater contributions.

Keywords: emerging micropollutant; wastewater; constructed pond; sediment bed; microcosm

1. Introduction

The presence of pharmaceuticals in receiving waters can be due to a high daily consumption [1] combined with incomplete removal by wastewater treatment plants [2,3]. They can also originate from combined sewer overflow, when a mixture of stormwater and wastewater is discharged into the receiving environment during storm event [4]. Separate storm sewers can also discharge pharmaceuticals during rainy as well as dry weather, their presence in storm sewer discharges comes from misconnected wastewater pipelines [5], cross-connections between storm and foul sewers, leakage between pipes, and overload of sewer pipelines [6–8]. A typical example is carbamazepine, which concentration in a combined sewer overflow peaks during the first flush of a rain event, ranging from 175 ng L⁻¹ to 923 ng L⁻¹ [9]. The concentration of pharmaceuticals and other pollutants in storm sewer runoff fluctuates over time, depending on the catchment, the condition of the sewer network, and the frequency and intensity of rainfall events. Often it is low compared to concentrations in raw wastewater [10]. Nevertheless, for substances where wastewater treatment plants have efficient removal ability, substances discharged from storm drainage systems can be a significant contribution to pharmaceuticals in the receiving water [11].

An increasing part of the urban stormwater runoff is treated prior to discharge by decentralized and low-tech treatment systems such as artificial ponds, commonly known as retention ponds, wet

ponds or wet detention basins [6,12,13]. They can hold the runoff water from days to weeks, allowing various natural processes to proceed in their water phase and sediments. Sorption and degradation are the main processes that determine the fate of organic pollutants in such sediment-water systems [14]. The former is especially critical in determining the transport and mobility of pollutants [15]. In the case of organic pollutants, sorption may influence degradation as well, as the adsorbed pollutant can become the object of further chemical and/or biological degradation. Hence, the combination of sorption and degradation has important environmental implications on the fate of organic pollutants in stormwater treatment systems.

It is well known that sorption of pollutants is strongly affected by the matrix' content of organic matter, clay minerals, temperature and the pH [16–18]. Degradation is more associated with the activity of microorganisms present in the sediment-water system [18,19], where redox potential and oxygen condition are main factors [20–23]. Studies have already shown that stormwater retention ponds can reduce pollutants including polycyclic aromatic hydrocarbons (PAHs), heavy metals and biocides by processes like adsorption, sedimentation and degradation [24–26]. However, less is known about the fate of pharmaceuticals in such ponds, especially the removal mechanisms and the main factors that govern removal rates.

The objective of this study was to contribute to the understanding of the fate of pharmaceuticals in stormwater retention ponds, with a focus on the role of sorption and degradation in pond sediments. This was achieved by (a) studying the sorption of selected pharmaceuticals to stormwater pond sediments under environmentally realistic pH conditions; (b) quantifying the degradation rate and overall removal efficiency in microcosms under different oxygen regimes.

2. Materials and Methods

2.1. Materials

The compounds selected for observation were naproxen (NAP), carbamazepine (CAR), sulfamethoxazole (SUL), furosemide (FUR), and fenofibrate (FEN). These compounds are representatives of five common therapeutic categories that have been frequently detected in surface water [27–30].

Standards of NAP (>98%), CAR (>98%), SUL (>98%), FUR (>98%), and FEN (>98%) were purchased as powder from Sigma-Aldrich. Isotopically labeled standard carbamazepine- d_2 was purchased from Santa Cruz Biotechnology and fenofibrate- d_6 were from Qmx Laboratories. Physicochemical properties of the five compounds are given in Table 1. Formic acid was purchased from Sigma-Aldrich. Stock solutions were prepared in methanol and acetonitrile (LC-MS grade, Th. Geyer).

Name and CAS	Charles about the	Physical and Chemical	Therapeutic	Species at pH				
Number	Structure	Characteristics	Category	5	6	7	8	
Naproxen 22204-53-1		MW: 230.3 log <i>K_{OW}</i> : 3.18 <i>pKa</i> : 4.15	Anti-inflammatory	_	_	_	_	
Carbamazepine 298-46-4	O NH2	MW: 236.3 log K _{OW} : 2.45 <i>pKa</i> : 13.9	Antiepileptic agent	0	0	0	0	
Sulfamethoxazole 723-46-6		MW: 253.3 log <i>K</i> _{OW} : 0.89 <i>pKa</i> : 1.6, 5.7	Antibiotic	0/-	0/-		_	

Table 1. Physicochemical properties and therapeutic category of the selected pharmaceuticals.

Name and CAS	Structure	Physical and Chemical	Therapeutic	Species at pH			
Number		Characteristics	Category	5	6	7	8
Furosemide 54-31-9		MW: 330.7 log K _{OW} : 2.03 <i>pKa</i> : 3.9	Diuretic	+/-(a)	_	_	_
Fenofibrate 49562-28-9	MW: 360.8 k_{OW} : 5.19 pKa : -		Lipid regulator	0	0	0	0

Table 1. Cont.

^a charge of the relevant species at the pH: (+/-) zwitter.

2.2. Sampling

All samples were collected at the same time in January 2017, from a stormwater retention pond in Brabrand, Denmark. The pond has a permanent water surface of 6400 m², with an averaged water depth of 1.14 m. Sediments were collected with a 5 cm diameter corer, at 0.5 m water depth, from three randomly chosen places close to the inlet of the pond. The top 5 cm of the sediments were used in the experiments. After transfer to the laboratory, the sediments from the three locations were gently mixed and homogenized before use. Water samples were collected into 5 L glass bottles. All collected samples were immediately transferred to the laboratory and kept in the dark at 5 °C. Sediment properties are shown in supplementary material Table S1.

2.3. Sorption Experiment

To determine the effect of pH on the sorption behavior of the selected pharmaceuticals, a batch equilibrium method following OECD guideline 106 [31] was applied. Briefly, the pond water was first filtered (0.3 μ m glass fiber filter) to remove particles, and 10 g of freeze-dried sediment and 100 mL of the filtered water were placed into 100 mL glass bottles. The suspensions were spiked with pharmaceuticals at six concentrations (50, 100, 200, 500, 1000, and 1500 μ g L⁻¹), and adjusted to fixed pH values (5, 6, 7 and 8) using 1 M HCl and 0.1 M NaOH. Although pharmaceutical in nature waters typically ranges from ng L⁻¹ to μ g L⁻¹, the high concentration used in sorption studies has been commonly used in lab [32–34]. The bottles were covered with aluminum foil and shaken continuously by a mechanical shaker (110 rpm) at 23 °C for 24 h. Initial trials had shown that equilibrium would be reached within this time period. A subsample from each bottle was then collected and centrifuged in a microcentrifuge tube at 7800 rpm for 15 min. After that, 800 μ L of the supernatant was transferred to a 2 mL low adsorption vial and stored at -18 °C in the dark until analysis. All experiments were conducted in triplicate.

The amount of adsorbed pharmaceuticals was calculated as the difference between the mass initially added and the mass remaining in the solution upon equilibrium, as Equation (1):

$$C_s = \frac{(C_0 - C_e) \times V}{M},\tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations in the water phase, respectively (μ g L⁻¹). *V* is the water volume (L) and *M* is the organic matter of the sediments (g) used in the batch tests. C_s is the concentration of pharmaceuticals adsorbed onto the sediments, normalized to the organic matter (OM) of the sediments (μ g (g OM)⁻¹). The sorption isotherms were then fitted to a Freundlich isotherm model as Equation (2):

$$C_s = K_f \times C_e^{1/n},\tag{2}$$

where K_f is the Freundlich distribution coefficient ($g^{1-1/n} L^{1/n} kg^{-1}$) and *n* is the linearity parameter.

Partitioning coefficient (K_d , L kg⁻¹), which describes the concentration ratio of the compound between the sediment organic matter content and the liquid phase at equilibrium was calculated. It is

used to assess the mobility and fate of chemicals in the environment [35,36]. In this study, K_d values were expressed as the slopes of the Freundlich isotherms at zero concentration.

2.4. Removal Kinetics in Microcosm

In an intact water-sediment system, a decrease of a compound in the water phase does not necessarily imply that the removed amount has been completely sorbed or completely mineralized. Its fate is governed by a combination of diffusion into the matrix, sorption, and biological and chemical degradation, for example, hydrolysis and oxidation. In stormwater ponds, oxygen conditions vary substantially over the day and over the seasons [37]. Usually the water phase and the sediment surface is aerobic while the deeper sediments are anaerobic. Therefore, to simulate a natural pond system, microcosm experiments were set up to study the effect of available oxygen on the removal of the pharmaceuticals and hereby achieve an improved understanding on the processes governing their fate.

Three types of microcosms (hereafter 'cosms') were established (Figure 1). The first two were kept aerobic (AE) and anaerobic (ANAE) by aerating the water phase with air and N₂, respectively. The third was designed to mimic a real-life water-sediment scenario (RE): no gas was sent in and the water was left undisturbed. For all cosms, the ratio of water volume to wet sediment mass was 2.44 mL g⁻¹. This ratio, on the high side of what is found in retention ponds, was chosen intentionally to manifest the sediment processes, which are the focus of the study. For the AE and ANAE cosms, 90 g of wet sediments and 220 mL of pond water were filled in glass bottles, resulting in approximately 2 cm deep sediment beds and 8 cm deep water phases. For RE cosms, 180 g of wet sediments and 440 mL of pond water were placed in 2 L crystallizing dishes, yielding sediment bed depths of approximately 1.5 cm and water depths of 2.5 cm (Figure 1). After being filled with sediments and water, all cosms were covered with aluminum foil to minimize photochemical reactions. AE and ANAE cosms were sealed with caps fitted with butyl rubber stoppers. Controls and blanks were conducted for all types of cosms, and each type of cosm was conducted in triplicate, resulting in a total of 27 cosms.



Figure 1. Schematic diagram of the process of the microcosm experiment (**left**) and experimental reactors for AE, ANAE and RE microcosms (**right**).

After the sediment beds had settled for approximately 3 days, the cosms were pre-conditioned to have the desired oxygen conditions. A one-week process achieved the conditions by flushing AE cosms with air for 20 min every 3 h, and flushing ANAE cosms with N_2 for 3 h each day. Prior to the introduction of pharmaceuticals, the oxygen was equilibrated for another week. During this week, the cosms were slowly shaken to evenly diffuse the gases without disturbing the settled sediment beds. Before the introduction of pharmaceuticals, the stability of the bed condition was confirmed by vertically profiling the cosms for redox potential and pH. AE cosms were also profiled for dissolved oxygen. Redox and pH microsensors with a tip diameter of 100 μ m using Ag/AgCl electrode as reference electrode were purchased from Unisense, Denmark, and oxygen microsensors with a tip diameter of 140 μ m were performed by a motorized micro-manipulator (Thorlabs, Sweden) with a spatial resolution of 100 μ m.

A mixture of pharmaceuticals was spiked into the water phase and incubated at 23 °C for 38 days. The procedure of aerating was kept the same as in the equilibrium period for the 38 days. The concentration change in the water phase was monitored by sampling 2 mL of water on days 0, 1, 2, 4, 7, 10, 16, 22, 28, and 38 using a glass syringe. The syringe was cleansed with 2 mL of 50/50 methanol/acetone after each sampling. The 2 mL subsample and the 2 mL of washing solution were combined in a Teflon centrifuge tube and mixed by ultra-sound sonication for 10 min. The mixture was then centrifuged at 7800 rpm for 15 min, 800 μ L of the supernatant was then collected and transferred into a 2 mL low adsorption vial. All collected samples were stored at -18 °C in the dark until LC-MS analysis. Prior to termination of the experiments, the sediment beds were again profiled.

A first-order decay model was applied to quantify the sediment elimination rate of the studied compounds using Equation (3). The dissipation half-lives (DT_{50}) of the compounds were estimated as the time to halve the amount of the compound in the water phase of the system using Equation (4). All simulations and statistics were performed in SigmaPlot (13.0).

$$C_{st} = C_{so} \times e^{-kt},\tag{3}$$

$$DT_{50} = \frac{ln2}{k},\tag{4}$$

where C_{so} and C_{st} (µg g⁻¹) are the concentrations of a pharmaceutical transferred into the sediments (normalized to dry weight) at time zero and time *t* (d), and *k* (d⁻¹) is a first-order rate constant.

2.5. Extraction

Pharmaceuticals were extracted from the sediments upon the termination of the cosm experiment using microwave-assisted solvent extraction. After decanting the water phase from the cosms, the sediments were freeze-dried and gently ground. For each cosm, four sediment sub-samples of approximately 1.5 g was placed in a 100 mL PTFE extraction vessel, to which a mixture of 20 mL of 35/35/30 of methanol/acetone/miliQ was added as an extraction solution. The microwave program followed the method used by [38] to extract pharmaceuticals from river water and sediments. The steps were: preheating at 700 W for 5 min up to 60 °C, followed by 600 W for 5 min up to 100 °C and extraction at 700 W at 100 °C for 20 min. The extracted solution was transferred to a Teflon centrifuge tube and centrifuged at 7800 rpm for 20 min. 800 µL of the supernatant was collected and stored at -18 °C in the dark until analysis. To assess the recovery of the extractions, the dry sediments were spiked with 100 µL of 10 mg L⁻¹ isotopically labeled fenofibrate-d₆ and went through the whole extraction as well as the analysis procedures. An individual recovery was determined for each extraction vessel by comparing the mass of extracted fenofibrate-d₆ to the mass initially spiked.

Results show that the average recovery was 91.1%, with a standard deviation of 9.5%. The extracts from each extraction vessel were corrected by their corresponding recovery.

Individual stock solutions of the pharmaceuticals were prepared from powder in 50/50 methanol/acetonitrile (LC-MS grade, Sigma-Aldrich, Steinheim, Germany). A mixture including all five pharmaceuticals was prepared from the individual stock solutions, to a concentration of 100 mg L^{-1} of each compound. The mixture was used to spike both the sorption and cosm experiments. Isotopically labeled carbamazepine-d₂ was added as an internal standard into each low adsorption vial before analysis by high-performance liquid chromatography equipped with a mass spectrometer (HPLC-MS, Dionex Ultimate 3000/MSQ Plus, Thermo-Scientific, Waltham, MA, USA) with an electrospray interface (ESI). The compounds were separated by a C-18 column (L = 150 mm, ID = 2 mm, particles size = 4 μ m, Thermo Scientific). A multi-step gradient of LC-MS grade water (A) and 0.1% formic acid in acetonitrile (B) used was: 0-1 min 10% B, 1-21 min 10 to 90% B, 21-24 min 90 to 10% B. The capillary voltage of the MS was set to 3000 V and the probe temperature was at 340 °C. Positive ionization mode was used for all the selected compounds in single ion monitoring (SIM), and the identification of substances was based on the retention time, together with the matching of the diagnostic ions and the standards (Table S2). The limit of detection (LOD) and quantification (LOQ) were determined as the lowest concentration which gave a signal to noise ratio at 3 and 10, respectively (Table S3).

3. Results and Discussion

3.1. Sorption

Sorption was assessed through simulation using a Freundlich model (Equation (2), Figure 2). To allow comparison between the determined sorption constants (K_f), all combinations of pharmaceuticals and pH were simulated applying the same exponent (n), obtained to 1.43 by minimizing the overall root mean error for all 20 combinations of the five pharmaceuticals and the four pH conditions. The Freundlich simulations yielded an average coefficient of determination (R^2) of 0.9655, ranging from 0.8218 for the weakest correlation (sorption of SUL at pH 7) to 0.9995 for the strongest correlation (sorption of FEN at pH 6) (Table S4).



Figure 2. Sorption isotherms of pharmaceuticals to sediments under four pH conditions, with all isotherms normalized to the organic matter of the sediments. The solid points show the measured data; the solid lines represent the best fit of a theoretical Freundlich isotherm. Note the differences in axis scales.

The sorption of the electroneutral compounds (CAR and FEN) differed at the four pH-values, but without any trend to increase or decrease with pH. However, sorption of the ionic compounds NAP, SUL and FUR, which were primarily present in their anionic form at the applied pH conditions, did exhibit a trend to decrease with increasing pH (except for SUL at pH 7). Schaffer et al. [39] reported similar observations for NAP in column experiments with a natural sandy aquifer material and [34] for SUL in natural agricultural soil. In both studies, the sorption affinity decreased with increases of pH. Since the sediment surfaces probably were predominantly negatively charged due to natural organic matter and clay mineral surfaces [40], it can be assumed that the sorption of NAP, FUR and SUL was mainly driven by the electrostatic interaction with sediment surfaces. This assumption is also in agreement with Martínez-Hernández et al. (2014) [41], who investigated the sorption of selected pharmaceuticals and personal care products to organic and inorganic particles.

Several studies have shown that the sorption of sulfonamide antibiotics tends to decline with the increase of pH [42–47]. However, in some cases, surface complexation may affect the overall behavior of sorption for organic compounds [40,48,49], which could be an explanation for the slight increase of K_d for SUL at pH 7.

There was a positive relationship between log K_d and log K_{ow} (Figure 3, right), which can be described by a log K_{ow} -based linear function. This finding is consistent with Maskaoui et al. (2007) [50], who assessed the partitioning of river colloids and selected pharmaceuticals. The deviation in the log K_d -log K_{ow} relationship in the present study might have been caused by pH. However, the relation with pH was not proportional to the dissociation of the compounds. During a sorption process, various interaction mechanisms between a compound and the sediments, such as ion exchange, chemical bonding and surface complexation, may influence the overall sorption behavior of the compound to different levels. Nevertheless, the obtained results confirm that both the pH of the sediment system and the hydrophobicity of the compound were important for the sorption capacity.



Figure 3. Partitioning coefficients (log K_d) versus pH of the sediment-water system and the octanol-water partitioning coefficient (log K_{ow}) of the substances.

3.2. Sorption and Degradation in Cosms

Upon spiking the cosms with pharmaceuticals, all compounds continuously declined in the water phases (Figure 4). Their removal was generally fastest in the cosms with high oxygen content (AE) compared to the anaerobic (ANAE) and undisturbed (RE) cosms. Pharmaceuticals in the latter two behaved more or less the same in terms of water phase decline. The controls showed that most substances were stable in the absence of a sediment bed. FEN, an exception, did decrease significantly in the AE and ANAE controls, and also to some degree in the RE controls. However, the decrease of

FEN was still much slower in the controls than in the cosms that contained sediment beds. The blanks showed that no cross-contamination occurred during the sub-sampling. Microsensor profiling showed that redox potential stayed high in the water and sediments of the AE cosms, while it decreased through the experiment in the RE cosms and the ANAE cosms (Figure S1). For all cosms, pH in the sediment beds increased throughout the experiment, from slightly below 7 to slightly above 7. Dissolved oxygen was profiled for the RE cosms only, and showed an increase over the course of the experiment.



Figure 4. The measured concentration of pharmaceuticals in the water phase in the aerobic (AE), anaerobic (ANAE) and undisturbed microcosms (RE).

It can be assumed that the elimination of pharmaceuticals in the cosms was a combination of sorption, diffusion and degradation, but the role played by each process is difficult to discern at a glance. For all the cosms and all pharmaceuticals, the removal from the water phase was fastest during the first 2 days, after which the rate tended to slow down (Figure 4). The fast initial removal can be explained by diffusive mass transfer into the sediments, followed by sorption to the sediment matrix. Upon saturation of the sediments' sorption capacity, removal of pharmaceuticals from the water phase will have been governed by degradation. For the sake of simplification of data interpretation, it was assumed that sorption and diffusion were the sole factors causing the removal from the water phase during the first 2 days of the experiment, upon which equilibrium was assumed to have been reached. Degradation was then assumed to take over and further sorption neglected. Hence, the degradation rates calculated using Equation (2) took day 2 as time zero.

Upon termination of the cosm experiment, the mass balance in the water-sediment system was quantified by extracting the pharmaceuticals from the sediments (Figure 5). The difference between the originally added amounts and the amounts recovered from the sum of the sediment and water compartments was assumed to correspond to the amount eliminated by processes in the sediments (Figure 5).

For all conditions, SUL was degraded the most, followed by NAP, FEN, FUR, and CAR (Figure 5). The conditions under which the degradation took place had some impact on the elimination of substances, albeit this was not conclusive. The undisturbed systems (RE) tended to have the highest removals for most substances.



Figure 5. Mass balance in the microcosms at the termination of the experiment. Note the change in axis scale.

Even though CAR only sorbed moderately to the sediments (Figure 2), sorption was the main cause of its elimination from the water compartment. This indicates that the initial elimination of CAR from the water phase was more associated with sorption onto and diffusion into the sediments than to degradation. At the end of the experiment, an average of $35 \pm 4.2\%$ of the initially added CAR remained in the water phase, while $36 \pm 2.8\%$ of it was extracted from the sediments (Figure 5). This left a missing mass of approximately $29 \pm 6\%$ which was assumed degraded. The low contribution from degradation to the overall removal from the water compartment indicates that the high stability of CAR was caused by a low degradability, which is consistent with [51] finding that this chemical is highly resistant to degradation during sewage treatment. The missing mass corresponded to a degradation rate ranging from 0.0186 ± 0.0012 day -1 to 0.0194 ± 0.0014 day -1 for anaerobic and aerobic cosms, respectively. CAR exhibited high recalcitrance towards degradation in the sediments under all tested conditions, resulting in an average DT50 of 36.5 ± 0.8 day (Table S5). The DT50 value obtained in this study is smaller than the 47 day reported by Löffler et al. (2005) [52], who studied the fate of pharmaceuticals in systems containing sediments and water from a creek. However, the organic matter of the sediments in that study was only half of that of the present study's sediments. On the other hand, they used a somewhat lower water/sediment ratio (1.5 mL g^{-1}), which would tend to counteract the effect of a lower organic matter content. In this context, it is important to note that the water/sediment ratios applied in various studies differ, which complicates comparison between studies. Under idealized conditions and assuming that degradation only takes place in or on the sediments, a doubling of the water/sediment ratio would cause a halving of observed water phase degradation rates and a doubling of DT₅₀ values.

FUR was slightly less resistant to degradation than CAR. Its shortest DT50 value, 22.2 ± 2.1 day, was achieved in the aerobic cosms (AE) (Table S5). The degradation rates in the anaerobic cosms

were less than half of those of the aerobic ones (AE) $(0.0144 \pm 0.0014 d-1 \text{ and } 0.0314 \pm 0.0029 \text{ day}-1$, respectively). Based on the mass balance, the aerobic cosms had the least FUR remaining in the water compartment $(24.1 \pm 5.1\%)$ with approximately $66.1 \pm 7.9\%$ degraded, while the anaerobic cosms had $37.1 \pm 8\%$ in the water phase with approximately $51.8 \pm 9.5\%$ been degraded. Although the sorption experiment showed that FUR and CAR had comparable adsorption affinities (Figure 3), the extracted amount was much less for FUR (average of $14 \pm 6.2\%$). This indicates that FUR was more degradable than CAR, and especially under aerobic conditions. So far, hydrolysis and photolysis have been mostly considered as the removal mechanisms of FUR in water [53], while its biodegradation has not been reported so far [54].

The degradation rate for FEN was one order magnitude higher than that of CAR and FUR (ranging from $0.210 \pm 0.006 \text{ d}^{-1}$ in anaerobic to $0.517 \pm 0.0076 \text{ d}^{-1}$ in aerobic cosms). Undisturbed cosms were found to have the shortest DT₅₀ value ($2.4 \pm 0.1 \text{ d}$), and aerobic cosms had the longest ($3.3 \pm 0.04 \text{ d}$). Overall, 96.8 $\pm 1.5\%$ of FEN was degraded during the experiment, with only $2.9 \pm 1.4\%$ adsorbed to the sediments (Figure 5). The adsorbed amount agreed poorly with the high sorption affinity found in the sorption experiment (Figure 3), which can be explained by that the adsorbed FEN was rapidly degraded in the sediments. This suggests that degradation is a fast and dominating process in FEN removal.

The removal of NAP and SUL were comparable, where both compounds had similar half-lives (average DT_{50} = 7.7 \pm 0.5 d and 5.2 \pm 1.4 d, respectively) and similar remaining percentages in the water phase (averages of $0.16 \pm 0.3\%$ and $0.3 \pm 0.5\%$, respectively). However, the sediments seemed to facilitate a faster removal of SUL under anaerobic conditions ($0.16 \pm 0.0008 \text{ d}^{-1}$), but showed no clear trend for NAP (Table S5). Nevertheless, the rate constant of NAP somewhat lower yet still comparable to that reported by Koumaki et al. (2017) [14], who studied the environmental fate of pharmaceuticals in a river water-sediment system under various redox conditions ($0.1835 \pm 0.0148 \text{ d}^{-1}$ at aerobic and $0.1063 \pm 0.0103 \text{ d}^{-1}$ at anaerobic conditions), but applying a higher water/sediment ratio (3 mL g⁻¹). For all tested conditions, almost all the SUL and NAP were eliminated from the water compartment (Figure 5), with the majority being degraded (99.6 \pm 0.6% and 98.6 \pm 0.5%, respectively). The readily degradability of NAP (more than 75%) was also reported by [55] in silica sand containing different sources of water, but the water/sand ratio was not stated and the data hence are not comparable. The extracted amount of SUL (0.04 \pm 0.02%) agrees well with its weak tendency towards adsorption (Figure 3), while less NAP than expected was extracted (1.2 \pm 0.3%), indicating that degradation played an important role in removing NAP, compared to adsorption. Wilt et al. [56] also found that NAP was almost completely removed by sediments from a constructed wetland in batch experiments, but at a lower water/sediment ratio (8 mL g^{-1}), with biodegradation contributing more than 70% of the total removal.

The present study suggests that degradation of the selected pharmaceuticals predominantly took place in the sediments of the cosms and that sorption attenuated some pharmaceuticals in this matrix. For many full-scale stormwater ponds the water/sediment ratio is roughly around $5-15 \text{ mL g}^{-1}$, depending on water depth and amount of deposited sediments, i.e., somewhat higher than the ratio of 2.44 mL g⁻¹ applied in the present study. Their water phase removal rates can hence be expected to be slower than in the cosms. Furthermore, the water residence time in stormwater retention ponds is often shorter than the expected half-life of some of the substances. Nevertheless, this study demonstrates that, stormwater ponds are capable of eliminating pharmaceuticals like FEN. Hence, under these circumstances, conventional wastewater treatment plant is not the only way to mitigate its environmental impacts. For substances with a lower degradability, sorption to the sediments might enhance subsequent degradation, as it allows attenuation of the substance and hence providing more time for degradation. However, for substances like CAR and FUR, with low degradability and moderate sorption affinity to sediments, stormwater detention ponds probably will have limited efficiency.

4. Conclusions

This study suggested that the sorption of selected pharmaceuticals to the sediments in stormwater retention ponds was affected both by pH and the hydrophobicity of the compound. Comparing all substances investigated, the impact of their hydrophobicity (log K_{OW} 0.89 to 5.19) was though more important for the overall sorption than was pH. For NAP and FUR, however, pH did play an important role as log K_d values decreased by approximately a value of one when pH increased from 5 to 8, while for FEN, CAR, and SUL, it played a lesser role, or no role at all.

SUL was the most readily degradable substance, followed by NAP, FEN, FUR, and CAR. Nearly all traces of the first three pharmaceuticals were removed from the water phase and degraded by or sorbed to the sediments within the 38 days the experiment ran. The last two substances were only moderately degraded or sorbed. The overall results indicate that stormwater retention ponds have the potential to mitigate SUL, NAP, and FUR, while these systems most likely will have little effect on FUR and CAR. It is hence clear that stormwater retention ponds can play a role in removing part of the less-persistent pharmaceuticals that they sometimes receive from storm drainage systems. The actual removal efficiency and the importance of sorption versus degradation will depend on the design of the system and its operational conditions. Overall it can be concluded that shallow systems with low water to sediment ratios and systems with long retention times will enhance mitigation of pharmaceuticals originating from an undesired discharge of wastewater into storm drainage systems.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/11/3/526/s1, Figure S1: Vertical profile of aerobic (AE), anaerobic (ANAE) and undisturbed (RE) microcosms before and after incubation in terms of redox potential (left), pH (middle) and dissolved oxygen concentration (right), Table S1: Properties of the sediment, Table S2: Identification of the selected pharmaceuticals in SIM mode by LC-MS, Table S3: Limit of detection and quantification of the compounds in water and sediments, Table S4: Freundlich model fitting result and sediment-water distribution coefficient. Kf (µg1-1/n L1/n g-1), Kd (L kg-1), Table S5: The fitting results of first-order decay model.

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References

- Daughton, C.G. Non-regulated water contaminants: Emerging research. *Environ. Impact Assess. Rev.* 2004, 24, 711–732. [CrossRef]
- 2. Clara, M.; Strenn, B.; Gans, O.; Martinez, E.; Kreuzingeru, N.; Kroissk, H. Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. *Water Res.* **2005**, *39*, 4797–4807. [CrossRef] [PubMed]
- 3. Verlicchi, P.; Galletti, A.; Petrovic, M.; Barceló, D.; Al Aukidy, M.; Zambello, E. Removal of selected pharmaceuticals from domestic wastewater in an activated sludge system followed by a horizontal subsurface flow bed—Analysis of their respective contributions. *Sci. Total Environ.* **2013**, 454–455, 411–425. [CrossRef] [PubMed]
- Launay, M.A.; Dittmeri, U.; Steinmetzd, H. Organic micropollutants discharged by combined sewer overflows-Characterisation of pollutant sources and stormwater-related processes. *Water Res.* 2016, 104, 82–92. [CrossRef]
- 5. Revitt, D.M.; Ellis, J.B. Urban surface water pollution problems arising from misconnections. *Sci. Total Environ.* **2016**, *551–552*, 163–174. [CrossRef]
- 6. Hvitved-Jacobsen, T.; Vollertsen, J.; Nielsen, A.H. *Urban and Highway Stormwater Pollution: Concepts and Engineering*; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2010.
- 7. Panasiuk, O.; Hedström, A.; Marsalek, J.; Ashley, R.M.; Viklander, M. Contamination of stormwater by wastewater: A review of detection methods. *J. Environ. Manag.* **2015**, *152*, 241–250. [CrossRef]

- Beckers, L.M.; Busch, W.; Krauss, M.; Schulze, T.; Brack, W. Characterization and risk assessment of seasonal and weather dynamics in organic pollutant mixtures from discharge of a separate sewer system. *Water Res.* 2018, 135, 122–133. [CrossRef]
- 9. Pongmala, K.; Autixier, L.; Madoux-Humery, A.; Fuamba, M.; Galarneau, M.; Sauvé, S.; Prévost, M.; Dorner, S. Modelling total suspended solids, E. coli and carbamazepine, a tracer of wastewater contamination from combined sewer overflows. *J. Hydrol.* **2015**, *531*, 830–839. [CrossRef]
- Al Aukidy, M.; Verlicchi, P.; Jelic, A.; Petrovic, M.; Barcelò, D. Monitoring release of pharmaceutical compounds: Occurrence and environmental risk assessment of two WWTP effluents and their receiving bodies in the Po Valley, Italy. *Sci. Total Environ.* 2012, *438*, 15–25. [CrossRef]
- 11. Christoffels, E.; Brunsch, A.; Wunderlich-Pfeiffer, J.; Mertens, F.M. Monitoring micropollutants in the Swist river basin. *Water Sci. Technol.* **2016**, *74*, 2280–2296. [CrossRef]
- Revitt, D.M.; Shutes, R.B.E.; Jones, R.H.; Forshaw, M.; Winter, B. The performances of vegetative treatment systems for highway runoff during dry and wet conditions. *Sci. Total Environ.* 2004, 334–335, 261–270. [CrossRef]
- Mohanty, S.K.; Valenca, R.; Berger, A.W.; Iris, K.M.; Xiong, X.; Saunders, T.M.; Tsang, D.C.W. Plenty of room for carbon on the ground: Potential applications of biochar for stormwater treatment. *Sci. Total Environ.* 2018, 625, 1644–1658. [CrossRef]
- 14. Koumaki, E.; Mamais, D.; Noutsopoulos, C. Environmental fate of non-steroidal anti-inflammatory drugs in river water/sediment systems. *J. Hazard. Mater.* **2017**, *323*, 233–241. [CrossRef]
- 15. Thomsen, A.B.; Henriksen, K.; Grøn, C.; Møldrup, P. Sorption, transport, and degradation of quinoline in unsaturated soil. *Environ. Sci. Technol.* **1999**, *33*, 2891–2898. [CrossRef]
- Arias-Estévez, M.; López-Periago, E.; Martínez-Carballo, E.; Simal-Gándara, J.; Mejuto, J.C.; García-Río, L. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agric. Ecosyst. Environ.* 2008, 123, 247–260. [CrossRef]
- 17. Meng, P.; Pei, H.; Hu, W.; Shao, Y.; Li, Z. How to increase microbial degradation in constructed wetlands: Influencing factors and improvement measures. *Bioresour. Technol.* **2014**, *157*, 316–326. [CrossRef]
- Kim, H.B.; Kim, S.H.; Jeon, E.K.; Kim, D.H.; Tsang, D.C.W.; Alessi, D.S.; Kwon, E.E.; Baek, K. Effect of dissolved organic carbon from sludge, Rice straw and spent coffee ground biochar on the mobility of arsenic in soil. *Sci. Total Environ.* 2018, 636, 1241–1248. [CrossRef]
- 19. Murdoch, R.W.; Hay, A.G. Genetic and chemical characterization of ibuprofen degradation by Sphingomonas Ibu-2. *Microbiology* **2013**, *159*, 621–632. [CrossRef]
- 20. Yang, Y.; Wang, Z.; Xie, S. Aerobic biodegradation of bisphenol A in river sediment and associated bacterial community change. *Sci. Total Environ.* **2014**, 470–471, 1184–1188. [CrossRef]
- 21. Delaune, R.D.; Devai, I.; Mulbah, C.; Crozier, C.; Lindau, C.W. The influence of soil redox conditions on atrazine degradation in wetlands. *Agric. Ecosyst. Environ.* **1997**, *66*, 41–46. [CrossRef]
- Faulwetter, J.L.; Gagnon, V.; Sundberg, C.; Chazarenc, F.; Burr, M.D.; Brisson, J.; Camper, A.K.; Stein, O.R. Microbial processes influencing performance of treatment wetlands: A review. *Ecol. Eng.* 2009, 35, 987–1004. [CrossRef]
- 23. Banzhaf, S.; Nödler, K.; Licha, T.; Krein, A.; Scheytt, T. Redox-sensitivity and mobility of selected pharmaceutical compounds in a low flow column experiment. *Sci. Total Environ.* **2012**, *438*, 113–121. [CrossRef]
- 24. Istenič, D.; Arias, C.A.; Matamoros, V.; Vollertsen, J.; Brix, H. Elimination and accumulation of polycyclic aromatic hydrocarbons in urban stormwater wet detention ponds. *Water Sci. Technol.* **2011**, *64*, 818–825. [CrossRef]
- 25. Istenič, D.; Arias, C.A.; Vollertsen, J.; Nielsen, A.H.; Wium-Andersen, T.; Hvitved-Jacobsen, T. Improved urban stormwater treatment and pollutant removal pathways in amended wet detention ponds. *J. Environ. Sci. Health Part A* **2012**, *47*, 1466–1477. [CrossRef]
- 26. Minelgaite, G.; Nielsen, A.H.; Pedersen, M.L.; Vollertsen, J. Photodegradation of three stormwater biocides. *Urban Water J.* **2017**, *14*, 53–60. [CrossRef]
- 27. Daughton, C.G.; Ternes, T.A. Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change? *Environ. Health Perspect.* **1999**, *107*, 907–938. [CrossRef]
- 28. Hörsing, M.; Ledin, A.; Grabic, R.; Fick, J.; Tysklind, M.; la Cour Jansen, C.; Andersen, H.R. Determination of sorption of seventy-five pharmaceuticals in sewage sludge. *Water Res.* **2011**, *45*, 4470–4482. [CrossRef]

- 29. Grossberger, A.; Hadar, Y.; Borch, T.; Chefetz, B. Biodegradability of pharmaceutical compounds in agricultural soils irrigated with treated wastewater. *Environ. Pollut.* **2014**, *185*, 168–177. [CrossRef]
- 30. Roberts, J.; Kumar, A.; Du, J.; Hepplewhite, C.; Ellis, D.J.; Christy, A.G.; Beavis, S.G. Pharmaceuticals and personal care products (PPCPs) in Australia's largest inland sewage treatment plant, and its contribution to a major Australian river during high and low flow. *Sci. Total Environ.* **2016**, *541*, 1625–1637. [CrossRef]
- 31. OECD. Test No. 106: Adsorption—Desorption Using A Batch Equilibrium Method; OECD: Paris, France, 2000. [CrossRef]
- 32. Hou, J.; Pan, B.; Niu, X.; Chen, J.; Xing, B. Sulfamethoxazole sorption by sediment fractions in comparison to pyrene and bisphenol A. *Environ. Pollut.* **2010**, *158*, 2826–2832. [CrossRef]
- Le Guet, T.; Hsini, I.; Labanowski, J.; Mondamert, L. Sorption of selected pharmaceuticals by a river sediment: Role and mechanisms of sediment or Aldrich humic substances. *Environ. Sci. Pollut. Res.* 2018, 1–12. [CrossRef]
- 34. Shen, G.; Zhang, Y.; Hu, S.; Zhang, H.; Yuan, Z.; Zhang, W. Adsorption and degradation of sulfadiazine and sulfamethoxazole in an agricultural soil system under an anaerobic condition: Kinetics and environmental risks. *Chemosphere* **2018**, *194*, 266–274. [CrossRef]
- 35. Karickhoff, S.W.; Brown, D.S.; Scott, T.A. Sorption of hydrophobic pollutants on natural sediments. *Water Res.* **1979**, *13*, 241–248. [CrossRef]
- 36. Franco, A.; Trapp, S. Estimation of the soil—Water partition coefficient normalized to organic carbon for ionizable organic chemicals. *Environ. Toxicol. Chem.* **2008**, 27, 1995–2004. [CrossRef]
- 37. Wium-Andersen, T.; Nielsen, A.H.; Hvitved-Jacobsen, T.; Brix, H.; Arias, C.A.; Vollertsen, J. Modeling the eutrophication of two mature planted stormwater ponds for runoff control. *Ecol. Eng.* **2013**, *61*, 601–613. [CrossRef]
- Varga, M.; Dobor, J.; Helenkár, A.; Jurecska, L.; Yao, J.; Záray, G. Investigation of acidic pharmaceuticals in river water and sediment by microwave-assisted extraction and gas chromatography-mass spectrometry. *Microchem. J.* 2010, 95, 353–358. [CrossRef]
- 39. Schaffer, M.; Boxberger, N.; Börnick, H.; Licha, T.; Worch, E. Sorption influenced transport of ionizable pharmaceuticals onto a natural sandy aquifer sediment at different pH. *Chemosphere* **2012**, *87*, 513–520. [CrossRef]
- Klement, A.; Kodešová, R.; Bauerová, M.; Golovko, O.; Kočárek, M.; Fér, M.; Nikodem, A.; Grabic, R. Sorption of citalopram, irbesartan and fexofenadine in soils: Estimation of sorption coefficients from soil properties. *Chemosphere* 2018, 195, 615–623. [CrossRef]
- 41. Martínez-Hernández, V.; Meffe, R.; Herrera, S.; Arranz, E.; de Bustamante, I. Sorption/desorption of non-hydrophobic and ionisable pharmaceutical and personal care products from reclaimed water onto/from a natural sediment. *Sci. Total Environ.* **2014**, *472*, 273–281. [CrossRef]
- 42. Gao, J.; Pedersen, J.A. Adsorption of sulfonamide antimicrobial agents to clay minerals. *Environ. Sci. Technol.* **2005**, *39*, 9509–9516. [CrossRef]
- 43. Kahle, M.; Stamm, C. Sorption of the veterinary antimicrobial sulfathiazole to organic materials of different origin. *Environ. Sci. Technol.* **2007**, *41*, 132–138. [CrossRef]
- 44. Figueroa-Diva, R.A.; Vasudevan, D.; Mackay, A.A. Trends in soil sorption coefficients within common antimicrobial families. *Chemosphere* **2010**, *79*, 786–793. [CrossRef]
- 45. Park, J.Y.; Huwe, B. Effect of pH and soil structure on transport of sulfonamide antibiotics in agricultural soils. *Environ. Pollut.* **2016**, *213*, 561–570. [CrossRef]
- 46. Chen, K.L.; Liu, L.C.; Chen, W.R. Adsorption of sulfamethoxazole and sulfapyridine antibiotics in high organic content soils. *Environ. Pollut.* **2017**, *231*, 1163–1171. [CrossRef]
- 47. Białk-Bielińska, A.; Maszkowska, J.; Mrozik, W.; Bielawska, A.; Kołodziejska, M.; Palavinskas, R.; Stepnowski, P.; Kumirska, J. Sulfadimethoxine and sulfaguanidine: Their sorption potential on natural soils. *Chemosphere* **2012**, *86*, 1059–1065. [CrossRef]
- Karcı, A.; Balcıoğlu, I.A. Investigation of the tetracycline, sulfonamide, and fluoroquinolone antimicrobial compounds in animal manure and agricultural soils in Turkey. *Sci. Total Environ.* 2009, 407, 4652–4664. [CrossRef]
- 49. Figueroa, R.A.; Mackay, A.A. Sorption of oxytetracycline to iron oxides and iron oxide-rich soils. *Environ. Sci. Technol.* **2005**, *39*, 6664–6671. [CrossRef]

- Maskaoui, K.; Hibberd, A.; Zhou, J.L. Assessment of the interaction between aquatic colloids and pharmaceuticals facilitated by cross-Flow ultrafiltration. *Environ. Sci. Technol.* 2007, 41, 8038–8043. [CrossRef]
- 51. Ternes, T.A. Occurrence of drugs in German sewage treatment plants and rivers. *Water Res.* **1998**, 32, 3245–3260. [CrossRef]
- 52. Löffler, D.; Römbke, J.; Meller, M.; Ternes, T.A. Environmental Fate of Pharmaceuticals in Water/Sediment Systems. *Environ. Sci. Technol.* **2005**, *39*, 5209–5218. [CrossRef]
- 53. Yagi, N.; Kenmotsu, H.; Sekikawa, H.; Takada, M. Studies on the photolysis and hydrolysis of furosemide in aqueous solution. *Chem. Pharm. Bull.* **1991**, *39*, 454–457. [CrossRef]
- 54. Chen, Y.; Vymazal, J.; Březinová, T.; Koželuh, M.; Kule, L.; Huang, J.; Chen, Z. Occurrence, removal and environmental risk assessment of pharmaceuticals and personal care products in rural wastewater treatment wetlands. *Sci. Total Environ.* **2016**, *566–567*, 1660–1669. [CrossRef]
- 55. Maeng, S.K.; Sharma, S.K.; Abel, C.D.; Magic-Knezev, A.; Amy, G.L. Role of biodegradation in the removal of pharmaceutically active compounds with different bulk organic matter characteristics through managed aquifer recharge: Batch and column studies. *Water Res.* **2011**, *45*, 4722–4736. [CrossRef]
- De Wilt, A.; He, Y.; Sutton, N.; Langenhoff, A.; Rijnaarts, H. Sorption and biodegradation of six pharmaceutically active compounds under four different redox conditions. *Chemosphere* 2018, 193, 811–819. [CrossRef]



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Paper- II

Microplastics in Urban and Highway Stormwater Retention Ponds

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Microplastics in urban and highway stormwater retention ponds



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HIGHLIGHTS

scapes.

way areas.

mass.

• An assessment of MP in stormwater re-

· Commercial and industrial areas emit-

PVC, PS, PP, PE and polyester were the

most common polymers found.PVC had the largest particle size and

ted more MP than residential and high-

tention ponds across various land-

GRAPHICAL ABSTRACT



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ABSTRACT

Urban and highway stormwater runoff seems an obvious pathway for conveying microplastics from land-based sources to the aquatic environment. The significance of this pathway is however largely unknown. This study presents first results on microplastics in urban and highway stormwaters by analysing microplastics (10–2000 μ m) in the water phase of stormwater treatment ponds in the North of Jutland, Denmark. The stormwater of seven ponds treating runoff drained from different landscapes were studied. Ponds serving highway and residential areas had the lowest microplastic concentration, while ponds serving areas with industry and commerce had the highest. The stormwater of the ponds contained 490–22,894 items m⁻³, corresponding to an estimated 85–1143 μ g m⁻³. The dominating polymers were polypropylene, polyvinylchloride, polyester, polyethylene and polystyrene. There was a tendency towards polyvinylchloride particles being the largest in size, while a mixed group of less common polymers were the smallest. Residential ponds generally held the largest microplastic particles and were in many aspects quite comparable to one another, in terms of concentrations, sizes, and polymer composition. This study shows that land-based sources are significant contributors to MP in the environment. It demonstrates that the stormwater retention ponds act not only as pollution hotspots, but also play a role in the transport of MP from land to the aquatic environment.

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1. Introduction

Plastic pollution is highly visible in the environment, and an emerging topic on the public, scientific, and political agenda. Reports on marine plastic pollution and concerns about its impact on marine vertebrates (Thompson et al., 2004; Lusher et al., 2013; Marques et al., 2018) have driven the awareness of the plastic-issue. Microplastics (MP), most frequently defined as plastic particles <5 mm in length (Arthur et al., 2009), have been found throughout the marine environment, including the gut of fish (Beer et al., 2017), zooplankton (Cole et al., 2013), as well as deposit and filter feeders (Van Cauwenberghe et al., 2015). Negative

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effects have been documented at the individual level in copepods (Cole et al., 2015), worms (Wesch et al., 2017), and bivalves (Bour et al., 2018). Meanwhile, concerns regarding human exposure through seafood (Van Cauwenberghe and Janssen, 2014; Lusher et al., 2017) and potable water (Pivokonsky et al., 2018) have also been raised.

The MP originate from sea-based and land-based sources, where urban areas are identified as important contributors of MP into the environment (Horton et al., 2017). The discharge of MP from urban wastewater treatment plants (WWTPs) has been studied in quite some detail (Mintenig et al., 2017; Talvitie et al., 2017; Simon et al., 2018). However, advanced WWTPs that include carbon and nutrient removal are efficient at retaining MP, and their discharge seems only to explain part of the MP in the receiving waters. For example did Simon et al. (2018) find that Danish WWTPs released on average 0.56 g of MP per capita and year, which does not seem to explain the occurrence of MP in Danish waters. For a British watershed, Kay et al. (2018) reported that the studied WWTPs led to elevated levels of MP, but that other sources also played an important role in explaining the detected levels of MP contamination. Estabbanati and Fahrenfeld (2016) measured MP upstream and downstream of four municipal WWTPs and found that downstream MP levels were elevated. However, the waters also contained MP at the upstream locations which, was contributed by other sources. Lasee et al. (2017) studied MP in three connected urban lakes receiving treated wastewater. Their results indicated that the treated wastewater alone could not explain the levels of MP and they reasoned that urban stormwater runoff must also have contributed to the levels in the lakes. Recent work has also shown that the ingestion of MP by river invertebrates downstream of WWTPs was not significantly higher than upstream (Windsor et al., 2019a). Sutton et al. (2016) drew a similar conclusion when investigating MP in the San Francisco Bay, concluding that there must have been other sources for MP than the treated wastewater, and suggested stormwater runoff as one of these. Horton et al. (2017) also presented data indicating that stormwater runoff might contribute to MP in the environment. They observed fragments of thermoplastic road markings downstream of a storm drain outfall and attributed these to road runoff.

Urban and highway stormwater runoff are direct pathways for landbased microplastics into freshwaters (Horton et al., 2017; Vaughan et al., 2017), which have been pointed out to be important in terms of microplastics impacts and pathways for emissions to the oceans. At the same time, they have been rather under-studied and only to a limited degree pinned down in terms of actual measurements (Rochman, 2018). Blettler et al. (2018) also identified freshwater environments as an area with little data and a need for investigations covering plastics in all size fractions and pointed out that the large rivers in countries with rapid growth and poorly managed waste have been especially overlooked. For the freshwater systems of the developed world, there is some data on MP in river systems (Liedermann et al., 2018; Rodrigues et al., 2018) and lakes (Hendrickson et al., 2018; Sighicelli et al., 2018) showing that MP are also ubiquitous in these waters. All these observations indicate that stormwater runoff is important for the conveyance of MP into the aquatic environment, but that the understanding of magnitudes and processes remains poor, as the field-based measurements are limited (Windsor et al., 2019b).

One issue in pinning down the sources of MP contamination is the use of widely different sampling approaches and analytical methods, combined with different MP size-ranges addressed. Furthermore, the vast majority of the published studies refer to MP in terms of particle number within some size range (Löder et al., 2017). Such data are highly important when assessing the environmental impacts of MP, but insufficient when assessing the load of MP on the environment or its fate therein. Here, the mass of the MP must also be quantified. This creates some analytical problems. The spectroscopic methods typically applied for MP analysis are well suited for the quantification of size and shape of MP particles. The current state of the science, they do however only allow MP mass to be estimated (Simon et al., 2018).

A further issue when quantifying MP in stormwater discharge from urban areas is the difficulty in obtaining a representative sample during a storm event. All cities drain stormwater by natural and constructed systems, where the latter typically is a piped drainage system. Some of the drainage systems are combined - where domestic and industrial wastewater and stormwater are conveyed in the same pipe, while others are separated - where one pipe conveys wastewater and another stormwater. Contrary to dry-weather WWTP discharges, the discharges during rain events are of intermittent nature. A combined drainage system, for example, only discharges when its hydraulic capacity is exceeded during a large storm event. A separate storm sewer, on the other hand, discharges at any rain event above a certain initial hydrological loss. The general pollutant concentration in the stormwater runoff is known to vary substantially between sites, and also between events at the same site (Bertrand-Krajewski et al., 1998). Furthermore, part of the stormwater of a modern city is not discharged directly, but undergoes some sort of treatment, often in artificial basins, called retention ponds, that mimic the natural treatment processes of small freshwater lakes (Hvitved-Jacobsen et al., 2010). Here, the stormwater stays for a period of days to weeks, allowing many of the particulates to settle, upon which part of the treated water is discharged by displacement during the following rain event.

The objective of the present study is to quantify microplastics in stormwater from retention ponds, partly because these have many similarities to small natural lakes subject to high pollution loads, and partly because stormwater is an important pathway for MP into the aquatic environment. Seven ponds were chosen as having different catchment characteristics, in order to evaluate whether the land use in the catchment influenced the amount of MP in the water of the ponds.

2. Material and methods

2.1. Sampling

Stormwater was sampled from September to October 2017 from seven retention ponds in Denmark (Table 1) - three ponds with residential catchments (R1, R2, R3), two with industrial ones (I1, I2), one with a commercial catchment (C1), and one with a highway catchment (H1). Three sampling rounds were performed during dry weather, with at least two weeks between them. Dry weather was defined as no rain occurring at least two days prior to the sampling. Samples were collected using a filtering device equipped with a removable filter cut from a 10 µm stainless steel mesh (100 mm in diameter) (Fig. S1). Water was pumped through the device by a positive displacement pump (Creusen Roermond, Netherlands). The filtering device was made in stainless steel, with the inflow and outflow pipes made in PVC. The suction hose was connected to a cuboid cage $(10 \times 10 \times 20 \text{ cm})$ made of a 2 cm stainless steel mesh to filter out large debris. The flow was logged with an electronic flowmeter (IFM SM7000, Germany). When sampling, the suction hose was held by a floater approx. 20 cm below the water surface. The cage was placed in the pond approx. 5-10 m from the shoreline, and the corresponding water depth was approx. 1 m. For each sampling of a pond, water was filtered until the filter clogged, which typically happened after 201 to 454 L. For each pond, the filters from the three sampling rounds were lumped and analysed as one sample. The total volumes sampled per pond are given in Table 1. The filters were stored in glass jars and soaked in a sodium dodecyl sulphate solution (SDS, 0.15 g L^{-1}) immediately after use. After transferring to the lab, filters from the same pond were combined into one beaker and soaked with 500 mL of the SDS solution in order to detach MP from other solids, hence to open up the surface space for subsequent MP extraction.

2.2. Sample processing

Samples were wet-oxidised on the filters for 2 days by adding 50 mL of 50% H_2O_2 to the 500 mL of SDS-solution holding the filters. The H_2O_2 was hence diluted in the final solution, to minimize the potential of

Tuble 1				
Pond locations	, catchment	characteristics	and sample	volumes.

Site	City	Coordinate (N, E)	Pond area (m ²)	Impervious catchment area (ha)	Sample volume (L)	Catchment type
R1	Silkeborg	(56°11′39.8″, 9°32′57.9″)	4000	7.1	1016	Residential with single family houses and part of an orbital road
R2	Aarhus	(56°10′18.4″, 10°05′49.9″)	11,880	42.6	1139	Residential with single family houses
R3	Aarhus	(56°10′18.4″, 10°06′22.6″)	11,900	46.6	958	Residential with single family houses
I1	Aarhus	(56°10′49.0″, 10°07′58.4″)	7460	10.9	722	Light industry
I2	Viborg	(56°28'29.3", 9°24'43.3")	6500	69.8	1078	Light industry, commerce, do-it-yourself shops
C1	Aarhus	(56°08'41.8", 10°08'12.2")	6050	19.0	850	Commercial (shopping centre), some residential use
H1	Aarhus	(56°13′13.9″, 10°07′43.5″)	5540	4.8	979	Highway

polymer degradation (Hurley et al., 2018). This step partly removed some organic matter, and partly opened up the matrix for a subsequent enzymatic digestion (Enders et al., 2015). Particles were removed from the filters by ultrasonic treatment and collected into 200 mL of SDS solution. The samples were incubated with the enzymes Cellubrix (500 µL, Sigma-Aldrich) and Viscozyme (350 µL, Sigma-Aldrich) at 50 °C for 3 days, upon which Alcalase (500 µL, Novozymes) was added and the solution incubated for another 3 days, also at 50 °C. Finally, the sample underwent a Fenton reaction by adding 146 mL 50% H₂O₂, 63 mL of 0.1 M FeSO₄ and 65 mL of 0.1 M NaOH to further remove organic matter (Simon et al., 2018). As the process is exothermic, the vessel was kept on ice, targeting a temperature of 15–19 °C. Lares et al. (2018) carried out a study where MP and fibers were successfully extracted from wastewater through a rigorous oxidation treatment (30% H₂O₂ with catalyst, followed by an enzyme treatment). The present study applied relatively lower concentrated reagents, therefore the degradation of MP and fibers were neglected. After 4 h, the reaction had slowed down sufficiently and the vessel was left for 2 days at room temperature. The samples were filtered on 10 µm steel filters (47 mm in diameter), the filters transferred to a 50 mL beaker with a 1.7 g cm^{-3} zinc chloride solution, removed from the filters by ultrasonic treatment and transferred to a 200 mL funnel for density separation. The funnel was topped off with zinc chloride solution.

The sample underwent density separation twice. The first time the liquid was left to settle for 2 h and the second time it was left overnight. Settled particles were drained off and the remaining liquid was filtered through a 10 μ m stainless steel filter. Collected particles were transferred into HPLC grade ethanol using ultrasonic treatment. The suspension was transferred into a glass vial and evaporated until it was dry by flushing with N₂ (N5.0). Five mL of 50% ethanol was added for quantification by μ FTIR imaging (Fourier-transform infrared spectroscopy). Initial tests had shown that such a solution minimized particles sticking to the inside of the glass vial.

2.3. MP identification and quantification

The suspension was homogenised and sub-samples were deposited onto a 13 mm diameter zinc selenide transmission window of 2 mm thickness, using disposable glass capillary pipettes. The surface of the window was restricted by a compression cell (Pike Technologies, USA) to 10 mm diameter. The windows were covered with a glass beaker and dried at 55 °C. Depositing a too large sample volume on a window would impede the subsequent interpretation of the data obtained by the μ FTIR imaging. Sub-samples were hence deposited and dried in increments of 100 μ L until a suitable amount was reached. The latter was verified under a microscope. For each sample, three individual windows were prepared and analysed, corresponding to analysing 6–12% of the entire sample volume. The final MP concentration of a sample was determined from the sum of MP found on the three windows.

The whole of all 10 mm diameter windows were scanned with an FPA-based (Focal Plane Array) FTIR imaging technique at 5.5 μ m pixel resolution (μ FTIR imaging). This resulted in three IR-maps of approx. 3.2 million spectra each, as the equipment scans rectangular areas. The equipment was a Cary 620 FTIR microscope coupled with a Cary

670 IR spectroscopy (Agilent). The microscope used a 15× Cassegrain objective and had a 128 × 128 Mercury Cadmium Telluride (MCT) FPA detector. The scans were performed in transmission mode in the spectral range of 3750–950 cm⁻¹ at 8 cm⁻¹ resolution, applying 30 co-added scans (Simon et al., 2018).

The maps from the μ FTIR imaging were analysed using MPhunter, a software for the automated detection of MP from μ FTIR chemical imaging datasets developed at Aalborg University, Denmark, in collaboration with Alfred Wegener Institute, Germany. MPhunter builds upon the work of Primpke et al. (2017) and compares the IR-spectrum of each map pixel with the spectra of a reference database and assigns a score to the quality of each match. The algorithm generating the score correlates the raw spectra, their 1st derivatives and their 2nd derivatives by a Pearson correlation, yielding three Pearson's correlation coefficients (r_0 , r_1 , r_2) per combination of map spectrum and reference spectrum. The r-values are squared, and the user assigns them global weights (k_0 , k_1 , k_2). A score between 0 and 1 is calculated, $S_{d(i,j)}$, where (i,j) are the coordinates of the pixel on the map and d the number of the reference spectrum (Eq. (1)). Negative correlations are omitted, i.e. if an r-value is below zero, it is set to zero.

$$S_{d(i,j)} = \frac{k_0 r_0^2 + k_1 r_1^2 + k_2 r_2^2}{k_1 + k_2 + k_3} \tag{1}$$

The analysis yields a correlation map per reference spectrum in the database. The applied database contained 113 reference spectra of plastics as well as natural organic materials that can be misinterpreted as plastics. The spectra were organised into material groups covering the plastics: ABS (acrylonitrile butadiene styrene), acrylic, acrylic paints, alkyd, aramid, cellulose acetate, diene elastomer, EPDM (ethylene propylene diene monomers), epoxy, EVA (ethylene vinyl acetate), PA (polyamide), PAN Acrylic fibre (polyacrylonitrile), PE (polyethylene), Pebax®, PEG (polyethylene glycol), phenoxy resin, PLA (polylactic acid), polycarbonate, polyester, POM (polyoxymethylene), PP (polypropylene), PS (polystyrene), PTFE (polytetrafluoroethylene), PU (polyurethane), PU paints (polyurethane paints), PVA (polyvinyl alcohol), PVAC (polyvinyl acetate), PVC (polyvinyl chloride), SAN (styrene acrylonitrile), SBR (styrene butadiene rubber) and vinyl copolymer. Even though SBR was included, this does not mean that car tyre rubber containing SBR could be quantified as FTIR in transmission or reflection mode is not able to determine tyre material, due to the carbon black added to the tyre material as a filler (Kole et al., 2017). Carbon black is absorbent throughout the infrared region, making the acquisition of transmission or reflection spectra problematic. The included nonplastic groups were cellulose and proteinaceous material.

MPhunter allocates particles to a material group through an algorithm based on score thresholds, which were set prior to the analysis by manually assessing which thresholds produced trustworthy particle recognition. Applying MPhunter, the user first sets three thresholds for each reference spectrum ($t_1 > t_2 > t_3$). To qualify as a particle belonging to a material, at least one pixel must have a score of $S_{d(i_j)} \ge t_1$. If several materials have a score above their respective t_1 value, the pixel is associated with the material with the highest score. As an example, if a particle exceeds both the threshold of polyamide and proteinaceous

materials, but has a score for proteinaceous materials that is higher than that for polyamide, then that particle is associated with proteinaceous materials.

The so-selected pixel $S_{d(i,i)}$ is used as the nucleus of a particle, where both MP and natural particles are identified. The algorithm develops the particle by evaluating the adjacent pixels (Eq. (2)). If any of them have a score of $S_d \ge t_2$ for any reference spectrum belonging to the same material group as the nucleus pixel, it becomes associated with the particle created around it. After having developed the particle around $S_{d(i,j)}$, the procedure is repeated around all pixels that have been added to the original particle nucleus. The above approach can give rise to particle sizes from one pixel upwards. However, practical experience has shown that particles of only one pixel tend to be artefacts. Hence, a minimum particle size of 3 pixels was set. The third threshold is solely used to make the dataset more manageable, where any correlation below t_3 is ignored in the visualisation. Setting the threshold t_1 low will increase the number of false positive detections but decrease the number of false negative detections. Setting it high will have the opposite effect. Setting t_2 low will increase the size of the particle, setting it high will decrease it.

$$\begin{bmatrix} S_{d(i-1,j+1)} & S_{d(i,j+1)} & S_{d(i+1,j+1)} \\ S_{d(i-1,j)} & S_{d(i,j)} \ge t_1 & S_{d(i+1,j)} \\ S_{d(i-1,j-1)} & S_{d(i,j-1)} & S_{d(i+1,j-1)} \end{bmatrix}$$
(2)

A so-constructed particle is characterised by a major dimension and a minor dimension. The major dimension was calculated as the longest linear distance between pixels constituting the particle. The minor dimension was estimated from the area of the particle and its major dimension – assuming an elliptical shape. The volume is estimated by assuming the particle is an ellipsoid with its third dimension being 0.6 times its minor dimension (Simon et al., 2018). The particle mass is calculated from the estimated volume and density of the polymer. Further details and graphics on MPhunter can be found in supplementary materials, S1.

Applying an automated approach to identifying MP from µFTIR imaging datasets is vastly superior to using the alternative: a manual checking of each of the thousands of possible particles of a scanned sample (Primpke et al., 2017). Not only is this approach much less time consuming, it also reduces the risk of overlooking particles as every single pixel of a scan is analysed, not just visually selected particles. However, the approach is not free of human bias, as the operator has to set the thresholds for the analysis as well as select the reference spectra dataset - the latter being quite critical when identifying MP (Primpke et al., 2018). During the development of MPhunter, the program was validated by analysis of MP standards created from pure polymers. For the present study, the identification of MP in real samples was evaluated to take into account that real MP might behave differently from pure polymer standards, as well as to take into account possible matrix effects. This was done by first setting the threshold t₁ rather low and manually walking through a limited number of particles belonging to the targeted material groups. If the automated detection caused a significant number of false positive detections, the threshold was increased until the number of false positive and false negative detections were minimized. Secondly, the threshold t_2 was adjusted by walking through the boundaries of a limited number of particles to evaluate if the particle boundaries were well identified. In this process, the grouping of reference spectra into polymer groups was also adjusted. For MP where the µFTIR imaging revealed a major dimension >500 µm, the actual size of the MP was further confirmed using the visual image. Large particles can be of substantial thickness, leading to saturation in µFTIR imaging spectra. Visual inspection was needed in these cases to ensure that particle size was not underestimated.

2.4. Experimental quality control

The use of a plastic suction hose (PVC) for the filtering device could not be avoided. Hence, potential contamination during sampling was assessed. To do so, the spectrum of the hose was collected using Attenuated Total Reflectance – FTIR (Cary 630 with a diamond ATR crystal, Agilent) and compared to all particles identified as PVC in the μ FTIR imaging of the samples. The spectra comparison was conducted in the OMNIC software (Thermo Fisher, USA). In case the two spectra matched, there was a risk that this PVC particle could have originated from the hose, and it was excluded from the results.

Precautions were taken to reduce contamination during sample processing. Only glass, or Teflon-coated labware was used. Teflon is excluded from the data analysis as this plastic has a density of about 2.2 g cm⁻³. It would, hence, be removed together with inorganic particles in the density separation. All labware was rinsed with Milli-Q water and steel filters were muffled at 500 °C before use. All open containers were covered with Watch glass dishes (Sigma-Aldrich) immediately after use. To counteract contaminations from air deposition, which may originate from clothes, human skin, or be present in the common dust of laboratories (Woodall et al., 2014; Dris et al., 2017), the air of the μ FTIR scanning room was continuously filtered by an air treatment device (Dustbox® Hochleistungsluftreininger, Germany) with a HEPA filter (H14, 7.5 m²).

However, MP can still occur due to their ubiquitous presence. Therefore, the background contamination from the sample preparation was assessed by three blanks: a total of 100 L filtered Milli-Q water (1.2 μ m GF filters) was filtered on three 10 μ m steel filters by the previously described sampling device and the filters processed as described for the stormwater samples.

2.5. Statistical analysis

The normality of datasets was tested by a Shapiro-Wilk normality test (Ašmonaite et al., 2018). To check if there were differences on MP sizes among the ponds, a non-parametric Kruskal-Wallis test was applied. If the difference was statistically significant, then a Wilcoxon rank sum test was used afterwards to assess the differences in the pairwise comparison between ponds (Brandon et al., 2016). Principle Component Analysis (PCA) was carried out to estimate the variables which explained most of the variations. All statistical analysis was performed in R (v3.5.1), and the significance level was set to 0.05 in all cases.

3. Results and discussion

3.1. Background contamination

None of the particles identified in the stormwater matched the PVCmaterial of the sampling hose, meaning that the suction hose did not cause contamination. During sample preparation and analysis the blanks did, however, revealed a slight contamination by PE, PA, polyester, and acrylic MP. For each of the three blanks, a sub-sample of 600 µL was deposited. In these, a total of eight MP were found, where three were of PE, two of PA, two of polyester and one of acrylic. The mass of the eight MP was estimated as 339 ng. The MP contamination could have come from the equipment and surrounding air, but presumably not from the filtered water used for the blanks. For instance, Lin et al. (2018) performed one procedural blank simultaneously throughout their experiment and suggested that lab-coats were the main origin of airborne contamination. Hence, the contamination is believed to be related to the lab processing of the sample, and not the volume filtered. Correspondingly, the contamination was 22.2 items per processed sample, corresponding to an estimated 942 ng per processed sample. On average, 954 L of stormwater was collected per sample, leading to an approximate contamination of 23.3 items m⁻³ or 987 ng m⁻³. Due to the low level of contamination, and the corresponding statistical uncertainty on the actual numbers, the results were not corrected for background contamination.

Although precautions are commonly taken and researchers are aware of the issue, background contamination is not always assessed and quantified (Browne et al., 2011; Cheung et al., 2016; Kalčíkoá et al., 2017; Di and Wang, 2018; Sighicelli et al., 2018). The contamination level reported in other studies ranged from 0.4 to 2110 items L⁻¹, or 4.4 \pm 1.4 items per sample (Mintenig et al., 2017; Talvitie et al., 2017; Lares et al., 2018; Simon et al., 2018). Compared to these numbers, the values of the present study are deemed similar or even lower.

3.2. MP abundance

A total of 3436 particles were identified as MP in the samples from the seven ponds. The lowest value was from H1 with 58 MP, and the highest value was from C1 with 1946 MP. The concentration per pond ranged from 490 to 22,894 item m⁻³ and 85 to 1143 µg m⁻³, with a median value between all ponds of 1409 (interquartile range (IQR) = 11,348–494) item m⁻³ and 231 (IQR = 664–128) µg m⁻³ (Table 2). Comparing to the contamination of the blanks, it is seen that H1 was close to the level of contamination (58 MP found in the analysed sample and 22.2 MP in the blanks). For the other ponds, the contamination was deemed acceptable or low (Table 2). Normality tests showed that the MP mass concentrations (µg m⁻³) were normally distributed between the seven ponds (p = 0.144) but not the number concentrations (item m⁻³) (p = 0.014). Hence, the overall concentration of MP in the ponds was described by the median value with an IQR (interquartile range) both for MP mass and number.

MP were detected in all ponds. The commercial pond (C1) had the highest concentration in terms of both number and estimated mass (22,894 item m⁻³ and 1143 µg m⁻³), while the lowest numbers were found in R2 (490 item m⁻³) and the lowest mass in H1 (85 µg m⁻³). The residential ponds (R1, R2 and R3) had an average MP concentration of 898 ± 468 item m⁻³ and 182 ± 52 µg m⁻³, while the industrial ponds (I1 and I2) had an average MP concentration of 8299 ± 4313 item m⁻³ and 593 ± 101 µg m⁻³.

As this study is among the first peer-reviewed study to have reported MP in stormwater ponds, so the obtained results were compared the data to other measurements in freshwater systems and treated wastewater. However, due to a lack of generally accepted definition of the sizes making up the analysed MP (Hartmann et al., 2019), together with the different sampling methods and analytical techniques applied, the comparison is challenging. A typical example is a study from Rodrigues et al. (2018), where the MP number concentration $(58-1265 \text{ item m}^{-3})$ was comparable with that of the present study, but the mass concentration was over 10-100 orders of magnitude higher $(5-51.7 \text{ mg m}^{-3})$. This could be attributed to the larger size range they used $(55-5000 \,\mu\text{m})$, resulting larger particles tend to be found. With a more similar approach in the sampling and MP extraction process, the MP concentration in the present study was lower than that reported in treated wastewater (Simon et al., 2018), where 54,000 item m^{-3} and 4200 $\mu g \; m^{-3}$ as the average value was found in the outlet of ten Danish wastewater treatment plants.

3.3. Overall polymer composition

Lumping together all data from the retention ponds, the MP could be allocated to 17 polymer groups: PE, PS, PVC, PP, PA, PU, polyester, epoxy,

Table 2

The abundance of MP in the water phase from seven stormwater retention ponds in terms of counted MP number and estimated MP mass.

	R1	R2	R3	I1	I2	C1	H1	Average
Item m ⁻³	796	490	1409	5249	11,348	22,894	494	1409 (IQR = 11348 - 494)
$\mu g \ m^{-3}$	186	128	231	521	664	1143	85	231 (IQR = 664-128)

PVAC, acrylic, SAN, vinyl copolymer, EVA, PVA, phenoxy resin, alkyd and acrylic paints. Some of these were only sparsely detected throughout the samples and were gathered into a group of "others" (PA, PU, epoxy, PVAC, acrylic, SAN, vinyl copolymer, EVA, PVA, phenoxy resin, alkyd and acrylic paints). The group of "others" contained 148 MP, equivalent to 4.3% of the total number of MP identified. Further details on MP in the polymer groups is given in Table S2.

PP was the dominant polymer both by mass and number (Fig. 1). When ranked according to number concentrations, the order of polymers was PP, PE, PVC, polyester and PS (71.5%, 9.1%, 7.4%, 5.5%, and 2.2%, respectively). When ranked according to mass concentrations, the order changed to PP, PVC, polyester, PE, and PS (48.9%, 39.1%, 5.0%, 3.9%, and 2.2%, respectively). The difference in the abundance of polymers when measured as number and mass concentrations is related to the difference in polymer density and particle size distributions. The most pronounced example is PVC versus PE. Although PVC compared to PE was not high in terms of particle numbers, its higher density and a tendency towards larger particles (Fig. 3B) led to its mass concentration being significantly higher than that of PE (Fig. 1).

The overall polymer composition in this study was comparable with other freshwater-related studies, for instance, Rodrigues et al. (2018) found PP, PE, and PS made up 68% of the MP counted in water and sediments from the Antuã River. Sighicelli et al. (2018) reported that PE, EPS (expanded polystyrene), and PP dominated (in total 78% in terms of MP counts) in the surface waters of Italian Subalpine lakes. PVC was also detected in the coastal waters of China by Qu et al. (2018), but at a much lower concentration in terms of MP number (2%). The occurrence of these polymers was consistent with the polymers demanded by market, where PP, PVC, Polyester, PE, and PS together made up more than half of the plastics produced (PlasticsEurope, 2017).

The polymer distribution differed significantly between ponds. For example was C1 dominated by PP with both mass and number concentrations above 90%, while other ponds showed much less PP (Fig. 2); PVC dominated in R1, R2, R3, and I1 in terms of mass, and polyester was abundant in H1. While the cause of these differences is unknown, it seems reasonable to assume that it has something to do with the land use in the catchment. C1 holds a large shopping centre where the handling of plastic wrappings, food packaging and littering might be an important source (PlasticsEurope, 2017). This pond is, furthermore, known to receive significant amounts of illicitly connected wastewater, which also could be a contributing factor. It is also noteworthy that C1 was the pond holding the most MP (Table 2). I2 held the secondhighest concentration. Its catchment also holds many retail outlets, but of a somewhat different nature (do-it-yourself shops), which might lead to similar issues regarding plastic pollution, albeit with a



Fig. 1. Polymer composition of the main polymers detected in terms of the relative MP mass and MP number concentrations.







Fig. 3. Boxplot of the measured major dimension of MP on a logarithmic scale versus stormwater pond (A) and versus polymer types (B). Estimated mass of MP on a logarithmic scale versus stormwater pond (C) and versus polymer types (D). Each point represents one of the identified MP. The solid black dots represent the mean values.
different material composition. Another cause for the differences could be the materials used to construct the drainage systems and the buildings in the catchment. For example are PVC, PP, and PE common materials used for urban drainage pipes (Vahidi et al., 2016). Finally, it cannot be excluded that atmospheric deposition can be a cause of MP in ponds where one otherwise would not expect it. For example the presence of polyester in the highway pond (H1) is unlikely to originate from the road drainage system or the traffic.

3.4. Size, mass and polymer type

Among all the MP identified, only five particles had major dimension of >500 μ m, and three of them were from C1 and two from I1. Their major dimensions ranged from 532 µm to 1030 µm. Four were of PP and one was of polyester. The rare presence of MP in this size range was also observed in the effluent of 12 German wastewater treatment plants (Mintenig et al., 2017), where MP > 500 μ m were visually sorted and identified by ATR-FTIR, and the concentration ranged from 0 to 40 items m⁻³. A likely reason for the absence of large MP in the stormwater ponds is partly that small particles, in the nature of things, must be more abundant than large particles. The large particles will furthermore have a higher tendency to either float to the water surface or settle to the bottom of the pond as the terminal velocity (rising or sinking) of a particle in a fluid is proportional to the square of its diameter (Stokes Law). In both cases, the particles would avoid being sampled with the approach used in the present study (extracting water 0.2 m below the water surface).

Comparing all MP from the ponds, particles in the commercial and industrial ponds tend to be on average smaller in the size, and lower in the mass (Fig. 3A, C). The residential ponds (R1, R2, and R3) contained MP with an average particle size of $82.7 \pm 11.8 \,\mu\text{m}$ and particle mass of $54.4 \pm 18.6 \,\text{ng}$ (see Table S1 for details). These ponds ranked the highest, followed by the highway pond (H1). The industrial ponds (I1 and I2) held MP with an average particle size of $46.5 \pm 1.3 \,\mu\text{m}$ and particle mass of $9.3 \pm 1.1 \,\text{ng}$, and ranked the lowest among all pond types. This was statistically significant (p < 0.05) for both size and mass of the individual MP when comparing C1, I1, and I2 to R1, R2, and R3. The highway pond was somewhere in between these two groups (see Table S4 for details). The three residential ponds did not differ significantly among themselves in terms of MP number and mass (p < 0.05). For commercial and industrial ponds, the picture was similar, with the exception of the MP size distribution between C1 and I2.

The median size of MP related to their polymer type followed the trend: PVC > PS > PP > polyester > PE > others (Fig. 3B). For the median mass, the order was slightly different: PVC > PS > polyester > PP > PE > others (Fig. 3D). In other words, PP and polyester changed place in the ranking (see Table S2 for details). A contributing factor for this shift is that polyester has a density of 1.3–1.4, while PP's density is slightly below one. However, differences in density cannot alone explain the difference. The second contributing factor is the shape and size distribution of the MP, where small differences in shape and size cause large differences in estimated MP volume, and hence mass.

A PCA analysis was applied to further assess what differentiated the ponds. The polymer composition of each pond was compared to the MP number concentrations (Fig. 4A) and the MP mass concentrations (Fig. 4B), as was the MP size of all the MP in each pond (Fig. 4C). For the latter, the logarithm of the measured major dimension was sorted into bins of 0.2 widths.

With respect to polymer composition, the ponds with residential catchments were grouped for MP number concentrations, and to some degree, for mass concentrations. The other ponds did not show any grouping and, all in all, the catchment type could not by itself explain the polymer composition in the water of a pond. The picture was clearer with respect to the MP size, where ponds serving areas with different land use could be differentiated (Fig. 4C). The MP in the highway pond tended to hold the largest size MP, while the commercial and industrial ponds had the smallest.

The PCA on the polymer composition with respect to MP number concentration showed that the first principle component (PC1) explained 49.7% of the variation, but that the differentiation was mainly driven by the industrial pond I2. Less abundant polymers (alkyd, phenoxy resin, PVAC, PVA, vinyl copolymer, acrylic, epoxy) had a high loading on PC1 (all above 0.9). PC2 explained 21.1% of the variation of the dataset, and most of the separation along it referred to PS (0.7), PP (-0.66), PU (-0.66), PA (0.63), and polyester (0.61). All the residential ponds (R1, R2, and R3) and the highway pond (H1) could be grouped based on the low PC1 value, while a rather high PC1 value was found for the industrial pond I2. The commercial pond (C1) and the industrial pond I1 tended to cluster at low PC2 values.

When the PCA analysis was performed on polymer composition related to polymer mass, PC1 explained more variation (61.2%), which was again mainly driven by pond I2. Again, less common polymers (PA, PU, epoxy, acrylic, SAN, vinyl copolymer, PVA, PVAC, phenoxy and alkyd) all had loadings above 0.9. The second principal component



Fig. 4. Biplot of PCA on polymer composition of each pond based on particle number (A) and particle mass (B) concentration. Biplot of PCA on particle size (major dimension, logarithmic scaled) of the MP (C). Capital letters represent the uncommon polymers: A – PA; B – PU; C – epoxy; D – acrylic; E – SAN; F – vinyl copolymer; G – EVA; H – PVA; I – PVAC; J – phenoxy resin; K – acrylic paints; L – alkyd.

(PC2) explained 16.2% of the variances, and the separation was mainly determined by EVA (-0.91), PS (0.69), polyester (0.67), and PE (0.58). Similar to the first PCA analysis, the residential ponds (R1, R2, and R3) and the highway pond (H1) had low PC1 values, while the industrial pond I2 stood alone with a distinguishably high PC1 value. The commercial pond (C1) and the industrial pond I1 were again grouped based on the low values of both PC1 and PC2.

PC1 regarding MP size accounted for 56.5% of the total variance, which was mainly driven by the highway pond (H1), and to a lesser degree by the industrial and commercial ponds. The large MP size bins (bins from 2.6 to 3.2, or 398 μ m to 1585 μ m) had low loadings on PC1 (all below - 0.9). Some medium MP size bins (bins from 2 to 2.4, or 100 μ m to 251 μ m) had high loadings on PC2, while smaller MP size bins (bins from 1.2 to 1.8, or 16 μ m to 63 μ m) had low loadings. The residential ponds tended to cluster at high PC2 values, while the industrial and commercial ponds also clustered at low PC2 values. The highway pond held MP with large particle sizes, which differentiated it from other ponds.

Overall, the study pointed towards some relation between land use and the content of microplastics in the stormwater of the treatment ponds. This was clearest for the ponds serving areas of industrial and commercial land use, versus those with residential and highway usages. The latter group held roughly an order of magnitude less MP. This clearly demonstrates that land use does play an important role for the amount of MP. With respect to the highway pond, it seems reasonable that it had the lowest MP concentrations, as there likely are fewer direct sources for plastic pollution – excluding tyre particles, as these could not be measured in the present study. The sources of the identified MP in the highway pond are unknown, but atmospheric deposition probably plays some role.

While the industrial and commercial ponds showed much variability among themselves, all three PCA analyses (Fig. 4), the size and mass relations (Fig. 3A, C), and the polymer compositions (Fig. 2) all indicated that ponds serving residential catchments held MP concentrations of comparable size and composition. This leads to some confidence in these data being representative of the microplastic concentration of the water phase of residential stormwater retention ponds sized similar to the studied ones.

The measured MP concentrations are likely to be somewhat indicative of the concentration of microplastics in the outflow during small storm events as retention ponds in such cases behave as plug-flow reactors, where incoming water displaces part of the standing pond water (Hvitved-Jacobsen et al., 2010). However, this will depend on local conditions and the actual rain event, and hence needs verification. Furthermore, the data should not be extrapolated to separate stormwater runoff from residential areas per se, partly because not all runoff undergoes treatment, and partly because the efficiency of treatments solutions might vary.

4. Conclusion

Microplastics was present in the water phase of all seven studied stormwater retention ponds, albeit with substantial differences in concentrations and polymeric composition. Land use was identified as an important parameter for explaining the differences between the investigated retention ponds. The ponds holding the highest microplastics concentrations served industrial or commercial catchments, and showed little similarity in terms of microplastics concentrations and polymer composition. Ponds with residential catchments, on the other hand, were more comparable in terms of the microplastics they held.

The most common polymers belonged to PVC, PS, PP, PE, and polyester, while a large number of other materials were found at low levels. The median particle sizes depended on the polymer groups, with PVC particles being the largest while particles belonging to the group of various less common polymers had the smallest size and estimated mass. In terms of particle mass, this difference was quite profound, with PVC microplastics being more than an order of magnitude heavier than microplastics of, for example, PE, polyester, and PP.

This study of seven stormwater ponds is among the first experimental investigation on the abundance of MP in stormwater runoff from urban and highway areas. It shows that the urban and highway runoff contributes MP to the aquatic environment even though it is treated in stormwater ponds, and that the stormwater runoff needs to be included as a pathway of MP from land to sea. It also shows that the land use of the contributing area should be taken into account when assessing MP loads to the aquatic environment.

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Author contributions

Fan Liu carried out the experiments, interpreted the results, and wrote the initial draft. Kristina B. Olesen and Amelia R. Borregaard contributed to the sampling and sample preparation. Jes Vollertsen developed the MPhunter software and supervised the project. All authors contributed to the final manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2019.03.416.

References

- Arthur, C., Baker, J., Bamford, H., 2009. Proceeding of the International Research Workshop on the Occurrence, Effects and Fate of Microplastic Marine Debris. Technical Memorandum NOS-OR&R-30. NOAA, Tacoma, WA.
- Ašmonaite, G., Larsson, K., Undeland, I., Sturve, J., Carney-Almroth, B., 2018. Size matters: ingestion of relatively large microplastics contaminated with environmental pollutants posed little risk for fish health and fillet quality. Environ. Sci. Technol. 52, 14381–14391. https://doi.org/10.1021/acs.est.8b04849.
- Beer, S., Garm, A., Huwer, B., Dierking, J., Nielsen, T.G., 2017. No increase in marine microplastic concentration over the last three decades – a case study from the Baltic Sea. Sci. Total Environ. 15 (621), 1272–1279. https://doi.org/10.1016/j. scitotenv.2017.10.101.
- Bertrand-Krajewski, J.L., Chebbo, G., Saget, A., 1998. Distribution of pollutant mass vs volume in stormwater discharges and the first flush phenomenon. Water Res. 32 (8), 2341–2356. https://doi.org/10.1016/S0043-1354 (97)00420-X.
- Blettler, M.C.M., Abrial, E., Khan, F.R., Sivri, N., Espinola, L.A., 2018. Freshwater plastic pollution: recognizing research biases and identifying knowledge gaps. Water Res. 143, 416–424. https://doi.org/10.1016/j.watres.2018.06.015.
- Bour, A., Haarr, A., Keiter, S., Hylland, K., 2018. Environmentally relevant microplastic exposure affects sediment-dwelling bivalves. Environ. Pollut. 236, 652–660. https://doi.org/10.1016/j.envpol.2018.02.006.
- Brandon, J., Goldstein, M., Ohman, M.D., 2016. Long-term aging and degradation of microplastic particles: comparing in situ oceanic and experimental weathering patterns. Mar. Pollut. Bull. 110, 299–308. https://doi.org/10.1016/j. marpolbul.2016.06.048.
- Browne, M., Crump, P., Niven, S.J., Teuten, E., Tonkin, A., Galloway, T., Thompson, R., 2011. Accumulation of microplastic on shorelines worldwide: sources and sinks. Environ. Sci. Technol. 45, 9175–9179. https://doi.org/10.1021/es201811s.
- Cheung, P.K., Cheung, LT.O., Fok, L., 2016. Seasonal variation in the abundance of marine plastic debris in the estuary of a subtropical macro-scale drainage basin in South China. Sci. Total Environ. 562, 658–665. https://doi.org/10.1016/j. scitotenv.2016.04.048.
- Cole, M., Lindeque, P., Fileman, E., Halsband, C., Goodhead, R., Moger, J., Galloway, T.S., 2013. Microplastic ingestion by zooplankton. Environ. Sci. Technol. 47, 6646–6655. https://doi.org/10.1021/es400663f.
- Cole, M., Lindeque, P., Fileman, E., Halsband, C., Galloway, T.S., 2015. The impact of polystyrene microplastics on feeding, function and fecundity in the marine copepod *Calanus helgolandicus*. Environ. Sci. Technol. 49, 1130–1137. https://doi.org/ 10.1021/es504525u.
- Di, M., Wang, J., 2018. Microplastics in surface waters and sediments of the Three Gorges Reservoir, China. Sci. Total Environ. 616–617, 1620–1627. https://doi.org/10.1016/j. scitotenv.2017.10.150.

Dris, R., Gasperi, J., Mirande, C., Mandin, C., Guerrouache, M., Langlois, V., Tassin, B., 2017. A first overview of textile fibers, including microplastics, in indoor and outdoor environments. Environ. Pollut. 221, 453–458. https://doi.org/10.1016/j. envpol.2016.12.013.

Enders, K., Lenz, R., Stedmon, C.A., Nielsen, T.G., 2015. Abundance, size and polymer composition of marine microplastics ≥ 10 mm in the Atlantic Ocean and their modelled vertical distribution. Mar. Pollut. Bull. 100, 70–81. https://doi.org/10.1016/j. marpolbul.2015.09.027.

Estahbanati, S., Fahrenfeld, N.L., 2016. Influence of wastewater treatment plant discharges on microplastic concentrations in surface water. Chemosphere 162, 277–284. https:// doi.org/10.1016/j.chemosphere.2016.07.083.

- Hartmann, N.B., Hüffer, T., Thompson, R.C., Hassellöv, M., Verschoor, A., Daugaard, A.E., Rist, S., Karlsson, T., Brennholt, N., Cole, M., Herrling, M.P., Hess, M.C., Ivleva, N.P., Lusher, A.L., Wagner, M., 2019. Are we speaking the same language? Recommendations for a definition and categorization framework for plastic debris. Environ. Sci. Technol. 53, 1039–1047. https://doi.org/10.1021/acs.est.8b05297.
- Hendrickson, E., Minor, E.C., Schreiner, K., 2018. Microplastic abundance and composition in Western Lake Superior as determined via microscopy, Pyr-GC/MS, and FTIR. Environ. Sci. Technol. 52 (4), 1787–1796. https://doi.org/10.1021/acs.est.7b05829.
- Horton, A.A., Walton, A., Spurgeon, D.J., Lahive, E., Svendsen, C., 2017. Microplastics in freshwater and terrestrial environments: evaluating the current understanding to identify the knowledge gaps and future research priorities. Sci. Total Environ. 586, 127–141. https://doi.org/10.1016/j.scitotenv.2017.01.190.
- Hurley, R.R., Lusher, A.L., Olsen, M., Nizzetto, L., 2018. Validation of a method for extracting microplastics from complex, organic-rich, environmental matrices. Environ. Sci. Technol. 52, 7409–7417. https://doi.org/10.1021/acs.est.8b01517.
- Hvitved-Jacobsen, T., Vollertsen, J., Nielsen, A.H., 2010. Urban and Highway Stormwater Pollution – Concepts and Engineering. CRC Press, Taylor & Francis Group.
- Kalčíkoá, G., Alič, B., Škalar, T., Bundschuh, M., Źgajnar Gotvajn, A., 2017. Wastewater treatment plant effluents as source of cosmetic polyethylene microbeads to freshwater. Chemosphere 188, 25–31. https://doi.org/10.1016/j.chemosphere.2017.08.131.
- Kay, P., Hiscoe, R., Moberley, I., Bajic, L., McKenna, N., 2018. Wastewater treatment plants as a source of microplastics in river catchments. Environ. Sci. Pollut. Res. 25 (20), 20264–20267. https://doi.org/10.1007/s11356-018-2070-7.
- Kole, P.J., Löhr, A.J., Van Belleghem, F.G.A.J., Ragas, A.M.J., 2017. Wear and tear of tyres: a stealthy source of microplastics in the environment. Int. J. Environ. Res. Public Health 14 (10), 1265. https://doi.org/10.3390/ijerph14101265.
- Lares, M., Ncibi, M.C., Sillanpää, M., Sillanpää, M., 2018. Occurrence, identification and removal of microplastic particles and fibers in conventional activated sludge process and advanced MBR technology. Water Res. 133, 236–246. https://doi.org/10.1016/j. watres.2018.01.049.
- Lasee, S., Mauricio, J., Thompson, W.A., Karnjanapiboonwong, A., Kasumba, J., Subbiah, S., Morse, A.N., Anderson, T.A., 2017. Microplastics in a freshwater environment receiving treated wastewater effluent. Integr. Environ. Assess. Manag. 13 (3), 528–532. https://doi.org/10.1002/ieam.1915.
- Liedermann, M., Gmeiner, P., Pessenlehner, S., Haimann, M., Hohenblum, P., Habersack, H., 2018. A methodology for measuring microplastic transport in large or medium rivers. Water. 10, 414. https://doi.org/10.3390/w10040414.
- Lin, L., Zuo, L.Z., Peng, J.P., Cai, L.Q., Fok, L., Yan, Y., Li, H.X., Xu, X.R., 2018. Occurrence and distribution of microplastics in an urban river: a case study in the Pearl River along Guangzhou City, China. Sci. Total Environ. 644, 375–381. https://doi.org/10.1016/j. scitotenv.2018.06.327.
- Löder, M.G.J., Imhof, H.K., Ladehoff, M., Löschel, L.A., 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 (24), 14283–14292. https://doi.org/10.1021/acs.est.7b03055.
- Lusher, A.L., Mchugh, M., Thompson, R.C., 2013. Occurrence of microplastics in the gastrointestinal tract of pelagic and demersal fish from the English Channel. Mar. Pollut. Bull. 67, 94–99. https://doi.org/10.1016/j.marpolbul.2012.11.028.
- Lusher, A., Hollman, P., Mendoza-Hill, J., 2017. Microplastics in Fisheries and Aquaculture: Status of Knowledge on their Occurrence and Implications for Aquatic Organisms and Food Safety. FAO Fisheries and Aquaculture Technical Paper No. 615 Rome, Italy.
- Marques, F.P., Cardoso, L.G., Haimovici, M., Bugoni, L., 2018. Trophic ecology of Magellanic penguins (*Spheniscus magellanicus*) during the non-breeding period. Estuar. Coast. Shelf Sci. 210, 109–122. https://doi.org/10.1016/j.ecss.2018.06.001.
- Mintenig, S.M., Int-Veen, I., Löder, M.G.J., 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 Res. 108, 365–372. https://doi.org/10.1016/j.watres.2016.11.015.

- Pivokonsky, M., Cermakova, L., Novotna, K., Peer, P., Cajthaml, T., Janda, V., 2018. Occurrence of microplastics in raw and treated drinking water. Sci. Total Environ. 643, 1644–1651. https://doi.org/10.1016/j.chemosphere.2016.07.083.
- PlasticsEurope, 2017. Plastics the Facts 2017, An Analysis of European Plastics Production, Demand and Waste Data. Plastics Europe, Association of Plastic Manufacturers, Brussels.
- 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. Anal. Methods 9, 1499–1511. https://doi.org/10.1039/C6AY02476A.
- Primpke, S., Wirth, M., Lorenz, C., Gerdts, G., 2018. Reference database design for the automated analysis of microplastic samples based on Fourier transform infrared (FTIR) spectroscopy. Anal. Bioanal. Chem. 410 (21), 5131–5141. https://doi.org/10.1007/ s00216-018-1156-x.
- Qu, X., Su, L., Li, H., Liang, M., Shi, H., 2018. Assessing the relationship between the abundance and properties of microplastics in water and in mussels. Sci. Total Environ. 621, 679–686. https://doi.org/10.1016/j.scitotenv.2017.11.284.
- Rochman, C.M., 2018. Microplastics research-from sink to source. Science. 360 (6384), 28–29. https://doi.org/10.1126/science.aar7734.
- Rodrigues, M.O., Abrantes, N., Gonçalves, F.J.M., Nogueira, H., Marques, J.C., Gonçalves, A.M.M., 2018. Spatial and temporal distribution of microplastics in water and sediments of a freshwater system (Antuã River, Portugal). Sci. Total Environ. 633, 1549–1559. https://doi.org/10.1016/j.scitotenv.2018.03.233.
- Sighicelli, M., Pietrelli, L., Lecce, F., Iannilli, V., Falconieri, M., Coscia, L., Di Vito, S., Nuglio, S., Zampetti, G., 2018. Microplastic pollution in the surface waters of Italian Subalpine Lakes. Environ. Pollut. 236, 645–651. https://doi.org/10.1016/j.envpol.2018.02.008.
- Simon, M., van Alst, N., Vollertsen, J., 2018. Quantification of microplastic mass and removal rates at wastewater treatment plants applying Focal Plane Array (FPA)based Fourier Transform Infrared (FT-IR) imaging. Water Res. 142, 1–9. https://doi. org/10.1016/j.watres.2018.05.019.
- Sutton, R., Mason, S.A., Stanek, S.K., Willis-Norton, E., Wren, I.F., Box, C., 2016. Microplastic contamination in the San Francisco Bay, California, USA. Mar. Pollut. Bull. 109 (1), 230–235. https://doi.org/10.1016/j.marpolbul.2016.05.077.
- Talvitie, J., Mikola, A., Setälä, O., Heinonen, M., Koistinen, A., 2017. How well is microlitter purified from wastewater? A detailed study on the stepwise removal of microlitter in a tertiary level wastewater treatment plant. Water Res. 109, 164–172. https://doi.org/ 10.1016/j.watres.2016.11.046.
- Thompson, R.C., Olsen, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W.G., Mcgonigle, D., Russell, A.E., 2004. Lost at sea: where is all the plastic? Science. 304 (5672), 838. https://doi.org/10.1126/science.1094559.
- Vahidi, E., Jin, E., Das, M., Singh, M., Zhao, F., 2016. Environmental life cycle analysis of pipe materials for sewer systems. Sustain. Cities Soc. 27, 167–174. https://doi.org/10.1016/ j.scs.2016.06.028.
- Van Cauwenberghe, L., Janssen, C.R., 2014. Microplastics in bivalves cultured for human consumption. Environ. Pollut. 193, 65–70. https://doi.org/10.1016/j. envpol.2014.06.010.
- Van Cauwenberghe, L., Claessens, M., Vandegehuchte, M.B., Janssen, C.R., 2015. Microplastics are taken up by mussels (*Mytilus edulis*) and lugworms (*Arenicola marina*) living in natural habitats. Environ. Pollut. 199, 10–17. https://doi.org/10.1016/j. envpol.2015.01.008.
- Vaughan, R., Turner, S.D., Rose, N.L., 2017. Microplastics in the sediments of a UK urban lake. Environ. Pollut. 229, 10–18. https://doi.org/10.1016/j.envpol.2017.05.057.
- Wesch, C., Elert, A.M., Wörner, M., Braun, U., Klein, R., Paulus, M., 2017. Assuring quality in microplastic monitoring: about the value of clean-air devices as essentials for verified data. Sci. Rep. 7 (1), 5424. https://doi.org/5424.10.1038/s41598-017-05838-4.
- Windsor, F.M., Tilley, R.M., Tyler, C.R., Ormerod, S.J., 2019a. Microplastic ingestion by riverine macroinvertebrates. Sci. Total Environ. 646, 68–74. https://doi.org/10.1016/j. scitotenv.2018.07.271.
- Windsor, F.M., Durance, I., Horton, A.A., Thompson, R.C., Tyler, C.R., Ormerod, S.J., 2019b. A catchment-scale perspective of plastic pollution. Glob. Chang. Biol., 1207–1221 https://doi.org/10.1111/gcb.14572.
- Woodall, L.C., Sanchez-Vidal, A., Canals, M., Paterson, G.L.J., Coppock, R., Sleight, V., Calafat, A., Rogers, A.D., Narayanaswamy, B.E., Thompson, R.C., 2014. The deep sea is a major sink for microplastic debris. R. Soc. Open Sci. 1, 140317. https://doi.org/10.1098/ rsos.140317.

Paper- III

Retention of Microplastics in Sediments of Urban and Highway Stormwater Retention Ponds

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Retention of microplastics in sediments of urban and highway stormwater retention ponds

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Abstract

Urban and highway surfaces discharge polluted runoff during storm events. To mitigate environmental risks, stormwater retention ponds are commonly constructed to treat the runoff water. This study is the first to quantify the retention of microplastics in the sediments of such ponds. It applied state-of-art FTIR-methods to analyse the composition, size, shape, and mass of microplastics in the range 10–2000 μ m. Seven ponds serving four land uses were investigated, and the results are related to catchment characteristics, sediment organic matter content, and hydraulic loading. We have not found a correlation between the microplastics abundance, polymer composition, size distribution and the land use in the catchment, as well as the sediment organic matter content. Both the highest (127,986 items kg⁻¹; 28,732 μ g kg⁻¹) and the lowest (1,511 items kg⁻¹; 115 μ g kg⁻¹) accumulation of microplastics were found in the sediments of ponds, where the sediments of the highest-loaded ponds held the most microplastics. This study shows that sediments in stormwater retention ponds can trap some of the microplastics and prevent them from being transported downstream. These systems need to be considered when assessing the fate of microplastics from urban and highway areas.

Capsule

The study demonstrated that stormwater retention pond is able to trap microplastics from urban and highway runoff in sediments, and the retention is correlated to the hydraulic loading of the pond.

1. Introduction

Plastic has become ubiquitous in the environment due to the continuous increase in its production (PlasticsEurope, 2018); and its inherent resistance to degradation (Koelmans et al., 2019; Windsor et al., 2019). Currently, an estimated 4.8–12.7 million metric tons enter the oceans annually (Jambeck et al., 2015). The role of microplastics (MPs) as part of plastic pollution has recently received scientific, public, and political attention. Compared with larger plastic debris, MPs have a higher surface-to-volume ratio, leading to an increased potential to release additives and adsorb organic chemicals (Velzeboe et al., 2014; Zhan et al., 2017; Hahladakis et al., 2018). Investigation of MPs in freshwater and terrestrial environments began quite recently (Eriksen et al., 2013). Since then, studies on freshwater-related MPs began to emerge, and

wastewater treatment plants (WWTP) have been well-documented as point sources (McCormick et al., 2014; Talvitie et al., 2017; Simon et al., 2018). In addition, urban and highway stormwater runoff is known to be a land-to-sea pathway for MPs, although it has received substantially less attention in terms of experimental studies (Auta et al., 2017). One of the few such studies shows that MP concentrations in urban and highway runoff could be related to how land in the drained catchment is used (Liu et al., 2019b).

Before discharging the runoff, an increasing portion of stormwater runoff is treated by sustainable stormwater management technologies such as stormwater retention ponds (Hvitved-Jacobsen et al., 2010). The runoff is drained into the pond and held from days to weeks before discharge, allowing pollution removal processes to occur. Sorption and degradation are the dominant processes for eliminating soluble pollutants like biocides and pharmaceuticals (Minelgaite et al., 2017; Liu et al., 2019a). For particulate materials, sedimentation and deposition are the main removal mechanisms. For these processes, the size, shape, and density of particles are critical parameters, as they affect directly the particle movement in water and determine their final deposition (Hvitved-Jacobsen et al., 2010). For synthetic particles, the formation of biofilm on the surface can further promote the particle deposition, which makes sedimentation occur even for low-density polymers (Rummel et al., 2017; Harrison et al., 2018). With their retention, sediments can largely reduce the mobility of MPs in water, hence decrease the transportation to another water environment. However, accumulation in the sediments protects MPs from solar UV light, which leads to the deposited MPs becoming less degraded compared to those subjected to direct UV exposure (Andrady, 2017; Da Costa et al., 2018). Therefore, retained MPs can accumulate in the sediments over the years, until the sediments eventually are removed, de-watered, and sent to a soil treatment facility for further processing (Hvitved-Jacobsen et al., 2010).

MPs found in sediments, typically collected as a grab sample by various means such as Van Veen grabs (Di and Wang, 2018; Haave et al., 2019), shovels (Wang et al., 2017), spatulas (Abidli et al., 2018), and sediment corers (Vaughan et al., 2017), can be understood to comprise a long-term average of MPs. The analytical methods for MPs identification and quantification are less straightforward, and the applied approaches vary substantially (Van Cauwenberghe et al., 2015; Cabernard et al., 2018; Hartmann et al., 2019). Over the later years, focal plane array (FPA)-based micro-Fourier-Transform Infrared (μ FTIR) microscopy combined with automated image analysis has proven to be a comparatively reliable method for MP quantification. This approach reduces the bias caused by manual particle sorting and allows for robust quantification of particles down to sizes of roughly 10 μ m (Primpke et al., 2017; Simon et al., 2018; Liu et al., 2019b).

The objective of this study was to quantify the retention of MPs, in the range 10–2000 μ m, in the sediments of stormwater retention ponds. FPA-based μ FTIR imaging was used to quantify MPs below 500 μ m, and attenuated total reflectance (ATR)-based FTIR was used to identify larger particles. We hypothesised that the accumulation of MPs in pond sediments would correlate with catchment characteristics, sediment characteristics, and hydraulic loading. Seven ponds with drainage areas covering four land use types were chosen for evaluation.

2. Material and methods

2.1. Sampling

Sediments were collected from seven stormwater retention ponds in Denmark in March and April 2017. The ponds received stormwater runoff from catchments of different land use. Three served residential areas (R1, R2, R3), two served industrial areas (I1, I2), one had a commercial catchment (C1), and one received runoff from a highway (H1). Six of the ponds were around 10 years old. One pond was much older, but had its sediments dredged some 10–15 years ago (Table 1).

The sampling was done in dry weather, with an antecedent dry weather period of at least two days. Samples were taken at 1 m water depth using a Van Veen bottom grab sampler and stored in 1 L glass jars. The jars were closed with non-sealing glass lids. Only the top 5 cm of the sediments were collected from each grab. At 1 m water depth, deposited sediments are not prone to wind-induced re-suspension (Bentzen et al., 2009) and sediment accumulation rates can be expected to range between 0.7–1.6 cm y⁻¹ (Damrat et al., 2013; Szmytkiewicz and Zalewska, 2014). Hence the samples are expected to represent the long-term average of approximately 3–7 years of sediment accumulation. For each pond, samples were collected the same day from three randomly locations; sediments from the same pond were combined and analysed as one sample (Wang et al., 2018). A minimum of 3 L of sediments was collected from each pond. All samples were immediately transferred to the laboratory and stored at 5°C until analysis. Sediment organic matter content was determined by the weight loss on ignition (LOI): the dried sediments were placed into a muffle furnace and heated to 550°C for 4 h (Hurley et al., 2018).

Site	City	Coordinate (N, E)	Hydraulic loading: catchment		Organic matter	
			impervious area per	Catchment type	(% dry	
			pond surface area		weight)	
			(m²/m²)			
R1	Silkeborg	(56°11'39.8", 9°32'57.9")	71000/4000	Residential with single-family		
				houses and part of an orbital	1.01	
				road. Constructed: 2008		
R2	Aarhus	(56°10'18.4" <i>,</i>	426000/11880	Residential with single family	2.10	
		10°05'49.9")		houses. Constructed: 2005		
R3	Aarhus	(56°10'18.4" <i>,</i>	466000/11900	Residential with single family	3.26	
		10°06'22.6")		houses. Constructed: 2005		
11	Aarhus	(56°10'49.0" <i>,</i>	109000/7460	Light industry. Constructed: 2007	3.61	
		10°07'58.4")				
12	Viborg	(56°28'29.3", 9°24'43.3")	698000/6500	Light industry, commerce, do-it-		
				yourself shops. Constructed		
				before 1995. Dredged for	8.96	
				sediments approx. 10-15 years		
				before sampling		

Table 1. Overview of stormwater ponds, their catchments, and the organic matter content of the sampled sediments

C1	Aarhus	(56°08'41.8", 10°08'12.2")	190000/6050	Commercial (shopping centre), some residential use. Constructed: 2008	1.13
H1	Aarhus	(56°13'13.9", 10°07'43.5")	48000/5540	Highway. Constructed: 2009	2.30

2.2. Sample processing

The isolation of MPs from the sediments followed a method derived from Masura et al. (2015) and Mintenig et al. (2017). First, particles larger than 2 mm were removed from the 3 L of the wet sediments by wet-sieving, using a 2 mm sieve (Retsch GmnH, Germany). The wet-sieving used 1.2 μ m GF filtered Milli-Q water (47 mm in diameter, Whatman), and the sieved sample was collected in 5 L glass beakers. To reduce the large water volume that resulted from the wet-sieving, the collected samples were settled for one week, after which the supernatant was filtered through a 10 μ m stainless steel mesh (47 mm in diameter, laser-cut from larger filter sheets, Filtertek A/S, Denmark). The filter was then collected in a glass beaker containing 20–30 mL Milli-Q water and sonicated for 15 min. Particles remaining on the filter were carefully flushed into the solution and transferred back into the 5 L beaker containing the settled sediments.

Sediments contain aggregates of organic matter and the fine inorganic particles which can trap MPs. This could reduce the extraction efficiency of the density separation as such agglomerated particles can have densities close to sand and clay, and hence lead to a loss of MPs (Kooi et al., 2018). To avoid this bias, the sediments went through a pre-oxidation designed to reduce the organic matter content and open up the matrix before the density separation. Peroxide-based treatment has proven efficient for organic matter removal, and a concentration of $30\% H_2O_2$ has commonly been used for such treatment (Hurley et al., 2018). However, prior to processing the pond samples, initial tests on the same matrix had shown that the use of 30% H₂O₂ can lead to an uncontrolled exothermic reaction and gas production for stormwater pond sediments, which may potentially cause loss of MPs. Hence the sediment samples were divided into several smaller batches, which each underwent oxidation at a lower peroxide concentration. Briefly, approx. 50 g of wet sediments were subsampled from the sieved sediments and placed in a 2 L glass beaker. The beaker was filled with 200 mL Milli-Q water before adding 30 mL of 30% H₂O₂ (achieving a final H_2O_2 concentration of 4%), thus achieving a diluted peroxide solution. The reactor was kept at 50°C by placing it on a heating plate and gently stirring it. The temperature was monitored and, in case the solution overheated due to the exothermic oxidation reaction, the beaker was placed in an ice-water bath until the thermal reaction slowed down. The oxidation was continued by adding another 30 mL of 30% H₂O₂ every 24 hours, until no foaming was observed when adding peroxide. The pre-oxidized sediments were transferred onto a glass dish and dried in an oven at 50°C. This procedure was repeated until all 3 L of sediments had been processed. The dried sediments were combined and subjected to further oxidation with 15% H₂O₂ on a heating plate (50°C) for 7 days. Temperature was monitored during the oxidation. Subsequently the sediemtns were oven-dried at 50°C.

A sub-sample of 200 g dry sediments underwent density separation using 1.5 L of zinc chloride solution (1.97 g cm⁻³), and the MPs abundance was quantified based on this dry weight. The

separation was performed twice in a 2 L glass funnel. In the first separation, the mixed solution was aerated with dry and dust-free compressed air for one hour and allowed to settle for 5 hours. The settled particles were drained off through the bottom of the funnel. In the second separation, the solution was aerated for 30 min and left to settle overnight, after which the settled particles were again drained off. The remaining liquid was filtered through a 10 μ m stainless steel filter. The pre-oxidation – intended to open up the matrix prior to density separation – was insufficient to remove all organic matter. The collected particles hence underwent a Fenton reaction by adding 146 mL 50% H₂O₂, 63 mL of 0.1 M FeSO₄, and 65 mL of 0.1 M NaOH (Simon et al., 2018). The reaction was kept at 15–19°C by putting the reactor on ice. After the reaction had slowed down sufficiently, the reactors were left for 2 days at room temperature. After that, the liquid was filtered through a 500 μ m stainless steel sieve, followed by a 10 μ m steel filter. The particles remaining on the sieve (500–2000 μ m) were collected into HPLC grade ethanol by ultra-sonication, then transferred into a glass vial and evaporated by nitrogen (N5.0) until dry. Finally, 5 mL of 50% ethanol was added to the vial.

2.3. MP identification and quantification

MPs <500 µm were analysed as described in Liu et al. (2019b) and Simon et al. (2018), yielding major dimension, minor dimension, and estimated mass for each particle. Briefly, a sub-sample of the 5 mL particle concentrate was deposited on a zinc selenide window, where a compression cell (Pike Technologies, USA) was used to restrict the surface to a diameter of 10 mm. The window was dried at 55°C and scanned at a pixel resolution of 5.5 μ m (μ FTIR imaging), using a Cary 620 FTIR microscope coupled with a Cary 670 IR spectrometer (Agilent Technologies). The microscope used a 15x Cassegrain objective and a 128x128 Mercury-Cadmium-Telluride (MCT) FPA detector. The resulting IR maps were analysed using MPhunter (Liu et al., 2019b). The wavenumber range was 900–3750 cm⁻¹. The library used by MPhunter contained 113 reference spectra, organized into 29 material groups: ABS (acrylonitrile butadiene styrene), acrylic, acrylic paints, alkyd, aramid, cellulose acetate, diene elastomer, EPDM (ethylene propylene diene monomers), epoxy, EVA (ethylene vinyl acetate), PA (polyamide), PAN Acrylic fibre (polyacrylonitrile), PE (polyethylene), Pebax®, PEG (polyethylene glycol), phenoxy resin, PLA (polylactic acid), polycarbonate, polyester, POM (polyoxymethylene), PP (polypropylene), PS (polystyrene), PTFE (polytetrafluoroethylene), PU (polyurethane), PU paints (polyurethane paints), PVA (polyvinyl alcohol), PVAC (polyvinyl acetate), PVC (polyvinyl chloride), SAN (styrene acrylonitrile), SBR (styrene butadiene rubber), and vinyl copolymer. In addition, to reduce the risk of false-positive detections, the database contained cellulose and proteinaceous material. Three replicates from the 5 mL particle concentrate were sub-sampled, deposited, scanned by µFTIR, and analysed by MPhunter. The results of the 3 scans were combined and interpreted as the final result (Liu et al., 2019b).

MPs >500 μ m were visually sorted with ultra-fine micro forceps under a stereomicroscope (Stereo Discovery V8, Zeiss, Oberkochen, Germany). The chemical composition of each potential MP particle was confirmed with ATR-FTIR (Cary 630 FTIR Spectrometer, Agilent Technologies, equipped with a single reflection diamond ATR crystal). Spectra were collected over the wavenumber range 650–4000 cm⁻¹. The particles were analysed by 32 co-added scans, with a

background correction of 64 co-added scans and a resolution of 8 cm⁻¹. The spectra of samples were analysed using OMNIC 8.3 software (Thermo Fisher Scientific, Madison, WI, USA) software by comparing them to the several reference polymer libraries, including the spectral library developed by JPI-OCEANS, BASEMAN (Primpke et al. 2018). The sample's polymer type was determined by a combination of the best-fitted spectra and the expertise of the operator on interpreting polymer IR spectra. Each identified particle was measured in both its major and minor dimensions, using the stereomicroscope's software (ZEN Core, Zeiss, Oberkochen, Germany). The mass of the particle was estimated based on the same assumptions used for particles <500 μ m: first, the volume was estimated while assuming that the thickness was 67% of the minor dimension and that the particle had an ellipsoid shape. The mass was estimated from the volume and density of the polymer material. Car tyre rubber could not be identified by the FTIR techniques, as it contains carbon black as a filler, which absorbs light throughout the infrared region (Kole et al., 2017).

2.4. Experimental quality control

To minimize contamination during sample processing, only glass, stainless steel, and PTFEcoated labware was used. PTFE was excluded in this study, as it has a density of 2.2 g cm⁻³, and these particles hence would be drained off with the inorganics in the density separation. All labware was flushed with Milli-Q water beforehand and covered with a watch glass or aluminium foil immediately after each treatment step. Sieves and steel filters were muffled at 500°C. Cotton lab coats were worn during all process steps. Samples were processed inside a fume hood whenever possible, and the air of the FTIR room was continuously filtered by an air treatment device (Dustbox[®] Hochleistungsluftreiniger, Germany) with a HEPA filter (H14, 7.5 m²). All open containers were covered with watching glass or aluminium foil. Even so, contamination could still occur from cloth, lab dust, etc. (Woodall et al., 2014; Dris et al., 2017). Hence, the background contamination from the sample processing was assessed by use of three blanks. Washed and muffled (500°C) sand of 75–1000 μ m (Baskarp Sand No. 15) was used. The blanks went through the same processes described for the sediment samples.

Recovery was tested in triplicate for the density separation step by spiking 300 items of red 100 μ m PS beads (Sigma-Aldrich, product no. 56969) into 200 g the muffled sand (Fig. S1). The spiked sand went through the separation following the steps described above, and the 10 μ m stainless steel filters were investigated under a stereomicroscope and the beads counted.

2.5. Statistical analysis

The Shapiro-Wilk normality test was used to test the normality of datasets. All statistical analysis was performed in R (v3.5.1), and the significance level in all cases was set to 0.05.

3. Results

3.1. Background contamination and recovery

For each of the three blank samples, a sub-sample of 400 μ L was deposited and scanned. Only five MPs were found in total in the blanks. All were of PE with a summed estimated mass of 17.5 ng. This corresponds to 20.8 items and 72.9 ng per sample processing. Compared to some other studies, the slightly higher MP number in the blanks could be explained by the different MP

identification and quantification method applied. For instance, Yang et al. (2019) and Allen et al. (2019) both found < 10 items in the procedural blanks. But they used manual sorting in their study, which could introduce human bias and lead to an underestimation of MPs especially for particles < 500 μ m (Hidalgo-Ruz et al., 2012). In the present study, all MPs found in the blanks were between 16.5 μ m and 75.1 μ m, and could easily have been missed if manual sorting had been applied instead of automated analysis. Compared to the studies applying a similar MP analysis method, the contamination in the present study was much lower. For instance, Simon et al. (2018) stated that 2110 MPs (84 μ g) had been found, while Mintenig et al. (2017) reported that 21 particulate and 130 fibrous MPs were detected in their blanks.

Since the blank tests were conducted o muffled sand, the contamination is related to the inorganic fraction of the processed sample. As 200 g of dry sediments were processed, the contamination accounted for 104 items kg⁻¹ and 0.36 μ g kg⁻¹, which corresponded to 1% and 0.02% of the average MP number and mass concentration of the field samples, respectively (Table S1). This was lower than the 6.8% reported by Su et al. (2016). Since the background contamination is subject to variation (Scheurer and Bigalke, 2018), and to avoid unknown biases and simplify data interpretation, the results were not corrected for this background contamination.

The density separation showed a recovery of 66 \pm 5.6 %. For comparison, Olesen et al. (2019) found a quite similar recovery (64%) for extraction of MPs from stormwater pond sediments. It should be noted that the actual recovery rate could differ from this value. One reason is that some of the microbeads – although recovered by the separation – were covered by other materials on the filter (Fig. S1). Another reason is that microbeads probably behave differently from the polymers found in the field samples because polymer types, shapes, and size differ. Hence to avoid these unknown biases, the results were not corrected by the recovery rate.

3.2. MP abundance and size

Various studies have shown that MP abundancy in terms of particle number increases with decreasing size (Mintenig et al., 2017; Cabernard et al., 2018; Simon et al., 2018). However, reported studies have applied different sampling methods and analytical techniques to different targeted size ranges (Hartmann et al., 2019). These differences make the reporting of MP abundancy challenging and complicate inter-study comparisons (Hartmann et al., 2019; Liu et al., 2019b). In this study we choose an upper cut-off in particle size of 2 mm as the number of large particles in the samples was low (Horton et al., 2017), and the finding of single large particles would be quite random, introducing a large bias in the mass estimate (Simon et al., 2018). The lower size limit set to 10 μ m as this was the pore size of the gilters used in the sample preparation. MP abundance was reported by the MP's major dimension, which was classed into size ranges that are commonly used in other studies (Leslie et al., 2017; Vaughan et al., 2017; Peng et al., 2018; Zhang and Liu, 2018). Five unevenly distributed fractions were used: 10–50 μ m, 50–250 μ m, 250–500 μ m, 500–1000 μ m, and 1000–2000 μ m (Fig. 1).

A total of 2232 particles were identified as MPs among all analysed samples, among which 1135 items were within the size range of 10–50 μ m, while only 5.3% (118 items) were above 250 μ m (Fig. 1A). The highest number concentration was found in the fraction of 10–50 μ m (8894 items kg⁻¹), while the lowest was in the fraction of 500–1000 μ m (118 items kg⁻¹, Fig. 1B). In contrast,

these two fractions had the lowest and highest mass concentration (43 μ g kg⁻¹ and 1054 μ g kg⁻¹, respectively, Fig. 1C), which was quite expectable as number of particles increase with decreasing particle size. The accumulated particle number and mass concentration from all size classes were 17490 items kg⁻¹ and 3085 μ g kg⁻¹, respectively. Comparing with other freshwater-related studies, the overall particle number concentration found was generally several orders of magnitude higher. For instance, MP concentration in river sediments from Shanghai was found to be 802 items kg⁻¹ (Peng et al., 2018), while it ranged from 178 ±69 to 544 ±107 items kg⁻¹ in sediments from the Beijing River littoral zone (Wang et al., 2017). Nel et al. (2017) reported that MPs were present at an overall average concentration of 160.1 ±139.5 items kg⁻¹ in a South African temperate urban river system during winter.

There are several possible reasons for the differences in MPs number concentrations. One is that that some studies used less dense solutions, such as NaCl and CaCl₂ (1.2 to 1.3 g mL⁻¹), to separate MPs from the inorganics. Such density is insufficient to extract high-density polymers such as PVC or polyester (Van Cauwenberghe et al., 2015; Leslie et al., 2017; Scheurer and Bigalke, 2018). In the present study, the high-density polymers constituted 13.5% of all MPs (244 polyester and 57 PVC, Table S2). Another reason is related to the different particle cut-off size applied. This study used 10 µm as the lower limit of detection, which is smaller than the sizes reported by most other studies. For instance, Horton et al. (2017) investigated MPs in the sediments of the River Thames (UK) and found 660 items kg⁻¹ of 1–4 mm MPs. A range of 18– 629 items kg⁻¹ of MPs was found in the Antuã River, Portugal, using 55 μ m as the cut-off size (Rodrigues et al., 2018). However, the present study showed that particles <50 µm constituted more than half (1135 items) of all MPs. Another difference relates to the analytical detection method. Other studies have applied manual sorting of particles under a microscope, followed by a material verification of the collected particles. The present study applied µFTIR imaging combined with automated MP identification, a method that minimizes false negatives and reduces human bias in the analytical procedure (Löder et al., 2017; Primpke et al., 2017). Finally, the sampled matrices do of course differ, and it cannot be expected that sediments from stormwater retention ponds should hold the same concentration of MPs as, for example, river sediments.

Compared to the few cases where mass concentrations have been reported, the mass concentrations of the present study were lower. This can be because of the vast majority of the identified MPs were small-sized particles, which had less mass contribution compared to larger particles in other studies. For instance, a Swiss floodplain was found to be contaminated by MPs at a concentration up to 55.5 mg kg⁻¹ (Scheurer and Bigalke, 2018), but the majority (88%) of the MPs were larger particles of 125–500 μ m.



Fig. 1. MP abundance in the sediments of the seven ponds. (A) shows the distribution of the 2232 MP particles found; (B) the calculated number concentrations in the size bins; and (C) the calculated mass concentration. The blue bars are the abundance in each size fraction, and the red lines show the corresponding accumulated abundance.

3.3 Relation between MP abundance and pond characteristics

As climate conditions at the seven sites are similar, the ratio between the impervious catchment area and the pond surface area is used as a surrogate for their specific hydraulic loading (Table 1). A positive correlation was observed between the pond hydraulic loading and the MP abundance, both in particle number (Fig. 2A) and mass concentration (Fig. 2B). Sediment's organic matter content also showed a correlation towards the MP mass concentration, but with less significance (P-value of 0.02, Fig. 2D). It should be noted that the low number of sampled ponds might introduce some uncertainty in the data interpretation and that the results hence should be handled with care. It is furthermore unknown to what extent MPs are lost in other parts of the stormwater drainage systems, such as deposition in gully pots that are regularly emptied or accumulated in the soil of permeable surfaces such as ditches and infiltration trenches. Therefore, the MPs accumulated in the sediments of the ponds can only to a limited extent reflect the MP abundance in the runoff. Despite these potential biases, the present study still found a strong correlation between the MP abundance in the sediments and the pond hydraulic loading (P-values for both particle number and mass concentration < 0.005), yielding a reasonable confidence in the found correlation.



Fig. 2. The relationship between MP abundance and the pond hydraulic loading (left), and the sediment organic matter content (right). The MP abundance are presented both as particle number concentration (up) and mass concentration. The solid blue line represents the regression line. The confidence intervals (95%) are highlighted as grey areas. Both the regression, the coefficient of determination (R^2), and the significance level (P) were presented.

The sediment MP concentrations showed no correlation with the land use of their catchment, since the least and the most contaminated sediments were both from ponds serving industrial catchments, and the three residential ponds also had MP accumulation varying with one order of magnitude (Table S1). This is in contrast with the findings of Liu et al. (2019b), who concluded that such correlation did exist for the water phase of the same seven ponds. Other freshwater-related studies reported that population density probably affected the MP pollution level in China's largest inland lake (Xiong et al., 2018), and for Laurentian Great Lakes of the United States, the urbanization level also correlated with the MP pollution (Eriksen et al., 2013).

3.4. Polymer composition, size, mass and shape

Analysis using MPhunter (Liu et al., 2019b) enabled MPs to be assigned to one of the following material groups: PE, PS, PVC, PP, PA, PU, polyester, ABS, epoxy, acrylic, SAN, vinyl copolymer, EVA, PVAC, polycarbonate, phenoxy resin, EPDM, acrylic paint, PU paint, and alkyd. Some of these polymers were not commonly detected and hence were gathered into a group of 'others' (ABS, epoxy, SAN, vinyl copolymer, EVA, PVAC, polycarbonate, phenoxy resin, EPDM, alkyd), which contained 70 items in total. Furthermore, acrylic paint (17 items) and PU paint (9 items) were grouped with acrylic and PU, respectively (Table S2).

PP clearly dominated in the ponds, in terms of both number and mass of particles (Fig. 3). When sorted by particle mass, PS ranked as the second most abundant polymer, followed by polyester, PE, PU, PVC, others, and PA. However, when sorted by number of particles PA was the second most abundant polymer, followed by polyester, PE, PS, PU, acrylic, others, and PVC. The high contribution of polymers with low densities indicted that, particle density was not the only factor determining MP sedimentation. But whether this was a result of these materials simply being

more abundant, an increased density due to the formation of biofilms on the particles, or a combination of various other factors cannot be determined by the present study (Eerkes-Medrano et al., 2015; Rummel et al., 2017).

Polymer density and particle size had a significant impact on the abundance when comparing number versus mass of particles. For instance, even though PVC was present at low numbers, its mass exceeded that of PA and acrylic due to its higher density. Another pronounced example is PA, which had the second highest number concentration, but as the particle size was the smallest of the polymers (Fig. S3B), it had the lowest mass concentration (Fig. 3).



Fig. 3. Polymer composition of the main polymers detected in the seven ponds. The concentration is given as particle mass and number of particles.

The polymer composition of the seven ponds analysed was comparable with results from other studies of freshwater sediments. For example, Thompson et al. (2004) find that acrylic, alkyd, PP, PE, PA (nylon), polyester, polymethylacrylate, poly (ethylene: propylene), and polyvinylalcohol were conclusively identified in estuarine and sub-tidal sediments around Plymouth, UK. Polyester was also commonly detected in river sediments in Shanghai (Peng et al., 2018), and PP, PE, and PS were commonly found in river sediments in Portugal (Rodrigues et al., 2018) as well as lake sediments in India (Sruthy and Ramasamy, 2017).

Low-density polymers (PP, PE) accounted for 65.2% by mass and 46.4% by the number of MPs identified overall (Fig. 3). Their abundance in the sediments of the stormwater ponds, as well as in many other sediment types previously reported (Klein et al., 2015; Haave et al., 2019), suggests that density is not the only factor that affects the distribution of polymers between water and sediments. Simple sedimentation in calm water is not sufficient to explain MP retention mechanisms. Other processes related to in-pond hydraulics, turbulence, and sediment organic matter may also have impacted the distribution (Thompson et al., 2004; Nel et al., 2017), as could aggregation with other particles, biofilm growth, and animal uptake (Besseling et al., 2017).

The polymer composition varied significantly between ponds (Fig. S2). For example, PVC was present in comparable concentrations in the residential ponds (R1, R2, R3) and highway pond H1, but it was rarely detected in commercial pond C1 and not detected at all in industrial pond I1. Beyond this, ponds serving the same catchment type did not hold similar distributions of polymers. PP dominated in industrial pond I2, but constituted a much smaller fraction of MPs

found in 11. Among the residential ponds, polyester dominated in R1, but PP was the most abundant polymer in R2. These results are in contrast with previous findings for the water phase of the same seven ponds. The water phase of the ponds serving residential and highway catchment, as well as the ones serving industrial and commercial catchments both had similar polymer distribution patterns (Liu et al., 2019b). The reason here fore is unclear, but could be related to the fact that water phase concentrations represent short term MP concentration in the runoff, while the sediments reflect accumulation over several years.

Stormwater retention ponds are physically close to the MP source and receive surface runoff from a well-defined drainage area. It hence seems reasonable to assume that their sediments reflect the MP sources in the drainage area. A similar argument has been brought forward by Rochman (2018), who states that compared with the open ocean, MPs in freshwater and terrestrial systems more readily reveal their original sources, because they are direct receivers of treated and untreated urban, industrial, and agricultural waste. In line with this argument, it seems reasonable to believe that at least some of the MPs found in stormwater ponds originate from the structures and activities in the catchment. However, it cannot be excluded that some of the MPs found in the ponds originated outside the pond drainage area, and had been transported into it by atmospheric deposition (Free et al., 2014). Hence the fact that PP was abundant in all sediments could be due to its use in the drainage area, or it could simply be a consequence of the fact that it is one of the most widely used polymers (PlasticsEurope, 2018), and hence is abundant in atmospheric particles and deposited during dry and wet weather.

When grouping the MPs from all seven ponds into polymer types, there was a clear trend of the median particle size of the polymers: PVC > PP > others > acrylic > PS > PE > polyester > PU > PA (Fig. S3, Table S2). This trend held almost true also for particle mass, except that acrylic and 'others' switched place in the ranking. When the MPs were grouped by ponds, there was also a trend in the particle size: R1 > I2 > R2 > I1 > C1 > R3 > H1 (Fig. S3, Table S3). This trend, though, did not correlate with land use, and was also in contrast with the findings of the pond water of the same seven ponds (Liu et al., 2019b). MP mass in the ponds also followed this trend, except that R2 had lower average particle mass than I1. A likely reason for this slight change is that pond R2 held a relatively higher percentage of PP. PP is the polymer that had the second-largest particle size (Fig. S3), whilst its low density pulled down the average particle mass.

Particles identified by ATR-FTIR were mostly fragments (38 items) followed by film (6 items), whilst only one fiber and one pellet were found (Fig. S4). The majority of the MPs in the smaller size range (10–500 μ m) were plump ellipsoids, with the median value of the major to minor dimension ratio at 1.9 (Fig. S6). To compare the shape between polymers, the major dimension was plotted against the minor dimension and fitted to a linear model (Fig. S5). PP particles were found to be the slimmest in shape, where the major dimension on average was close to three times the minor dimension. Although this ratio on its own is not sufficient to determine whether these were truly fibres, it is reasonable to assume that compared to other polymers, PP particles had a higher tendency to be fibres. PU particles were the plumpest in shape, with the major dimension only slightly longer than the minor.

The shape of particles < 500 μ m in the present study was determined based on the assumption that, all the particles were of ellipsoid shaped (Simon et al., 2018; Liu et al., 2019b). This assumption is a simplification made to allow mass estimation, and the shape information only

used for comparison between the polymer types within this study. The shape of particles > 500 μ m was an actual measurement by the stereomicroscope, and this fraction can hence be compared with other studies. So did for example Sruthy and Ramasamy. (2017) – in contrast to the present study – found that film and foam shapes dominated in sediment of Vembanad Lake in India, whilst fibres were the most common shape in Taihu Lake, China (Su et al., 2016). However, it is rather complex to distinguish which specific factors drove the difference in MP shape distribution, as it is a result of a combination of a multitude of anthropogenic activities and environmental processes.

Several important questions remain largely unanswered: What causes the variation in particle shape and how it depends on polymer types? What explains the variation in particle sizes in between polymers and ponds? and within the same stormwater retention pond, what causes the difference in polymer composition between the water phase and the sediment phase? While this first study on MPs in the sediments of stormwater retention ponds raises at least as many questions as it answers, the results are an important step towards a better understanding of MPs in urban and highway runoff and the role of the retention ponds, which mitigating MP pollution from downstream by retain them in sediments.

Conclusion

This study is the first evaluation of MPs in the sediments of stormwater retention ponds. It shows that microplastics, and especially small particles (10–250 μ m) were prevalent in these sediments. The variation in MP abundance, size distribution, and polymer composition between the ponds was large. Hydraulic loading was an explanatory factor for the difference in MP abundance, while other potential explanations such as land use and sediment organic matter content were not supported. Furthermore, the determination of whether or not stormwater ponds are efficient for controlling overall plastic pollution from urban and highway areas remains a question for future research. It does, though, seem clear that stormwater pond sediments do retain MPs and hence plays a role in managing MPs from urban and highway areas.

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Reference

Andrady, A.L., 2017. The plastic in microplastics: A review. Mar. Pollut. Bull. 119 (1), 12-22. https://doi.org/10.1016/j.marpolbul.2017.01.082

Auta, H.S., Emenike, C.U., Fauziah, S.H., 2017. Distribution and importance of microplastics in

the marine environmentA review of the sources, fate, effects, and potential solutions. Environ. Int. 102, 165–176. https://doi.org/10.1016/j.envint.2017.02.013

- Abidli, S., Antunes, J.C., Ferreira, J.L., Lahbib, Y., Sobral, P., Trigui El Menif, N., 2018. Microplastics in sediments from the littoral zone of the north Tunisian coast (Mediterranean Sea). Estuar. Coast. Shelf Sci. 205, 1–9. https://doi.org/10.1016/j.ecss.2018.03.006
- Allen, S., Allen, D., Phoenix, V.R., Le Roux, G., Durántez Jiménez, P., Simonneau, A., Binet, S., Galop, D., 2019. Atmospheric transport and deposition of microplastics in a remote mountain catchment. Nat. Geosci. 12, 339–344. https://doi.org/10.1038/s41561-019-0335-5
- Bentzen, T., Larsen, T., Rasmussen, M., 2009. Predictions of resuspension of highway detention pond deposits in interrain event periods due to wind-induced currents and waves. J. Environ. Eng. 135, 1286–1293. https://doi.org/10.1061/(asce)ee.1943-7870.0000108
- Besseling, E., Quik, J.T.K., Sun, M., Koelmans, A.A., 2017. Fate of nano-and microplastic in freshwater systems: A modeling study. Environ. Pollut. 220, 540–548. https://doi.org/10.1016/j.envpol.2016.10.001
- Cabernard, L., Roscher, L., Lorenz, C., Gerdts, G., Primpke, S., 2018. Comparison of Raman and Fourier transform infrared spectroscopy for the quantification of microplastics in the aquatic environment. Environ. Sci. Technol. 52, 13279–13288. https://doi.org/10.1021/acs.est.8b03438
- Damrat, M., Zaborska, A., Zajaczkowski, M., 2013. Sedimentation from suspension and sediment accumulation rate in the River Vistula prodelta, Gulf of Gdańsk (Baltic Sea).
 Oceanologia 55, 937–950. https://doi.org/10.5697/oc.55-4.937
- Dris, R., Gasperi, J., Mirande, C., Mandin, C., Guerrouache, M., Langlois, V., Tassin, B., 2017. A first overview of textile fibers, including microplastics, in indoor and outdoor environments. Environ. Pollut. 221, 453–458. https://doi.org/10.1016/j.envpol.2016.12.013
- Da Costa, J.P., Nunes, A.R., Santos, P.S.M., Girão, A. V, Duarte, A.C., Rocha-Santos, T., 2018.
 Degradation of polyethylene microplastics in seawater: Insights into the environmental degradation of polymers. J. Environ. Sci. Heal. Part A Toxic/Hazardous Subst. Environ.
 Eng. 53, 866–875. https://doi.org/10.1080/10934529.2018.1455381
- Di, M., Wang, J., 2018. Microplastics in surface waters and sediments of the Three Gorges Reservoir, China. Sci. Total Environ. 616–617, 1620–1627. https://doi.org/10.1016/j.scitotenv.2017.10.150
- Eriksen, M., Mason, S., Wilson, S., Box, C., Zellers, A., Edwards, W., Farley, H., Amato, S., 2013.
 Microplastic pollution in the surface waters of the Laurentian Great Lakes. Mar. Pollut.
 Bull. 77, 177–182. <u>https://doi.org/10.1016/j.marpolbul.2013.10.007</u>
- Eerkes-Medrano, D., Thompson, R.C., Aldridge, D.C., 2015. Review microplastics in freshwater systems: A review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. Water Res. 75, 63–82. https://doi.org/10.1016/j.watres.2015.02.012
- Free, C.M., Jensen, O.P., Mason, S.A., Eriksen, M., Williamson, N.J., Boldgiv, B., 2014. Highlevels of microplastic pollution in a large, remote, mountain lake. Mar. Pollut. Bull. 85,

156-163. https://doi.org/10.1016/j.marpolbul.2014.06.001

- Hvitved-Jacobsen, T., Vollertsen, J., Nielsen, A.H., 2010. Urban and highway stormwater pollution: Concepts and engineering. CRC Press, Taylor & Francis Group.
- Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M., 2012. Microplastics in the marine environment: A review of the methods used for identification and quantification. Environ. Sci. Technol. 46, 3060–3075. https://doi.org/10.1021/es2031505
- Hodson, M.E., Duffus-Hodson, C.A., Clark, A., Prendergast-Miller, M.T., Thorpe, K.L., 2017.
 Plastic bag derived-microplastics as a vector for metal exposure in terrestrial invertebrates. Environ. Sci. Technol. 51 (8), 4714–4721.
 https://doi.org/10.1021/acs.est.7b00635
- Horton, A.A., Svendsen, C., Williams, R.J., Spurgeon, D.J., Lahive, E., 2017. Large microplastic particles in sediments of tributaries of the River Thames, UK – Abundance, sources and methods for effective quantification. Mar. Pollut. Bull. 114, 218–226. https://doi.org/10.1016/j.marpolbul.2016.09.004
- Hurley, R.R., Lusher, A.L., Olsen, M., Nizzetto, L., 2018. Validation of a method for extracting microplastics from complex, organic-rich, environmental matrices. Environ. Sci. Technol. 52, 7409–7417. https://doi.org/10.1021/acs.est.8b01517
- Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E., Purnell, P., 2018. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. J. Hazard. Mater. 344, 179-199. https://doi.org/10.1016/j.jhazmat.2017.10.014
- Harrison, J.P., Hoellein, T.J., Sapp, M., Tagg, A.S., 2018. Microplastic-associated biofilms: a comparison of freshwater and marine environments. Freshwater Microplastics, Springer, Cham. pp. 181–201. https://doi.org/10.1007/978-3-319-61615-5
- Haave, M., Lorenz, C., Primpke, S., Gerdts, G., 2019. Different stories told by small and large microplastics in sediment first report of microplastic concentrations in an urban recipient in Norway. Mar. Pollut. Bull. 141, 501–513.
 https://doi.org/10.1016/j.marpolbul.2019.02.015
- Hartmann, N.B., Hüffer, T., Thompson, R.C., Hassellöv, M., Verschoor, A., Daugaard, A.E., Rist, S., Karlsson, T., Brennholt, N., Cole, M., Herrling, M.P., Hess, M.C., Ivleva, N.P., Lusher, A.L., Wagner, M., 2019. Are we speaking the same language? Recommendations for a definition and categorization framework for plastic debris. Environ. Sci. Technol. 53, 1039–1047. https://doi.org/10.1021/acs.est.8b05297
- Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. Science. 347 (6223), 768–771. https://doi.org/https://doi.org/10.1126/science.1260352
- Klein, S., Worch, E., Knepper, T.P., 2015. Occurrence and spatial distribution of microplastics in river shore sediments of the rhine-main area in Germany. Environ. Sci. Technol. 49, 6070–6076. https://doi.org/10.1021/acs.est.5b0049
- Kole, P.J., Löhr, A.J., Van Belleghem, F.G.A.J., Ragas, A.M.J., 2017. Wear and tear of tyres: A stealthy source of microplastics in the environment. Int. J. Environ. Res. Public Health. 14 (10), 1265. https://doi.org/10.3390/ijerph14101265
- Kooi, M., Besseling, E., Kroeze, C., van Wezel, A.P., Koelmans, A.A., 2018. Modeling the Fate

and Transport of Plastic Debris in Freshwaters: Review and Guidance, in: Wagner, M., Lambert, S. (Eds.), Freshwater Microplastics : Emerging Environmental Contaminants? Springer International Publishing, Cham, pp. 125–152. https://doi.org/10.1007/978-3-319-61615-5_7

- Koelmans, A.A., Mohamed Nor, N.H., Hermsen, E., Kooi, M., Mintenig, S.M., De France, J.,
 2019. Microplastics in freshwaters and drinking water: Critical review and assessment of
 data quality. Water Res. 155, 410-422. https://doi.org/10.1016/j.watres.2019.02.054
- Law, K.L., 2017. Plastics in the marine environment. Ann. Rev. Mar. Sci. 9, 205–229. https://doi.org/10.1146/annurev-marine-010816-060409
- Leslie, H.A., Brandsma, S.H., Van Velzen, M.J.M., Vethaak, A.D., 2017. Microplastics en route: Field measurements in the Dutch river delta and Amsterdam canals, wastewater treatment plants, North Sea sediments and biota. Environ. Int. 101, 133–142. https://doi.org/10.1016/j.envint.2017.01.018
- Löder, M.G.J., Imhof, H.K., Ladehoff, M., Löschel, L.A., 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, 14283–14292. https://doi.org/10.1021/acs.est.7b03055
- Liu, F., Nielsen, A.H, Vollertsen, J., 2019a. Sorption and degradation potential of pharmaceuticals in sediments from a stormwater retention pond. Water 11, 526. https://doi.org/10.3390/w11030526
- Liu, F., Olesen, K.B., Borregaard, A.R., Vollertsen, J., 2019b. Microplastics in urban and highway stormwater retention ponds. Sci. Total Environ. 671, 992-1000. https://doi.org/10.1016/j.scitotenv.2019.03.416
- McCormick, A., Hoellein, T.J., Mason, S.A., Schluep, J., Kelly, J.J., 2014. Microplastic is an abundant and distinct microbial habitat in an urban river. Environ. Sci. Technol. 48, 11863–11871. https://doi.org/10.1021/es503610r
- Masura, J., Baker, J., Foster, G., Arthur, C., Herring, C., 2015. Laboratory methods for the analysis of microplastics in the marine environment: Recommendations for quantifying synthetic particles in waters and sediments. NOAA. Technical Memorandum NOS-OR&R-48.
- Minelgaite, G., Nielsen, A.H., Pedersen, M.L., Vollertsen, J., 2017. Photodegradation of three stormwater biocides. Urban Water J. 14, 53–60. https://doi.org/10.1080/1573062X.2015.1076489
- Mintenig, S.M., Int-Veen, I., Löder, M.G.J., 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 Res. 108, 365–372. https://doi.org/10.1016/j.watres.2016.11.015
- Mani, T., Primpke, S., Lorenz, C., Gerdts, G., Burkhardt-Holm, P., 2019. Microplastic Pollution in Benthic Midstream Sediments of the Rhine River. Environ. Sci. Technol. 53, 6053–6062. https://doi.org/10.1021/acs.est.9b01363
- Mintenig, S.M., Löder, M.G.J., Primpke, S., Gerdts, G., 2019. Low numbers of microplastics detected in drinking water from ground water sources. Sci. Total Environ. 648, 631–635. https://doi.org/10.1016/j.scitotenv.2018.08.178

- Nuelle, M.T., Dekiff, J.H., Remy, D., Fries, E., 2014. A new analytical approach for monitoring microplastics in marine sediments. Environ. Pollut. 184, 161–169. https://doi.org/10.1016/j.envpol.2013.07.027
- Nel, H.A., Dalu, T., Wasserman, R.J., 2017. Sinks and sources: Assessing microplastic abundance in river sediment and deposit feeders in an Austral temperate urban river system. Sci. Total Environ. 612, 950–956. https://doi.org/10.1016/j.scitotenv.2017.08.298
- Olesen, K.B., Stephansen, D.A., Alst, N. Van, Vollertsen, J., 2019. Microplastics in a Stormwater Pond. Water 11, 1466. https://doi.org/10.3390/w11071466
- Panel, E., Chain, F., 2016. Presence of microplastics and nanoplastics in food, with particular focus on seafood. EFSA J. 14 (6), 4501. https://doi.org/10.2903/j.efsa.2016.4501
- 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. Anal. Methods 9, 1499–1511. https://doi.org/10.1039/c6ay02476a
- Peng, G., Xu, P., Zhu, B., Bai, M., Li, D., 2018. Microplastics in freshwater river sediments in Shanghai, China: A case study of risk assessment in mega-cities. Environ. Pollut. 234, 448– 456. https://doi.org/10.1016/j.envpol.2017.11.034
- PlasticsEurope, 2018. Plastics-the Facts 2018. Brussels.
- Primpke, S., Wirth, M., Lorenz, C., Gerdts, G., 2018. Reference database design for the automated analysis of microplastic samples based on Fourier transform infrared (FTIR) spectroscopy. Anal. Bioanal. Chem. 410, 5131–5141. <u>https://doi.org/10.1007/s00216</u>
- Rummel, C.D., Jahnke, A., Gorokhova, E., Kühnel, D., Schmitt-Jansen, M., 2017. Impacts of biofilm formation on the fate and potential effects of microplastic in the aquatic environment. Environ. Sci. Technol. Lett. https://doi.org/10.1021/acs.estlett.7b00164
- Rochman, C.M., 2018. Microplastics research-from sink to source. Science. 360 (6384). 28-29. https://doi.org/10.1126/science.aar7734
- Rodrigues, M.O., Abrantes, N., Gonçalves, F.J.M., Nogueira, H., Marques, J.C., Gonçalves,
 A.M.M., 2018. Spatial and temporal distribution of microplastics in water and sediments of a freshwater system (Antuã River, Portugal). Sci. Total Environ. 633, 1549–1559. https://doi.org/10.1016/j.scitotenv.2018.03.233
- Szmytkiewicz, A., Zalewska, T., 2014. Sediment deposition and accumulation rates determined by sediment trap and ²¹⁰Pb isotope methods in the Outer Puck Bay (Baltic Sea). Oceanologia 56, 85–106. https://doi.org/10.5697/oc.56-1.085
- Su, L., Xue, Y., Li, L., Yang, D., Kolandhasamy, P., Li, D., Shi, H., 2016. Microplastics in Taihu Lake, China. Environ. Pollut. 216, 711–719. https://doi.org/10.1016/j.envpol.2016.06.036
- Sruthy, S., Ramasamy, E. V, 2017. Microplastic pollution in Vembanad Lake, Kerala, India: The first report of microplastics in lake and estuarine sediments in India. Environ. Pollut. 222, 315–322. https://doi.org/10.1016/j.envpol.2016.12.038
- Scheurer, M., Bigalke, M., 2018. Microplastics in Swiss Floodplain Soils. Environ. Sci. Technol. 52, 3591–3598. https://doi.org/10.1021/acs.est.7b06003
- Simon, M., Alst, N. Van, Vollertsen, J., 2018. Quantification of microplastic mass and removal rates at wastewater treatment plants applying Focal Plane Array (FPA)-based Fourier Transform Infrared (FTIR) imaging. Water Res. 142, 1–9.

https://doi.org/10.1016/j.watres.2018.05.019

- Thompson, R.C., Olsen, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W.G., McGonigle, D., Russell, A.E., 2004. Lost at sea: Where is all the plastic? Science. 304 (5672), 838. https://doi.org/10.1126/science.1094559
- Talvitie, J., Mikola, A., Setälä, O., Heinonen, M., Koistinen, A., 2017. How well is microlitter purified from wastewater? A detailed study on the stepwise removal of microlitter in a tertiary level wastewater treatment plant. Water Res. 109, 164–172. https://doi.org/10.1016/j.watres.2016.11.046
- Velzeboer, I., Kwadijk, C.J.A.F., Koelmans, A.A., 2014. Strong sorption of PCBs to nanoplastics, microplastics, carbon nanotubes, and fullerenes. Environ. Sci. Technol. 48, 4869–4876. https://doi.org/10.1021/es405721v
- Van Cauwenberghe, L., Devriese, L., Galgani, F., Robbens, J., Janssen, C.R., 2015. Microplastics in sediments: A review of techniques, occurrence and effects. Mar. Environ. Res. 111, 5– 17. https://doi.org/10.1016/j.marenvres.2015.06.007
- Vaughan, R., Turner, S.D., Rose, N.L., 2017. Microplastics in the sediments of a UK urban lake. Environ. Pollut. 229, 10–18. https://doi.org/10.1016/j.envpol.2017.05.057
- Woodall, L.C., Sanchez-Vidal, A., Canals, M., Paterson, G.L.J., Coppock, R., Sleight, V., Calafat, A., Rogers, A.D., Narayanaswamy, B.E., Thompson, R.C., 2014. The deep sea is a major sink for microplastic debris. R. Soc. Open Sci. 1 (4), 140317–140317. https://doi.org/10.1098/rsos.140317
- Wang, J., Peng, J., Tan, Z., Gao, Y., Zhan, Z., Chen, Q., Cai, L., 2017. Microplastics in the surface sediments from the Beijiang River littoral zone: Composition, abundance, surface textures and interaction with heavy metals m-FTIR. Chemosphere. 171, 248–258. https://doi.org/10.1016/j.chemosphere.2016.12.074
- Wang, W., Wang, J., 2018. Comparative evaluation of sorption kinetics and isotherms of pyrene onto microplastics. Chemosphere 193, 567–573. https://doi.org/10.1016/j.chemosphere.2017.11.078
- Wang, Z., Su, B., Xu, X., Di, D., Huang, H., Mei, K., Dahlgren, R.A., Zhang, M., Shang, X., 2018. Preferential accumulation of small (<300 Mm) microplastics in the sediments of a coastal plain river network in eastern China. Water Res. 144, 393–401. https://doi.org/10.1016/j.watres.2018.07.050
- Windsor, F.M., Durance, I., Horton, A.A., Thompson, R.C., Tyler, C.R., Ormerod, S.J., 2019. A catchment-scale perspective of plastic pollution. Glob. Chang. Biol. 25 (4), 1207–1221. https://doi.org/10.1111/gcb.14572
- Xiong, X., Zhang, K., Chen, X., Shi, H., Luo, Z., Wu, C., 2018. Sources and distribution of microplastics in China's largest inland lake – Qinghai Lake. Environ. Pollut. 235, 899–906. https://doi.org/10.1016/j.envpol.2017.12.081
- Yang, D., Shi, H., Li, L., Li, J., Jabeen, K., Kolandhasamy, P., 2015. Microplastic pollution in table salts from China. Environ. Sci. Technol. 49, 13622–13627. https://doi.org/10.1021/acs.est.5b03163
- Yang, L., Li, K., Cui, S., Kang, Y., An, L., Lei, K., 2019. Removal of microplastics in municipal sewage from China's largest water reclamation plant. Water Res. 175–181. https://doi.org/10.1016/j.watres.2019.02.046

Zhan, F., Zhang, H., Wang, J., Xu, J., Yuan, H., Gao, Y., Su, F., Chen, J., 2017. Release and gasparticle partitioning behaviors of short-chain chlorinated paraffins (SCCPs) during the thermal treatment of polyvinyl chloride flooring. Environ. Sci. Technol. 51, 9005–9012. https://doi.org/10.1021/acs.est.7b01965

Zhang, G.S., Liu, Y.F., 2018. The distribution of microplastics in soil aggregate fractions in southwestern China. Sci. Total Environ. 642, 12–20. https://doi.org/10.1016/j.scitotenv.2018.06.004

Paper- IV

How Well can Microplastics be Removed from the Treated Wastewater? A Pilot Study of Biofilters Polishing Treatment Plant Effluents

Manuscript. The title is tentative

How well can microplastics be removed from treated wastewater? A pilot study of biofilters polishing treatment plant effluents

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Abstract

Microplastic (MP) pollution is a global environmental issue. Traditional wastewater treatment plant (WWTP) has been identified as a point source to transport land-based microplastics into aquatic environment. To reduce the environmental risk via the WWTP effluent discharge, this study evaluated the performance of a pilot-scale biofilter, which was constituted with four filtration layers, to further remove MP from the secondary effluent from a conventional WWTP in Denmark. The raw effluent had a MP number concentration of 917 item m⁻³ and mass concentration of 24.8 μ g m⁻³. After the biofilter, the concentration was decreased to 171 item m⁻³ and 1.1 μ g m⁻³, indicating an overall removal efficiency of 79% on the particle number and 89% on the particle mass. We also observed a tendency that MP with larger size and higher particle mass were more likely to be retained. After the last filtration level, all MP larger than 100 were all removed. The results obtained from this study demonstrated that biofilter is able to lower the MP abundance in treated wastewater significantly, but an compete removal is not guaranteed, hence some MP can still be discharged to the receiving environment.

1. Introduction

Plastic litter is a global pollution issue both in the aquatic and terrestrial environment (Enders et al., 2015)(Horton et al., 2017b) (Strungaru et al., 2019). Microplastics (MP), often defined as plastic particles < 5 mm in diameter (Arthur et al., 2008), are of particular concern due to their persistence in the environment, and the potential to transport and release of chemical compounds (Teuten et al., 2009). Nowadays, MP has been detected not only in various water bodies (Dris et al., 2018)(Wang et al., 2017), soils and sediments (Scheurer and Bigalke, 2018)(Horton et al., 2017a), but also in indoor air (Vianello et al., 2019), table salts (Lee et al., 2019), and even in the atmosphere in remote areas (Allen et al., 2019). More recently, ingestion and entanglement of MP was also found by freshwater and deep-sea organisms (Taylor et al., 2016)(Taylor et al., 2019b)(Savoca et al., 2019)(Valente et al., 2019), which raised the

concern that the human food chain is under risk of MP contamination (Panel and Chain, 2016)(Toussaint et al., 2019).

Land-based sources have been suggested as the main contributor to plastic pollution entering the aquatic environment, atmospheric and other terrestrial systems (Windsor et al., 2019a). The pathway for such transportation includes stormwater, wastewater, mismanaged plastic wastes, and even wind (Jambeck et al., 2015)(Lebreton et al., 2017). Here, wastewater plays an important role, as it receives plastic litter directly from residential, industrial, agricultural, and commercial areas. Despite the fact that wastewater treatment plant is efficient to remove MP, with the removal efficiency generally been above 90% (Carr et al., 2016)(Sun et al., 2019), tons of MP can still be released through the effluents yearly (Talvitie et al., 2017b)(Simon et al., 2018)(Gatidou et al., 2019).

Studies have shown that the secondary treatment in traditional wastewater treatment plants, which intended to treat nutrients, suspended and dissolved materials, was sufficient to remove most of the MP (Mason et al., 2016). On top of that, some tertiary treatment technologies can improve the removal further, for instance, membrane bioreactors, rapid sand filters, and discfilters (Talvitie et al., 2017a)(Gatidou et al., 2019). Among these advanced effluent polishing techniques, biofilters, however, have not been studied for MP removal.

The aim of this study was to investigate the performance of biofilters in removing MP, using a pilot-scale biofilter column treating secondary wastewater effluents. This evaluation includes the removal efficiency in terms of MP mass and number, as well as details on sizes, masses, and polymer composition of the particles retained by the filters.

2. Materials and methods

2.1. Experiment setup

Two pilot-scale biofilters were set-up in the fall of 2017 at Avedøre wastewater treatment plant (WWTP) in Hvidovre, Denmark. The water used in the set-up was wastewater effluents after secondary sewage treatment. The biofilters were packed in 1 m³ stainless steel tanks, and from top to bottom consisted of a drainage layer of approx. 1.1 m of stonewool (ROCKWOOL^{*}, Hedehusene, Denmark), 40 cm of Filtralite^{*} CLEAN HR 3-6 (Leca Rælingen, Norway), and 10 cm granite gravel (11-15 mm grain size). The 1m stonewool filling was separated into 6 small layers, where the top layer was 0.1 m in depth and the following 5 layers were 0.2 m. Each stonewool layer was cut into four pieces evenly, and with shifted position to avoid a major water pathway through the filter. The different materials, and the valves on the side were separated/covered by a layer of glass fibre mat (CSM 300 gr. Emulision m⁻², Lintex), to avoid migration of materials. On the side of the tank, four sampling valves were mounted, each covering different levels of the inside material (Fig. 1). Flow from valve 1, 2, 3 were the effluents

which passed through the filtration of the top, middle and bottom stonewool layers, respectively. Flow from valve 4 sampled the whole stonewool filtration and the filtrilate filtration.

Before the sampling, the setup was fed with raw effluent for 2.5 months to ensure that biofilms are sufficiently grown. During this period, as well as the time during sampling, the filter was kept submerged with water by elevating the outlet pipe. The flow through the setup was driven by gravitation.



Figure 1 Overview of the biofilter. The effluent water from the treatment plant flows in from the top (inlet), and out at the bottom (outlet).

2.2. Sampling

Samples were collected in June, 2018, using a filtering device. The device was made of stainless steel, and equipped with a removable 10 μ m stainless steel filter (100 mm in effective diameter) (Simon et al., 2018)(Liu et al., 2019a). The samples were drawn from the 4 levels and the outlets by a plastic-free positive displacement pump (Creusen Roermond, Netherlands). A pressure gauge was placed between the pump and the filter to indicate the hydraulic capacity of the filter. The pump was stopped when the pressure had risen to 2 bar, and the filter changed.

The water treated by each filtration level was sampled individually, with valves of only the inlet, outlet and the corresponding filtration level open while others were closed. Before filtering the water into the sampling device, the three valves were kept open and the setup was kept running for 20 min, to ensure that the water level on the top of the setup tank was stable and no overflow occurred. For each filtration level, the sampling was continued till three filters had clogged, which corresponded to sample volumes between 509 and 995 L. The three filters were then combined and stored in a glass jar, filled with sodium dodecyl sulphate solution (SDS, 0.15 g L⁻¹) immediately to cover the top surface of the filters (Liu et al., 2019a). The jar was sealed with a glass lid and wrapped with aluminium foil to prevent contamination of air-borne MPs. The inlet to the filter (the raw effluent from the treatment plant) was sampled by filtering the water directly into the sampling device without passing through the biofilter. The final sampled

volume of each filtration level is given in Table S1. All samples were transferred to the lab and stored at 5 °C until analysis.

2.3. Sample processing

The processing of the samples followed the method by (Liu et al., 2019a). Briefly, the filters containing the samples were wet-oxidized by adding 50 mL 50% H_2O_2 in 500 mL of SDS solution and left for 2 days, followed by Cellubrix (500 µL, Sigma-Aldrich), Viscozyme (350 µL, Sigma-Aldrich), and Alcalase (500 µL, Novozymes) enzyme treatment for 6 days. Fenton reaction was carried out afterwards to further remove remaining organic matter. The reactors were kept in a water bath, where the temperature was monitored and maintained between 15-19 °C. In order to separate MP from inorganic particles, the oxidized samples underwent a density separation using zinc chloride solution (1.8 g cm⁻¹). The separation was done in a 200 mL glass funnel, where dust-free nitrogen gas was bubbled through the solution for 30 min. The solution was left for 2 h after the first floatation, and the settled particles were drained off through the bottom. After that, the solution was topped op with clean zinc chloride solution until 200 mL and went for another floatation for 30 min. This time the solution was left overnight, and the settled particles were drained off again. Particles floating on the solution surface, as well as the ones suspended in the top 2 cm layer of the separation liquid were collected. The collected particles were filtered through a 10 µm stainless steel filter, and concentrated in a 5 mL 50% ethanol solution.

2.4. Microplastic identification and quantification

The identification of MP followed the method from (Simon et al., 2018)(Liu et al., 2019b)(Vianello et al., 2019). Briefly, a subsample of 600 μ L was deposited onto a zinc selenide transmission window, which was restricted to a dimension of 13 mm using a compression cell. The whole window was dried at 50 °C and scanned with a FPA (Focal Plane Array) based FTIR imaging technique (Agilent Cary 620 microscope equipped with a 128 pixel FPA and combined with a Cary 670 spectrometer). The resulted FTIR imaging map was analysed with MPhunter, a free software developed at Aalborg University (Liu et al., 2019a). If MPhunter identified an MP of dimension larger than 500 μ m, the particle was further investigated visually with ultra-fine micro forceps under a stereomicroscope (Stereo Discovery V8, Zeiss, Oberkochen, Germany), to reduce the risk of underestimation of actual size due to the saturation of μ FTIR imaging spectra.

2.5. Statistical analyse

All statistical analysis was performed in R (3.5.1). The removal efficiency was calculated as: $\frac{MP \ concentration \ in \ inlet \ water - MP \ concentration \ after \ treatment}{X} \times 100\%$

MP concentration in inlet water

3. Results and discussion

3.1. MP abundance and removal efficiency

Within all the samples analysed, a total of 195 particles were identified as MP, where 83 of them were from the inlet to the filter (i.e. untreated effluents from the treatment plant) (Table S1). The MP concentration in the inlet and at each filtration level was reported as particle mass and particle number (Fig. 2). Particle mass was estimated assuming that the MP particle was ellipsoid shaped, and the third dimension was 0.6 of the minor dimension (Simon et al., 2018)(Liu et al., 2019a). There was a clear tendency of decrease in the MP concentration from the inlet to the filtered levels. Although there was a slight concentration variation between the four filtration levels, compared with the change in the raw effluent of the inlet, this was not significant. One possible source of the variation is that the samples were taken in a sequential order over 3 days, and the MP concentrations hence likely to vary somewhat (Talvitie et al., 2017c).



Fig 2. MP mass concentration and number concentration of inlet and four filtration levels.

The highest MP abundance was found in the inlet (24.8 μ g m⁻³ and 916.8 item m⁻³), and the lowest was in the second filtration level (1.5 μ g m⁻³ and 111.1 item m⁻³, Table S1). When the removal efficiency was calculated for each filtration level individually, the highest efficiency was in level 2 in terms of particle number (87.9%) and level 4 in terms of particle mass (95.6%) (Table S1). Among the four filtration levels, the average removal efficiency was 79% for particle number, and 90% for particle mass. When lumping the four levels and consider them as one filtration level, the removal efficiency was 78.5% for particle number and 88.9% for particle mass (Table S2). The top filtration level of the pilot scale setup was stonewool, a material which is made from heated basalt rock. Mineral wools are normally closely packed during manufacturing, and each single particle is fiber-shaped (Chapelle, 2016). The material has a high surface-volume ratio and provides a large surface are for biofilms to form on. The attached biofilm can increase the capture area of the stonewool fibers and reduce the pore space in-between, hence increasing the potential capacity for retaining particles (Lobelle and Cunliffe, 2011). Besides, studies have shown that there is a rapid development of microbial biofilms on the surface of plastics (Lobelle and Cunliffe, 2011)(Miao et al., 2019), meaning that the retained MP particles also can have developed biofilms, further increasing the possibility of capture.

Some other techniques used to polish wastewater effluents were also evaluated for the removal of microplastics, for instance membrane bioreactor, discfilter, rapid sand filtration and dissolved air floatation. Among these methods, the membrane bioreactor was found to be the most efficient treatment method, with the removal efficiency 99.9% (Talvitie et al., 2017a)(Lares et al., 2018a)(Lv et al., 2019).

3.2. Polymer composition

Of all the polymers identified, PE was mostly abundant in particle mass (38%), followed by PP, PVC, polyester, PS, acrylic, and PA. Meanwhile, polyester dominated in the particle number (34%) (Fig. 3). Followed by PE, PP, PVC, PS, PA, and acrylic. Epoxy and PU were rare both in particle mass and number, both constituting less than 1%.



Fig.3. Polymer composition of the polymers detected in terms of the relative MP mass and MP number concentrations.

When looking at the polymer distribution between the inlet and different filtrations, no trend of decrease with the filtration level was observed for any identified polymer type (Fig. 4). Nevertheless, compared with the inlet, less polymer types were detected after the four filtration levels. PE, PP, and polyester were the most commonly detected polymers, both in terms of particle number and mass (Fig. 4). The high presence of these polymer types were also reported in other wastewater treatment plant effluents (Lares et al., 2018b)(Lv et al., 2019)(Magni et al., 2019) and even urban stormwater runoff (Liu

et al., 2019b)(Wagner et al., 2019). This is not surprising, since these are the polymers in the most demand (PlasticsEurope, 2017), and wastewater has been identified as an important point source to transport MP to the environment (Carr et al., 2016)(Magni et al., 2019)(Sun et al., 2019).





The distribution of MP belonging to the targeted polymer groups, both in terms of particle number and polymer mass, were plotted for the inlet and after each filtration level (Fig. 4). Comparing the inlet and the effluents at the four filtration levels, less polymer groups were detected after the final filtration. More specifically, PU, PS, and acrylic were all removed by the filter. Among the identified polymers, acrylic had the largest median particle size, and PU had the smallest, while PS ranked in the middle. The

size of the removed particles varied significantly, which indicates that the retention of MP particles was not entirely associated with the particle size. The distribution of MP in the water between the four filtration levels varied, however, with not specific trend in terms of the polymer distributions.

3.3. Particle size and mass

Fig. 5 shows the major and minor dimension of each MP particle, where the estimated mass is presented as the relative size of the circle. All the MP identified were small-sized particles, with the major dimension below of 300 μ m, and the minor below 100 μ m. The absence of particles larger than 300 μ m indicates that the conventional treatment of Avedøre wastewater treatment plant is efficient to remove large sized MPs, a finding which is in agreement with for example (Talvitie et al., 2017b)(Magni et al., 2019).

Despite the small sizes in general, there was still a tendency that larger-sized particles were retained by the filters, and the median value of particle size decreased with the increase of filtration level except for level 2 (Table S1). Over 70% of particles larger than 100 μ m were fond in the inlet, (the untreated effluent of the treatment plant), while MP larger than 100 μ m were absent after the final filtration step (Fig. 5). Similarly, there was a tendency for retaining of particles with higher mass, where the median value of estimated particle mass decreased with the increase of treatment level, but also here with the exception at level 2 (Table S1). Of course, the uncertainty caused by day-to-day variation in MP in the effluent of wastewater treatment plants (Talvitie et al., 2017a) should be considered when interpreting the data. However, compared with other studies, the sampled volume in the present study was in general one order of magnitude higher (Simon et al., 2018)(Yang et al., 2019)(Wolff et al., 2019), hence it is reasonable to assume that the impact from this type of variation was lower in this study.


Figure 5. The major dimension of the particle versus the minor dimension. The size of the data points represents the estimated mass of the particle.

The retention efficiencies between the four filtration levels were difficult to compare, partly because the variation caused by the sampling time was hard to evaluate, and partly because of the statistical uncertainties. However, it was clear to see that most of the MP retention happened in the first treatment level. Comparing the inlet to the filter with the water after the four treatments, it is clear to see that MP with larger size and higher mass were efficiently retained.

4. Conclusion

Wastewater effluents after secondary treatment still contains MP, which potentially puts the receiving environment at risk, considering the large amounts of treated water discharged every day. The studied biofilter, established as an advanced tertiary treatment step, was able to reduce MP from wastewater effluents by 79-89%. The bulk of this removal occurred in the top of the filter, while the deeper layers of the filter yielded limited additional treatment efficiency. The biofilter was preferentially retaining large sized MP particles, and no particle larger than 100 μ m were found in the final effluent of the filter. The biofilter was hence able to lower the MP abundance in the treated wastewater significantly, but did not ensure a complete retainment. Hence some MP will still become discharged to the environment with the treated wastewater.

Reference

- Allen, S., Allen, D., Phoenix, V.R., Le Roux, G., Durántez Jiménez, P., Simonneau, A., Binet, S., Galop, D., 2019. Atmospheric transport and deposition of microplastics in a remote mountain catchment. Nat. Geosci. 12, 339–344. https://doi.org/10.1038/s41561-019-0335-5
- Arthur, C., Baker, J., Bamford, H., 2008. Proceedings of the International Research Workshop on the Occurrence, Effects, and Fate of Microplastic Marine Debris, in: National Oceanic and Atmospheric Administration, 2009. NOAA Technical Memorandum NOS-OR&R-30, p. 530.
- Carr, S.A., Liu, J., Tesoro, A.G., 2016. Transport and fate of microplastic particles in wastewater treatment plants. Water Res. 91, 174–182. https://doi.org/10.1016/j.watres.2016.01.002
- Chapelle, L., 2016. Characterization and modelling of the mechanical properties of mineral wool. Technitical University of Denmark.
- Dris, R., Gasperi, J., Rocher, V., Tassin, B., 2018. Synthetic and non-synthetic anthropogenic fibers in a river under the impact of Paris Megacity: Sampling methodological aspects and flux estimations. Sci. Total Environ. 618, 157–164. https://doi.org/10.1016/j.scitotenv.2017.11.009
- Enders, K., Lenz, R., Stedmon, C.A., Nielsen, T.G., 2015. Abundance, size and polymer

composition of marine microplastics $\geq 10 \ \mu m$ in the Atlantic Ocean and their modelledverticaldistribution.Mar.Pollut.Bull.100,70–81.https://doi.org/10.1016/j.marpolbul.2015.09.027

- Gatidou, G., Arvaniti, O.S., Stasinakis, A.S., 2019. Review on the occurrence and fate of microplastics in Sewage Treatment Plants. J. Hazard. Mater. 367, 504–512. https://doi.org/10.1016/j.jhazmat.2018.12.081
- Horton, A.A., Svendsen, C., Williams, R.J., Spurgeon, D.J., Lahive, E., 2017a. Large microplastic particles in sediments of tributaries of the River Thames, UK – Abundance, sources and methods for effective quantification. Mar. Pollut. Bull. 114, 218–226. https://doi.org/10.1016/j.marpolbul.2016.09.004
- Horton, A.A., Walton, A., Spurgeon, D.J., Lahive, E., Svendsen, C., 2017b. Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities. Sci. Total Environ. https://doi.org/10.1016/j.scitotenv.2017.01.190
- Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. Science (80-.). 347, 768–771. https://doi.org/https://doi.org/10.1126/science.1260352
- Lares, M., Ncibi, M.C., Sillanpää, Markus, Sillanpää, Mika, 2018a. Occurrence, identification and removal of microplastic particles and fibers in conventional activated sludge process and advanced MBR technology. Water Res. 133, 236–246. https://doi.org/10.1016/j.watres.2018.01.049
- Lares, M., Ncibi, M.C., Sillanpää, Markus, Sillanpää, Mika, 2018b. Occurrence, identification and removal of microplastic particles and fibers in conventional activated sludge process and advanced MBR technology. Water Res. 133, 236–246. https://doi.org/10.1016/j.watres.2018.01.049
- Lebreton, L.C.M., Van Der Zwet, J., Damsteeg, J.-W., Slat, B., Andrady, A., Reisser, J., 2017. River plastic emissions to the world's oceans. Nat. Commun. 8. https://doi.org/10.1038/ncomms15611
- Lee, H., Kunz, A., Shim, W.J., Walther, B.A., 2019. Microplastic contamination of table salts from Taiwan, including a global review. Sci. Rep. 9, 10145. https://doi.org/10.1038/s41598-019-46417-z
- Liu, F., Olesen, K.B., Borregaard, A.R., Vollertsen, J., 2019a. Microplastics in urban and highway stormwater retention ponds. Sci. Total Environ. 671, 992–1000. https://doi.org/10.1016/j.scitotenv.2019.03.416
- Liu, F., Olesen, K.B., Borregaard, A.R., Vollertsen, J., 2019b. Microplastics in urban and highway stormwater retention ponds. Sci. Total Environ. 671, 992–1000. https://doi.org/10.1016/j.scitotenv.2019.03.416

- Lobelle, D., Cunliffe, M., 2011. Early microbial biofilm formation on marine plastic debris. Mar. Pollut. Bull. 62, 197–200. https://doi.org/10.1016/j.marpolbul.2010.10.013
- Lv, X., Dong, Q., Zuo, Z., Liu, Y., Huang, X., Wu, W.M., 2019. Microplastics in a municipal wastewater treatment plant: Fate, dynamic distribution, removal efficiencies, and control strategies. J. Clean. Prod. 225, 579–586. https://doi.org/10.1016/j.jclepro.2019.03.321
- Magni, S., Binelli, A., Pittura, L., Avio, C.G., Della Torre, C., Parenti, C.C., Gorbi, S., Regoli, F., 2019. The fate of microplastics in an Italian Wastewater Treatment Plant. Sci. Total Environ. 652, 602–610. https://doi.org/10.1016/j.scitotenv.2018.10.269
- Mason, S.A., Garneau, D., Sutton, R., Chu, Y., Ehmann, K., Barnes, J., Fink, P., Papazissimos, D., Rogers, D.L., 2016. Microplastic pollution is widely detected in US municipal wastewater treatment plant effluent. Environ. Pollut. 218, 1045–1054. https://doi.org/10.1016/j.envpol.2016.08.056
- Miao, L., Wang, P., Hou, J., Yao, Y., Liu, Z., Liu, S., Li, T., 2019. Distinct community structure and microbial functions of biofilms colonizing microplastics. Sci. Total Environ. 650, 2395–2402. https://doi.org/10.1016/j.scitotenv.2018.09.378
- Panel, E., Chain, F., 2016. Presence of microplastics and nanoplastics in food, with particular focus on seafood. EFSA J. 14. https://doi.org/10.2903/j.efsa.2016.4501
- PlasticsEurope, 2017. Plastics-the Facts 2017. Brussels.
- Savoca, S., Capillo, G., Mancuso, M., Faggio, C., Panarello, G., Crupi, R., Bonsignore, M., D'Urso, L., Compagnini, G., Neri, F., Fazio, E., Romeo, T., Bottari, T., Spanò, N., 2019. Detection of artificial cellulose microfibers in Boops boops from the northern coasts of Sicily (Central Mediterranean).
 Sci. Total Environ. 691, 455–465. https://doi.org/10.1016/j.scitotenv.2019.07.148
- Scheurer, M., Bigalke, M., 2018. Microplastics in Swiss Floodplain Soils. Environ. Sci. Technol. 52, 3591–3598. https://doi.org/10.1021/acs.est.7b06003
- Simon, M., Van Alst, N., Vollertsen, J., 2018. Quantification of microplastic mass and removal rates at wastewater treatment plants applying Focal Plane Array (FPA)-based Fourier Transform Infrared (FT-IR) imaging. Water Res. 142, 1–9. https://doi.org/10.1016/j.watres.2018.05.019
- Strungaru, S.A., Jijie, R., Nicoara, M., Plavan, G., Faggio, C., 2019. Micro- (nano) plastics in freshwater ecosystems: Abundance, toxicological impact and quantification methodology. TrAC - Trends Anal. Chem. 110, 116–128. https://doi.org/10.1016/j.trac.2018.10.025
- Sun, J., Dai, X., Wang, Q., van Loosdrecht, M.C.M., Ni, B.J., 2019. Microplastics in wastewater treatment plants: Detection, occurrence and removal. Water Res. https://doi.org/10.1016/j.watres.2018.12.050
- 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 Res. 123, 401–407. https://doi.org/10.1016/j.watres.2017.07.005

- 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 Res. 109, 164–172. https://doi.org/10.1016/j.watres.2016.11.046
- Talvitie, J., Mikola, A., Setälä, O., Heinonen, M., Koistinen, A., 2017c. How well is microlitter purified from wastewater? A detailed study on the stepwise removal of microlitter in a tertiary level wastewater treatment plant. Water Res. 109, 164–172. https://doi.org/10.1016/j.watres.2016.11.046
- Taylor, M.L., Gwinnett, C., Robinson, L.F., Woodall, L.C., 2016. Plastic microfibre ingestion by deep-sea organisms. Sci. Rep. 6. https://doi.org/10.1038/srep33997
- Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Barlaz, M.A., Jonsson, S., Björn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P.H., Tana, T.S., Prudente, M., Boonyatumanond, R., Zakaria, M.P., Akkhavong, K., Ogata, Y., Hirai, H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., Takada, H., 2009. Transport and release of chemicals from plastics to the environment and to wildlife. Philos. Trans. R. Soc. B Biol. Sci. 364, 2027–2045. https://doi.org/10.1098/rstb.2008.0284
- Toussaint, B., Raffael, B., Angers-Loustau, A., Gilliland, D., Kestens, V., Petrillo, M., Rio-Echevarria,
 I.M., Van den Eede, G., 2019. Review of micro- and nanoplastic contamination in the food
 chain. Food Addit. Contam. Part A. https://doi.org/10.1080/19440049.2019.1583381
- Valente, T., Sbrana, A., Scacco, U., Jacomini, C., Bianchi, J., Palazzo, L., de Lucia, G.A., Silvestri, C., Matiddi, M., 2019. Exploring microplastic ingestion by three deep-water elasmobranch species: A case study from the Tyrrhenian Sea. Environ. Pollut. 253, 342–350. https://doi.org/10.1016/j.envpol.2019.07.001
- Vianello, A., Jensen, R.L., Liu, L., Vollertsen, J., 2019. Simulating human exposure to indoor airborne microplastics using a Breathing Thermal Manikin. Sci. Rep. 9, 8670. https://doi.org/10.1038/s41598-019-45054-w
- Wagner, S., Klöckner, P., Stier, B., Römer, M., Seiwert, B., Reemtsma, T., Schmidt, C., 2019.
 Relationship between discharge and river plastics concentrations in a rural and an urban catchment.
 Environ.
 Sci.
 Technol.
 acs.est.9b03048.
 https://doi.org/10.1021/acs.est.9b03048
- Wang, J., Peng, J., Tan, Z., Gao, Y., Zhan, Z., Chen, Q., Cai, L., 2017. Microplastics in the surface sediments from the Beijiang River littoral zone: Composition, abundance, surface textures and interaction with heavy metals m-FTIR. Chemosphere 171, 248–258. https://doi.org/10.1016/j.chemosphere.2016.12.074
- Windsor, F.M., Durance, I., Horton, A.A., Thompson, R.C., Tyler, C.R., Ormerod, S.J., 2019a. A catchment-scale perspective of plastic pollution. Glob. Chang. Biol. 25, 1207–1221. https://doi.org/10.1111/gcb.14572

- Windsor, F.M., Tilley, R.M., Tyler, C.R., Ormerod, S.J., 2019b. Microplastic ingestion by riverine
macroinvertebrates.Sci.TotalEnviron.646,68–74.https://doi.org/10.1016/j.scitotenv.2018.07.271
- Wolff, S., Kerpen, J., Prediger, J., Barkmann, L., Müller, L., 2019. Determination of the microplastics emission in the effluent of a municipal waste water treatment plant using Raman microspectroscopy. Water Res. X. https://doi.org/10.1016/j.wroa.2018.100014
- Yang, L., Li, K., Cui, S., Kang, Y., An, L., Lei, K., 2019. Removal of microplastics in municipal sewage from China's largest water reclamation plant. Water Res. 175–181. https://doi.org/10.1016/j.watres.2019.02.046

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