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Developing Monitoring Strategies for Quantifying and Examining the Fate of Microplastic Emissions in Urban Wastewater Drainage Systems

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إلى أغلى الناس،

إلى حبيبى الذى فارقنى و أنا على مرمى حجر،

إلى معلمى الأول، أخضرَ اليدِ و العمل،

إلى **يوسُفُ** أبى ... (1949 - 2020)

to Mahbouba, Ximena and Mateo…
to Rula, Rana, Mohammed, Ruba, Rasha, Osama and Rawan

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Abstract

The development of synthetic polymers in the early 20th century marked a revolution in society, leading to broad use in everyday items and industrial applications. The "plastic era" began post-World War II, with global production continuously and rapidly increasing. Research on marine plastic litter began in the 1960s and was increasingly linked to the entry of macroplastic from terrestrial sources. The term "microplastic" (MP) was coined in 2004. It defines water-insoluble plastics with a size of 1–1,000 micrometers (μm), excluding rubber. Microplastics are categorized into primary (manufactured in micro size) and secondary (macroplastic broken down through chemical or mechanical processes) and enter the environment through various pathways, with urban areas playing a significant role. The type of drainage systems (combined or separate) in urban areas, as well as weather conditions, are crucial for the entry and transport of microplastics into the environment. Tracking waterborne MP in urban areas is complex due to the diversity of sources, the different material compositions of MPs, and the low concentrations. Previous studies thus mostly focused on point sources from wastewater treatment plants. Recent studies suggest that entries from combined sewer overflows and separate district outfalls are of considerable relevance for the entry of MP from the sewer system into the environment. To assess the significance of each entry path, the development of sampling and monitoring strategies is required, and their standardization is crucial for a comprehensive understanding of the occurrence and relevance of MP in urban drainage systems. This work aimed to develop robust monitoring strategies to estimate MP emissions from urban wastewater streams and to address the lack of standardized methods for monitoring MP. Furthermore, a guideline for the sampling and preparation of microplastics was developed, and the investigations were expanded beyond treatment plants to the sources and entry paths in their catchment areas. This work presents results of systematic investigations of stormwater runoffs and compares them with emissions during dry weather. Going beyond the usual consideration of MPs as aggregate parameters, polymer types and relevant size fractions were determined. Moreover, specific sampling volumes and frequencies are recommended for the studied wastewater streams, based on weather conditions and the complexity of the sewer system. The results show that wastewater treatment plants eliminate at least 96% of the introduced MP load, with polyethylene (PE) being the dominant polymer type in all influent and effluent samples. Wet weather emissions are dominated by PE and styrene-butadiene rubber (SBR). The results suggest that wet weather emissions, primarily from combined sewer overflows and separate district outlets, introduce 2-4 times more MP load into the effluents compared to dry weather emissions from wastewater treatment plants. Furthermore, no correlations could be identified between MP fractions and wastewater matrix parameters (COD, TS, LoI). Future work will require further sampling campaigns to validate the insights gained here. Additionally, flexible sampling systems and online measurements for MP could improve real-time monitoring, thereby contributing to the continuous improvement of representative MP monitoring.

Kurzfassung

Die Entwicklung synthetischer Polymere zu Beginn des 20. Jahrhunderts markierte eine Revolution in der Gesellschaft und führte zu breiter Anwendung in Alltagsgegenständen sowie industriellen Prozessen. Das "Zeitalter des Plastiks" nahm nach dem Zweiten Weltkrieg Fahrt auf, wobei die weltweite Produktion kontinuierlich und rapide anstieg. Die Erforschung von marinem Plastikmüll begann in den 1960er Jahren und wurde zunehmend mit dem Eintrag von Makroplastik aus terrestrischen Quellen in Zusammenhang gebracht. Der Begriff "Mikroplastik" (MP) wurde 2004 geprägt. Er definiert wasserunlösliche Kunststoffe mit einer Größe von 1–1.000 Mikrometer (µm), wobei Gummi ausgenommen ist. Mikroplastik wird in die Kategorien primär (in Mikrometergröße hergestellt) und sekundär (durch chemische oder mechanische Prozesse zerkleinertes Makroplastik) eingeteilt und gelangt über verschiedene Wege in die Umwelt, wobei urbane Gebiete eine bedeutende Rolle spielen. Art der Entwässerungssysteme (Misch- oder Trennsystem) in urbanen Gebieten, sowie Wetterbedingungen sind entscheidend für den Eintrag und Transport von Mikroplastik in die Umwelt. Die Verfolgung von wasserbürtigem MP in städtischen Gebieten gestaltet sich aufgrund der Verschiedenheit der Quellen, der unterschiedlichen stofflichen Zusammensetzung von MP sowie der niedrigen Konzentrationen als komplex. Bisherige Studien konzentrierten sich daher überwiegend auf punktuelle Einträge aus Abwasserreinigungsanlagen. Neuere Studien geben Hinweise darauf, dass Einträge aus Mischwasserentlastungen und Trenngebietsauslässen von erheblicher Relevanz für den Eintrag von MP aus dem Abwassersystem in die Umwelt sind. Um die Bedeutung der jeweiligen Eintragspfade beurteilen zu können, bedarf es der Entwicklung von Probenahme- und Monitoringstrategien. Deren Standardisierung ist von entscheidender Bedeutung für ein umfassendes Verständnis des Vorkommens und der Relevanz von MP in urbanen Entwässerungssystemen. Das Ziel dieser Arbeit war es, robuste Überwachungsstrategien zu entwickeln, um die MP-Emissionen aus städtischen Abwasserströmen abzuschätzen und den Mangel an standardisierten Methoden zur Überwachung von MP zu beheben. Des Weiteren wurde ein Leitfaden für die Probenahme und die Aufbereitung von Mikroplastik entwickelt und die Untersuchungen über Kläranlagen hinaus um die Quellen und Eintragspfade in deren Einzugsgebiet erweitert. Diese Arbeit zeigt Ergebnisse systematischer Untersuchungen von Regenwasserabflüssen und vergleicht diese mit den Emissionen bei Trockenwetter. Über die bisher

übliche Betrachtung von MP als Summen-Parameter hinausgehend wurden Polymerarten sowie relevante Größenfraktionen bestimmt. Zudem werden spezifische Probenahmevolumina und -häufigkeiten für die untersuchten Abwasserströme, basierend auf den Wetterbedingungen und der Komplexität des Kanalsystems, empfohlen. Die Ergebnisse zeigen, dass Kläranlagen mindestens 96 % der eingeleiteten MP- Fracht eliminierten, wobei Polyethylen (PE) als dominierender Polymertyp in allen Zulauf- und Ablaufproben vorlag. Emissionen bei Regenwetter sind dominiert von PE und Styrol-Butadien-Kautschuk (SBR). Die Ergebnisse deuten darauf hin, dass Regenwetteremissionen vor allem aus Mischwasserentlastungen und Trenngebietsauslässen im Vergleich zu Trockenwetteremissionen aus Kläranlagen 2–4-mal mehr MP-Fracht in die Vorfluter einbringen. Zudem konnten keine Korrelationen zwischen MP-Fraktionen und Abwasser-Matrixparametern (CSB, AFS, AFS63, GV) festgestellt werden. Zukünftige Arbeiten erfordern weitere Probenahmekampagnen zur Validierung der hier gewonnenen Erkenntnisse. Zudem könnten flexible Probenahmesysteme und Online-Messungen für MP die Echtzeitüberwachung verbessern und somit zur kontinuierlichen Verbesserung einer repräsentativen MP-Überwachung beitragen.

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List of Abbreviations

A_{EIA}	Effective impervious area
AFS_{63}	German, Abfiltrierbaren Feststoffe kleiner als 63 µm
ATR-FTIR	Attenuated Total Reflectance FTIR
$B_{MP,a,ca}$	Yearly per population equivalent MP load from a certain catchment area in g/(p.e.*a)
$B_{MP,a,ha}$	Yearly MP load per unit drained area in g/(ha*a)
$B_{MP,ha,R.a}$	Yearly wet weather flow MP load per unit drained area in g/(ha*a).
$B_{MP\text{-}SBR,ha,R.a}$	Yearly wet weather flow MP load per unit drained area in g/(ha*a) excluding SBR component.
BAM	Bundesanstalt für Materialforschung und -prüfung (In German).
BHN	Brinell hardness number
BR	Butadiene Rubber
$b_{R,a,AFS63}$	Annual removal of AFS_{63}
$C_{R,\ AFS63}$	AFS63 concentration in stormwater runoff, annual mean
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
DWD	Deutscher Wetterdienst
EC	European Commission
EPA	Environmental Protection Agency
F	sampling Frequency
FPA-FTIR	Focal Plane Array FTIR
FTIR	Fourier-Transform-Infrared-Spectroscopy
GAC	Granulated Activated Carbon.
GPa	Gigapascal
GW	Greywater.
HDPE	High density polyethylene
L	confidence interval
LDPE	Low density polyethylene
LLDPE	linear low-density PE
LOD	Limit of Detection
LoI	Loss on Ignition
LOQ	Limit of Quantification
LVS	Large Volume Samplers.

MaP	Macroplastic
mg/L	milligram per Liter
MP	Microplastic(s)
Mpa	Megapascal (N/m^2)
Mt	Megatons
n	number of samples (statistics)
Nm	Nanometer
NR	Natural Rubber
OM	Organic Matter.
OMP	Organic Micropollutant(s)
P	Phosphorus
PA	Polyamide
PACs	Polycyclic Aromatic Hydrocarbons
PE	Polyethylene
p.e.	population equivalents.
PM	Particulate Matter
PMMA	Poly(methyl) methacrylate
POPs	Persistent Organic Pollutants
PP	Polypropylene
PS	Polystyrene
PSD	Particle size distribution
PVC	Polychloride vinyl
$Q_{d,min}$	Minimum daily dry weather flow within 21 days period, 10 days before and 10 days after measurement including the measurement day.
$Q_{d,min20}$	$Q_{d,min}$ multiplied by a factor of 1.2
$Q_{DW,0mm}$	Average dry weather flow with 0 mm precipitation and actual and previous days.
$Q_{DW,m,0mm}$	Mean dry weather flow with 0 mm precipitation and actual and previous days.
RM	Raman microspectroscopy.
S	standard deviation of sample (statistics)
SB	Sedimentation Box.
SBR	Styrene-butadiene rubber
SUDS	Sustainable Urban Drainage System(s)
T	duration of monitoring campaign
TED-GC/MS	Thermal Extraction Desorption-Gas Chromatography/Mass Spectroscopy
t_f	Longest flow time to the stormwater tank in the catchment
TS	Total Solids
TW	Tire Wear

TWP	Tire Wear Particles
UDS	Urban Drainage System(s)
UV	Ultraviolet
$V_{R,a}$	Annual stormwater runoff volume, long-term average
WW	Wastewater
WWTP	Wastewater treatment plant

1 Introduction

The invention of synthetic polymers (plastics) of hydrocarbon origin revolutionized many aspects of our lives. The use of these man-made materials spans from basic everyday applications, such as food packaging, to complex applications in medical and automotive industries. The production of hydrocarbon-based polymers began at the beginning of the 20th century with the invention of Bakelite resin in 1907. Thereafter, the production of new synthetic polymers picked up a rapid pace in the first half of the same century. The most important milestones were achieved with the invention of Polychloride vinyl (PVC) in 1912, Poly(methyl methacrylate) (PMMA, Plexiglas) in 1924, Polyethylene (PE) in 1933, Polystyrene (PS) in 1944 and Polypropylene (PP) in 1954 (Chalmin 2019). However, the "plastic era" was inaugurated after the end of World War II. In 1950s, annual global plastic production was estimated to be as low as 1.5 Megatons (Mt)/a. Ever since, the global market expanded immensely to reach a global production of about 367 Mt/a by 2020 (Plastics Europe 2021). Based on previous production trends from 1950-2020, various projections suggest that annual global plastic production would triple by 2060 (Geyer 2020; OECD 2022). According to the trade association Plastics Europe, packaging (with 40.5 % of market share) and building and construction sectors (20.4 %) represent the largest share of final plastic products in Europe. Automotive sector, electrical and electronics, household and agriculture represent ca. 19 % of the market share combined (Plastics Europe 2021). With a view to the types of polymers used in urban activities, the polyolefin group (e.g., high density PE (HDPE), low density PE (LDPE) and PP) is highly represented with a market share of more than 50 % (Plastics Europe 2021). This can be associated to its wide range of physical and chemical properties that are of great use in industrial and domestic applications.

The interest in studying marine plastic litter arose in early 1960s after receiving reports on plastic litter in north Atlantic sea (Ryan 2015). Kenyon and Kridler (1969) have reported on finding small plastic particles inside decaying carcasses of Albatrosses along Hawaiian beaches. These reports and others motivated a generation of researchers to investigate the problem in depth, and by the end of 1980s the scale of the crisis was largely fathomed (Ryan 2015). Although for the last 40 years the focus was mainly on marine environment, this shifted recently towards terrestrial sources and entry pathways into receiving waters from urban and agricultural areas (Ryan 2015).

The term "*microplastic*" (MP) was used for the first time by Thompson et al. (2004) to describe small plastic fragments found in the marine environment as a result of large plastic debris breaking down. However, neither the new term nor the previous use of "*small plastic litter*" gave a clear definition of this emerging pollutant (Frias and Nash 2019). Early studies defined MP being synthetic polymer particles with an upper size limit of 5 mm (Arthur et al. 2008; Cole et al. 2011; Frias and Nash 2019). The lack of clear definition for MP combined with a boom in the research area meant that the results of many studies were hardly comparable to one another.

In this work, the recent definition from the international organization for standardization (ISO) is applied with MP being solid and insoluble hydrocarbon materials containing high polymers and traces of additives that improve its properties, and a particle size ranging between 1 to 1000 µm (DIN CEN ISO/TR 2020). The definition mentioned above, does not include elastomers (e.g., natural and synthetic rubber), but they are considered here as microplastics due to similarity in particle formation (Braun et al. 2018). Other physical and chemical properties of MP, such as color, shape, density, ability to crystallize or remain amorphous under various environmental conditions, are not explicitly stated in the previous definition. Nevertheless, these properties are highly relevant while describing the fate and toxicity of detected MP in environment (Mark 2007).

MPs are classified into two categories: primary and secondary MP. This classification refers to the initial production size of the synthetic material, whether it was intended to be used in this size, hence primary MP, or an unavoidable mechanical or photodegradation forced a "*macroplastic*" to break down into smaller fragments, hence secondary MP (Bertling et al. 2018; Cole et al. 2011). The mechanisms, in which secondary MP is produced, are weathering, fractioning, surface embrittlement (Andrady 2011, 2015), and mechanical abrasion during a human activity, e.g., vehicle Tire Wear Particles (TWP) (Unice et al. 2019). As a result, both primary and secondary MP are expected to enter environmental compartments (soil, air, and surface water) from a wide range of diffuse sources and through various entry pathways. Based on Marine MP research, Andrady (2011) estimates that at least 80% of all MP found in environment originates from land-based sources. Land-based sources can be further classified into waterborne or airborne MP depending on the transport pathways they are forced to take. In urban areas, MP sources are emitted from indoor sources, e.g., hygiene products (Leslie 2015) or textile fibers in sport outfits (Dris et al. 2017; Hernandez et al. 2017), or outdoor sources, e.g., tire wear and littering. (Coalition Clean Baltic 2017). Although airborne microplastics as dust and fibers are possessing real danger to urban environment (Treilles et al. 2021; Dris et al. 2015), this work focuses on MP emitted in urban areas and transported into surface waters through urban drainage systems (UDS).

1.1. MP in Urban Drainage Systems (UDS)

Urban drainage systems had known in the past two main designs; combined and separate drainage systems. A combined drainage system drains stormwater runoff along with domestic and industrial wastewater using only one sewer network, while a separate drainage system drains stormwater runoff and wastewater streams in separate sewer networks. Each drainage system represents a distinct entry pathway for different MP types, both quantitatively and qualitatively, depending on the diffuse and point sources connected to it. Hence, it is recommended to monitor both systems separately to understand their significance in transporting MP over UDS. In addition to the design of UDS, the weather conditions play a role in favoring the transport, accumulation, and degradation of MP.

Similar to the conflict of finding a consensus on a comprehensive definition for MP, researchers from different scientific backgrounds deployed numerous sampling and analytical methods to detect MP in environmental samples. While this surge in the number of studies enlarged the knowledge base on the topic (Ryan 2015), the necessity for standardizing monitoring procedures soared. The standardization of sampling and detection strategies is essential for comparing data sets from varying urban areas and catchments, as well as to minimize uncertainties tied to the detection process.

MP as an emerging pollutant in our UDS represents, along with heavy metals, organic micropollutants (OMP) and polycyclic aromatic hydrocarbons (PACs), a serious challenge to urban water management systems. Alongside the classical goals assigned to these systems of sanitary disposal of wastewater (WW) streams and flood protection, UDSs are critical infrastructures. Identifying and characterizing the types and sizes of MP is a helpful tool to identify sources and in turn suggests effective avoidance and mitigation strategies. In addition, the quantification of MP along the different entry pathways is important to estimate the fate and removal potential of MP at the many treatment and retention structures within UDS, improve existing ones and better plan future structures. Ultimately, understanding the occurrence and dynamics of this particular pollutant is essential to apply best management practices and move closer to a green circular economy.

The research on MP occurrence and its effects on humans and environment is still emerging. So that up till now, there are no specific European laws regulating MP emissions from land-based sources (EC 2022). As part of the union's long-term policy on plastics, the European Commission (EC) is addressing the issue by introducing the *"initiative on Microplastics"*. This initiative is divided into two main stages. The first stage aims at promoting a ban of *"intentionally added"* (primary) MP. While stage two focuses on minimizing the unintentional (secondary) release of MP by introducing a series of standards and methods to close the knowledge gap on the topic, and suggesting a new labeling system to prevent the release of MP during products' life cycles (EC 2022). Although a collective directive for MP is still missing on a pan-European level, existing directives on urban WW, sewage sludge and waste management affect the release and retention of MP in urban areas (EC 2022; Plastics Europe 2021).

In Germany, the federal water act promotes the protection of water bodies as a natural resource and a habitat for animals and plants (Bundestag 2009). In Analogy to European directives, other federal laws and directives affect the emission and retention potential of MP. The novel German guidelines on stormwater management (DWA A-102) propose treatment and prevention measures for polluted stormwater runoff from urban areas. The mentioned guidelines classify urban catchment areas into three main categories based on the emission potential of the novel parameter Total Solids (TS) smaller than 63 µm in diameter; German, *Abfiltrierbaren Feststoffe kleiner als 63 µm (AFS$_{63}$)* (DWA/BWK 2020). Also, the sewage sludge act (AbfKlärV 2017) limit the use of sewage sludge from wastewater treatment plants (WWTP) as a fertilizer in agriculture from 2029 onwards.

The research activities in this work were largely conducted as part of the research project RUSEKU that was funded by the Federal Ministry of Education and Research Germany (BMBF) from April 2018 till September 2021. The project RUSEKU aimed at developing representative investigation procedures and strategies for the quantification of MP in urban wastewater systems.

1.2. Problem statement

Synthetic polymers and the additives added to them are foreign substances to inland and marine aquatic environments. Studies on the effects of MP on aquatic life showed that several zooplankton species mistakenly ingest MP causing negative effects on their growth, reproduction and migration processes (Botterell et al. 2019). The further fractionation of micro- and macroplastics (MaP) due to weathering increase the adsorption potential to other pollutant groups (Takada and Karapanagioti 2019). Therefore, MP may act as well as an adsorbent and carrier of other pollutant groups from urban areas to receiving environmental compartments, e.g., persistent organic pollutants (POPs), PACs and heavy metals (Rios Mendoza and Balcer 2020).

The lack of knowledge on quantity and particle size distributions (PSD) of MP leaves planners and operators of UDS unaware of the effectiveness of the many treatment elements in retaining MP particles. Moving towards resilient and sustainable urban drainage systems (SUDS) requires filling the knowledge gap on all pollutant groups, including MP. This new knowledge pillar would also improve the decision-making tools on aspired capabilities of future SUDS, including blue-green systems.

Tracking waterborne MP in urban areas is a challenging task due to the various sources and transport pathways involved. In addition, MP occur in low concentrations in most wastewater and stormwater streams (Murphy et al. 2016; Bertling et al. 2018; Carr and Thompson 2020; Fuhrmann et al. 2021; Järlskog et al. 2021; Tanentzap et al. 2021; Venghaus et al. 2021), large sample volumes are thus needed to monitor the occurrence and size variations in water samples. The large samples needed are not only a challenge during sampling, but also while preparing the samples for further analytics. Maintaining a balance between large volume sampling and realistic time or cost involved is, however, a tough decision for planners. In addition, UDSs have been constructed since the 19th century to convey all different types of wastewater streams in combined or separate streams, yet as quickly as possible. The rapid growth of cities and metropoles in the last century led, in return, to the growth of drainage systems serving those areas. Since then, UDSs have gone through expansion and development phases to meet civic needs and environmental goals all at once. So that tracking pollutants of small order of magnitude in such complex system is rather challenging.

Previous studies on MP emissions from urban catchments have considered UDS as *"black boxes"*. Thus, most of the sampling activities took place at the farthest downstream point in catchments; namely at WWTPs. These studies showed, nevertheless, that municipal WWTPs can capture the vast majority of MP entering the plants to highest extent (> 97%) regardless of weather-condition and catchment characteristics (Mintenig et al. 2014; Carr et al. 2016; Dyachenko et al. 2017; Kay et al. 2018; Carr and Thompson 2020; Fältström et al. 2021). Although the investigations at WWTPs are important in order to understand the relevance of this entry pathway, little information can be derived about potential sources and transport dynamics within the catchment itself. The close-to-source investigations are crucial to identify sources of MP and to estimate the specific MP emissions per population equivalent or area unit. Furthermore, sampling upstream of WWTP is necessary to understand the relevance of the many entry pathways and drainage patterns (combined, separate). Besides, MP found in urban drainage systems show different properties (i.e., density, morphology, and chemical stability) and experience different residence times, which in return means that potential changes in these properties may occur (Andrady 2011). Thus, studying the occurrence of MP close-to-source is more reasonable.

Urban drainage systems (UDS) had historically known two main layouts; combined and separate drainage systems. Each drainage system represents a distinct entry and transport pathway for different MP, both quantitatively and qualitatively, depending on the diffuse and point sources connected to them. Hence, both systems should be monitored separately to understand their significance in transporting MP of urban origin. In addition, the dynamics and spatiotemporal release patterns within UDSs represent a major challenge for any future comprehensive monitoring strategy. Particularly when considering dry and wet weather conditions, combined and separate systems convey probably different MP matrices depending on factors like, percentage of combined to separate systems and storm characteristics.

In recent years, large number of researchers and research institutes stormed the arena of MP studies motivated by various goals and objectives (Cole et al. 2011; GESAMP 2016; Lusher et al. 2017; Bertling et al. 2018; Heß et al. 2018) and, also, deploying mostly incomparable sampling strategies. In addition, early studies applied visual and automated particle counting methods and MP mass balancing was rather difficult, e.g., in the field of aquatic biology (Ng and Obbard 2006). The design of standardized sampling strategies would extend the knowledge retrieved, both spatially and qualitatively, and accelerate the transition into a well-established field of study. In addition, standardizing sampling strategies leads to enhanced understanding of possible uncertainties involved and gives planners a better chance to adjust their practices accordingly.

1.3. Main objectives and research approach

The main goal of this work is to develop monitoring strategies of waterborne MP of urban origin, quantify their abundance and distributions and evaluate their fate within UDS and receiving waters.

This main goal will be accomplished by achieving the following set of objectives:

I. Development of representative and reproducible **sampling strategies** of MP for **combined** and **separate** drainage systems

II. **Quantification** of MP release from selected catchment areas under dry and wet weather conditions.
    a. Identify the most abundant **MP types** occurring in urban drainage areas and their **PSD**s in urban WW flows.
    b. Estimating relevant **sources** of MP in the studied areas

III. Investigating the relationship between MP emissions and
    a. canalization pattern, i.e., **combined, and separate**,
    b. WW parameters, i.e., Total Suspended Solids **(TS)**, Chemical Oxygen Demand (**COD**) and Loss on Ignition (**LoI**),
    c. as well as **boundary conditions**, i.e., population density, traffic density, runoff characteristics, dry weather periods, catchment size and common anthropogenic activities in catchment.

IV. Anticipating **the fate of MP** from UDS along the **transport pathways** by estimating the synergetic effects of ongoing treatment effort and future advancements, i.e., removal of organic trace elements and ongoing stormwater runoff management.

The **approach** (Figure 1-1) to reach the set of mentioned goals starts by selecting a **UDS** to be a **study area** for most of research activities. The UDS of the city of Kaiserslautern was selected for the comparability to other UDSs in terms of functionality and size, its proximity to the University and the familiarity of the research team to its components. In addition, the generic information on layout, sewer length, land use, population, and traffic densities were retrieved from operators for subsequent data analysis.

After gathering generic information on the UDS, potential representative hotspots for MP sampling in terms of release and transport were defined, and preliminary chemical and physical characteristics of WW streams were identified. The information on WW characteristics were then utilized to design **preliminary monitoring strategies** in terms of equipment, frequency, sampling type and samples volumes. The first monitoring campaign tackled predefined hotspots under **dry weather** conditions or **indoor MP sources,** while planning the following campaign to tackle hotspots under **wet weather** conditions or **outdoor MP sources**. During both monitoring campaigns, sampling practices and protocols, as well as sample preparation methods are being continuously improved to minimize the margin of uncertainty.

Based on the results of sampling campaigns and the subsequent data analysis, the **quantification** of MP emissions from the targeted WW streams is done thoroughly in regard of catchment and population sizes, land use and, in case of stormwater runoff, characteristics of stormwater events. Subsequently, the release patterns of MP and possible **correlations** with WW standard parameters (COD, TS and LoI) are investigated coherently on single size fraction level.

MP emissions experience different **fates** along the transport pathways. This different fate is decided, among others, by the type of canalization, weather conditions and removal potential at existing retention structures. The effects of these conditions and structures are analyzed separately to estimate the effectiveness of UDS in retaining MP emissions under status quo and future developments (i.e., ongoing decentralization). The described approach includes many steps, starting with the choice of monitoring strategy to arithmetic quantitative analysis. Figure 1-1 illustrates the generic approach of this work.

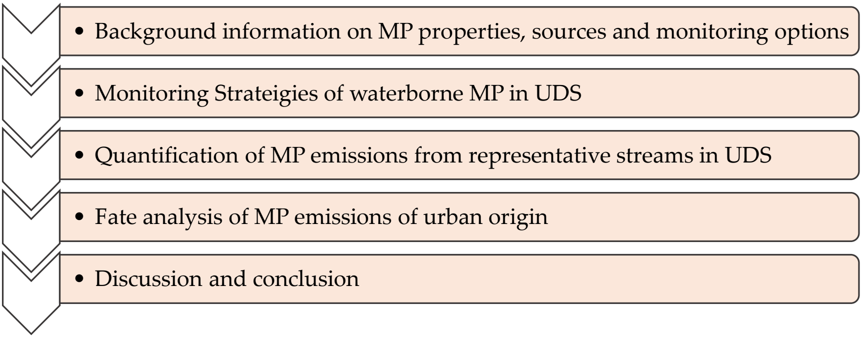

Figure 1-1 Approach of the work

1.4. Thesis outline

Chapter 1 introduces the origins of MP problem and gives an introduction and background of present research activities, then explains the problem statement from urban drainage point of view and introduces the road map for reaching the goal and objectives of this work.

Chapter 2 highlights the relevant chemical and physical properties of MP, in order to determine possible monitoring strategies, analysis limitations and the fate in UDSs.

Chapter 3 describes the hotpots for sampling and explains the deployed **materials and methods** of the monitoring concept. This concept stretches from sampling strategies over sample preparation techniques, to arithmetic quantification of MP per population equivalent or drained area. In addition, the methodology of extending the knowledge from catchment area or WWTP level to entire UDS is explained.

Chapter 4

- describes the results of monitoring campaigns under dry and wet weather conditions. Also, possible correlations between the release patterns of MP and other WW matrix parameters and event characteristics are discussed in detail,
- extends the results acquired in chapter 4 and tracks the fate of detected MP emissions along the UDS and gives prediction on the final destination of these emissions under status quo of UDS and future advancements.
- highlights major takeaways from the monitoring campaigns, gives practical suggestions on running representative monitoring campaigns and handling the different samples.

Finally, **chapter 5** delivers comprehensive discussion and conclusions of entire work and reflects on the future work and remaining knowledge gap.

2 Fundamentals and Background

The term "Microplastic", as a collective parameter, is used by many researchers to describe different small size synthetic polymers. A precise definition for MP, in terms of size and composition, is still debatable. Thus, it is usually derived from the goal behind the specific research, or the boundary conditions governing the detection process in use. However, to understand the available definitions and classifications, three notions should be explained: **polymers, synthetic polymers, plastics, thermoplastics, and elastomers.**

Polymers are macromolecules containing branched or chain repeating units of smaller molecules (Monomers) (Rudin and Choi 2013), while synthetic polymers are man-made materials produced using polymerization reactions. In Material science, synthetic polymers are classified into plastics (thermoplastics and thermosetting), elastomers and composites of synthetic and natural polymers. Thermoplastics and thermosetting polymers are materials that can be melted and formed into end products multiple cycles (thermoplastics) or for limited number of cycles. Figure 2-1 shows the classification of polymers according to its chemical composition, strain-stress behavior, and size.

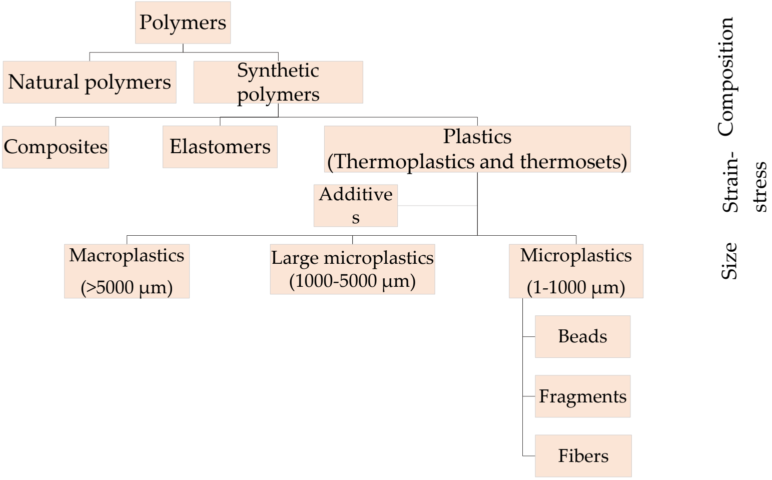

Figure 2-1 Classification of synthetic polymer materials according to ISO TR 21960

Besides the main synthetic polymeric material, plastic resins are usually mixed with many chemical additives that improve its physical and chemical properties and extend their life span (i.e., flexibility, Ultraviolet (UV) resistance, thermal stability, and slippery surfaces) (Hahladakis et al. 2018). During their lifetime, plastics exposed to weathering effects are able to adsorb other chemicals and contaminants present in neighboring environments (Galloway 2015). Hence, plastics and their smaller size counterparts “microplastics” indicate, when detected, the presence of additives, as well as other trace pollutants.

In this chapter, I will try to clarify the most important characteristic of MP to better understand their occurrence in the studied urban wastewater streams. Starting by the different definitions suggested in the field and the need for consensus, and discussing the characteristics, shapes, and stability of the most produced plastics worldwide. These plastics are also the ones that are looked for in this work. Then, a glimpse of potential sources and transport pathways will be given to support the decisions taken later on in this work regarding sampling locations and monitoring strategies. In addition, the applied basic rules and methods of sampling and sample preparation are briefly explained, since they are the starting point before achieving customized practices for MP monitoring. Finally, the available MP detection methods are described to show their potential impact on monitoring strategies, as well as the limitations and advantages they offer.

2.1. Definition of MP: a changing conception

Since the field of study emerged in early 2000s, agreeing on a proper definition for MP has been considered a topic on its own (Frias and Nash 2019). The lack of a solid definition motivated scholars to suggest some collective definitions. The first definition from Thompson et al. (2004) evolved from the question; “what happens to smaller plastic particles in marine environment?”. However, this definition failed to mention size boundaries nor chemical composition of these “small plastics”. In 2008, an upper size limit of 5 mm was first suggested by Arthur et al. (2008) to shed the focus on ecological hazards of MP and not only on the ones related to digestive tract congestions in marine and coastal animals. Arthur et al. also suggested a lower threshold size of 333 µm to keep in line with the only available sampling technique in time, namely the Neuston plankton nets. However, the lower limit vanished instantly due to new emerging techniques that allowed for fine separation below the 333 µm limit.

The working group GESAMP[1] (GESAMP 2016) considered plastic particles larger than 1 µm and smaller than 1000µm to be MP. Although the "founding fathers" of the field were themselves uncertain of it and made it conditional to advancement in detection methodologies, the upper limit of 5 mm established itself and became a de facto threshold in the vast majority of MP studies. In conclusion, early definitions reflected the scientific backgrounds of the researchers that have been working in the field and focused primarily on the size aspect.

A well-defined and multi-criterion definition is necessary to compare the results from the substantial number of studies available and better estimate the extent of the problem. A standardized definition is, in addition, a foundation to regulate and minimize MP immissions in environmental compartments (i.e., water, soil and air) adjacent to urban settlements. Following size-oriented definitions, Bertling et al. (2018) suggested the integration of source, solubility in water, solid state and chemical composition of the polymer into definition. Accordingly, primary MP and secondary MP were introduced. MP of type A are plastics and waxes that were intentionally produced in the small size, while MP of type B result from mechanical or photodegradation of macroplastic. Frias and Nash (2019) proposed an all-inclusive definition that is similar to Bertling's definition but adding to it a remark to consider all shapes of MP.

Hartmann et al. (Hartmann et al. 2019) proposed a baseline framework towards a robust definition that aims to untie any proposed definition from available analytical capacities and encourage researchers to continuously refine available definitions. The framework identifies the main criteria to establish a definition, defining and auxiliary criteria. Defining criteria include chemical composition of polymers, solid state, and solubility. Auxiliary criteria are descriptors that might be helpful in a specific research area, i.e., size, shape, color, and origin (primary and secondary).

The International Organization for Standardization (ISO) adopted the main criteria from Hartmann's framework, as well the descriptive size criterion, and defined MP as "*any solid plastic particle insoluble in water with any dimension between 1 µm and 1000 µm*" (CEN ISO/TR 2020). Therefore, rubber materials are excluded, color, shape and origin are not specified. Moreover, the previous norm defines plastic particles between 1000-5000 µm as "large MP". Only the latest ISO definition for MP is considered in this work since other means rather than color and origin are applied to track possible sources.

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[1] Joint group of experts on the scientific aspects of marine environmental protection.

2.2. Basic physical characteristics of polymers

In polymer science, the physical properties of polymers are described in terms of their mechanical, electrical, and optical behavior. In this chapter, I would like to explain some basic mechanical properties of plastics. These properties are of high importance while analyzing the stability, toxicity, and mobility of polymers in environmental compartments, both in macro and micro scale. (Rudin and Choi 2013)

The macro properties of MP, such as density and hardness, are mainly determined by the morphology of its building polymeric chains. The so-called degree of **crystallinity** is a measure of how well packed the polymeric chains are. The more irregular or less compact these chains are, the less crystalline this polymer is, or the more **amorphous.** However, polymer materials cannot reach a degree of crystallinity of 100%. (Smith and Hashemi 2006)

Density (specific gravity), tensile strength, elongation at yield, modulus of elasticity and Brinell hardness number (BHN) are, among others, the main mechanical parameters to describe polymers' mechanical performance. **Density** (kg/m^3) is the parameter that determines the probability of a polymer to float in a water medium or be captured at a sedimentation unit. Specific gravity is a modified term that gives the relative density of polymers to the density of water medium. Thermoplastic densities stretch over a broad scale and can be as low as 0.6 g/cm^3 for Polybutylene, or as high as 2.28 g/cm^3 for Polytetrafluoroethylene (Kholodovych and Welsh 2007). **Tensile strength** in megapascal (MPa) or MN/m^2 is the ratio of a perpendicular force (F) applied on polymer's cross section area that causes elongation or stretch to the polymer. **Elongation** at yield in % is the linear contraction of polymeric material due to tensile stress applied. **Modulus of elasticity** or tensile modulus, also Young's modulus, in gigapascal (GPa) a measure of polymer's stiffness and describes its elastic features as a ratio of stress to strain. Finally, **Brinell hardness number** in kg/mm is a measure of the permanent impression caused by the force of a hardened steel ball with specific diameter on polymer's surface. Table 2-1 shows the densities and mechanical properties of some relevant thermoplastics and thermosets to urban MP pollution.

Table 2-1 Physical properties of selected thermoplastics and thermosets (Engineering ToolBox 2001);(Mark 2007; Smith and Hashemi 2006; Thermo Fisher Scientific, Inc. 2022)

Polymer	Density - ϱ - (kg/m^3)	Tensile Strength - σ - (MPa)	Elongation (%)	Modulus of Elasticity - E - (GPa)	Brinell Hardness Number	Melting Point - T - (°C)
PP	890	34	200 - 700	0.69	10	160 - 176
PE (LD-HD)	925 - 950	20 - 27	350 - 100	0.7	2	85 - 138
PS	1050.0	48	3.0	3.4	25	270
Nylon	1160	60	90	2.4	10	217 - 260
PMMA	1160 - 1200	70	2.5	2.9	20	85 - 105
Acrylic (metacrylate)	1190.0	74	6.0	3	34	160
Cellulose Acetate	1300	40	10 - 60	1.4	12	230 - 300
PVC	1330	48	200	3.4	20	100 - 160
PTFE	2100	13	100	0.3		320 - 330

Mechanical properties vary with time depending on surrounding conditions, mainly temperature. Besides mechanical properties, polymers exhibit distinct **spectroscopic fingerprints** that allow “surface chemists” to identify their structure and type precisely (Rudin and Choi 2013). These spectroscopic attributes are also of great importance for detecting and quantifying MP in UDS. More information on the later will be given in (2.5).

For more information on the mechanical and thermodynamic properties of polymers, I suggest the following references:

- Physical properties of polymer handbook by James E. Mark,
- The elements of polymer science and engineering by Alfred Rudin and Phillip Choi, and
- Foundations of materials science and engineering by William F. Smith and Javad Hashemi.

2.2.1. Biodegradation and weathering of plastics

In polymer science there are two, often mistaken with one another, terms; biodegradability and bio-disintegration. The former term describes the extracellular breakdown of polymers into carbon dioxide (CO_2) and water with help from microorganisms and enzymes, while the latter refers to biologically assessed fragmentation of the polymer. Although all organic materials must gradually degrade, synthetic polymers are showing extremely slow degradation kinetics in comparison to natural polymers, such as tree leaves and wood. Generally, synthetic polymers with higher molecular weight, high crystallinity and insoluble in water are more recalcitrant in the environment. (Andrady 2007) According to Chamas et al. (2020), the size and improved stability of plastic debris in marine environment affect the pace of its surface degradation. While plastic bottles made from HDPE require on average 58 years to degrade, conduits from the same material have to wait 1000 years more for the same fate. However, accumulation and wash-off processes on urban surfaces hinder the capture of MP so long till biodegradation takes place.

Weathering or fragmentation of plastics is by definition the reason behind the release of secondary MP (type B). The disintegration of MaP is caused largely by extensive oxidation due to solar UV radiation on land, before plastic debris reaches water surfaces (Andrady 2022), and surface thermal oxidation (Kholodovych and Welsh 2007). Besides fragmentation of MaP , photodegradation and thermal oxidation cause cracking and increase brittleness of both MaP and MP particles. As a direct result of this phenomenon, the surface area of MP increases tremendously and with it the transport potential of other pollutants.

2.2.2. Types of common plastics and MP

Since the beginning of “plastic era”, the chemical industry has been producing large number of plastic materials to serve in wide range of applications. Yet, a handful of thermoplastics dominate the global market in large. According to PlasticEurope (Plastics Europe 2021), the types PE, PP, PVC, PET and PS counted combined for almost 74% of all plastic resins produced globally. These popular thermoplastics have found their way to countless urban activities and products, especially to products in direct contact with UDS. Thus, emissions to urban water cycle are inevitable.

In this section, six commonly produced thermoplastics are selected to be interpreted in terms of their **chemical composition**, **stability under environmental conditions** and **common applications**. In addition, the characteristics of SBR, which is clearly a synthetic rubber, are discussed. The selection is based on their potential abundance in UDS, and the limitation prompted by the adopted analytical process in this work, namely the thermal extraction and desorption combined with gas chromatography/mass spectrometry (TED-GC/MS). Although the latter process allows for PVC analysis, customized individual runs with adjustments had to be applied each time to detect PVC. Therefore, PVC was omitted from the analytical pool to avoid massive extra costs[2].

SBR was added to the analytical pool in this work due to its similar characteristics compared to thermoplastics, the potential abundance due traffic in urban areas and technical feasibility allowed by analytical process (TED-GC/MS).

In the sections (2.2.2.2) to (2.2.2.6), the handbook *"Thermoplastics And Thermoplastic Composites"* by Michel Biron and Odile Marichal (Biron and Marichal 2018) is used to describe the relevant properties of the six studied thermoplastic groups and their aging behavior as urban deposits or waterborne solids. For SBR properties (2.2.2.7), the "*Handbook of Thermoplastic Elastomers*" by Jiri G. Drobny (Drobny 2014) is retrieved. The recent trends on production, consumption and selected applications of common plastics are retrieved from the statistics of the organization Plastics Europe Market Research Group (PEMRG).

2.2.2.1. Polyethylene (PE)

Polyethylene $(C_2H_4)_n$, in its three common forms HDPE, LDPE, and linear low-density PE (LLDPE), is the most produced plastic resin worldwide . PE dominates the global polymer market because of the many preferable characteristics that are wished in a wide range of industries, and the nature of products it is utilized in. LDPE is utilized for instance in reusable bags, packaging, trays, and agricultural sheets in green houses. HDPE is used intensively in products like shampoo bottles, pipes, and houseware. In total, more than 31% of all plastic resins formed worldwide belong to the PE family (Plastics Europe 2021).

The attractiveness of PE resins for industry is linked largely to economic reasons. In comparison to natural materials, no other raw material delivers the same value for money and maintains good mechanical and chemical behavior through their life-time. In addition, impact resistance, chemical and physiological inertness and electrical insulation are properties that suggest endless number of application possible (Biron and Marichal 2018).

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[2] According to the analytical laboratory, each detection run with TED-GC/MS would cost 800€ on average.

Although PE properties are well maintained indoors, many products suffer heavily under the influence of heat, UV, and solar light. Therefore, UV and solar sensitivity is seen as the main downside of PE (Dümichen et al. 2015). As a result, PE surfaces (especially LDPE films) are prone to fractionation and small secondary MP particles are released (Biron 2018). We might all recall this time when we tried to remove a plastic bag that was stuck in the grass on the sidewalk, and how brittle the material was after a long stay under the sun. In the case of UDSs, the force that was applied in the previous example by our fingers on the wrapper, could be caused this time by stormwater runoff or a moving object in the catchment area.

2.2.2.2. *Polypropylene (PP)*

Polypropylene $(C_3H_6)_n$, with a production quota of about 20%, is the second most produced plastic worldwide after PE. Besides the pure homopolymer variation, PP monomers can be polymerized with other olefins to produce copolymers, or with elastomers to enhance impact resistance. PP also offers many preferable physical and chemical properties for considerably low price. The most common applications are found in packaging, construction (e.g., piping) and automotive industries. PP is also utilized intensively in household appliances and sport gadgets (Plastics Europe 2021).

Adding to the advantages mentioned before, PP is widely utilized because of the relative processing ease, also at processing plants in low developing countries. Good fatigue and impact resistance allowed the manufactures of piping and sanitary products to integrate PP into many solutions in the field (Plastics Europe 2021).

Similar to PE, PP are not expected to do well under continuous UV and solar radiation. Although the plastic industry developed new PP resins that are more resistant to UV, high temperatures coupled with other weathering conditions leave PP products prone to fractionation. From material science point of view, the low density of both PE and PP (refer to Table 2-1) is interpreted in a positive manner. However, low density increases the chance for MP of the two plastic families to become waterborne pollutants (Biron and Marichal 2018).

2.2.2.3. Polyethylene terephthalate (PET[3])

Polyethylene terephthalate $(C_{10}H_8O_4)_n$ is of the polyester family. The most common application is the use as bottles for soft drinks. According to Plastics Europe (Plastics Europe 2021), PET accounts for 8.4% of worlds plastic production. In literature, the term PET can be used to describe both the bottles material and the famous polyester textiles.

PET products are selected for their low cost, insulation properties, impermeability to CO_2 and high transparency. Polyesters show in general better heat resistance and tensile strength after weathering, although it is regarded as UV sensitive (Biron and Marichal 2018).

2.2.2.4. Polystyrene (PS)

Polystyrene $(C_8H_8)_n$ is a thermoplastic that is preferred for applications when rigidity is required. About 6% of global plastic resins are related to PS products. The common applications are rigid food packaging, insulation sheets and electrical equipment (Plastics Europe 2021).

PS products tend to show good mechanical properties and a high degree of transparency, and they are easily processed for a low price. Similar to PE and PP, heat and UV sensitivity is a drawback. In addition, PS materials have weak scratch resistance and lose 10-20% of their tensile strength after several months in an outdoor environment (Biron and Marichal 2018).

2.2.2.5. Acrylics

Acrylics is a group of thermoplastics knows for its glass-like optical properties. The most popular type of which is Plexiglass or PMMA. Among many others, applications like lab containers or aquarium protection walls are common.

Acrylics are chosen mainly for their optical properties, such as brightness and stability of colors, and for their outstanding UV resistance. Therefore, a fractionation of PMMA due to sun exposure is rather unlikely. However, they show low heat and impact resistances, which lead to potential fractionation when wrongfully disposed in the environment (Biron and Marichal 2018).

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[3] Some publications abbreviate Polyester when used as textile fiber as *PES.* This work adopts the abbreviation PET for all polyester derivatives.

2.2.2.6. Styrene-butadiene rubber (SBR)

SBR is clearly not a thermoplastic, but since it is exceptionally included in the definition of MP and because its basic properties are similar to thermoplastics, the basic characteristics and weathering behavior is explained here. SBR is a synthetic copolymer elastomer which results from the copolymerization of the monomers styrene and butadiene. It was first prepared by a research team from the German firm Bayer and was later marketed as Buna S synthetic rubber. The first copolymerization recipe involved the use of 75% butadiene and 25% styrene. (Drobny 2014) However, the actual mass production of SBR accompanied the American war effort during world war II (Sisanth et al. 2017). Worldwide, SBR production accounts for 21% of all rubber (natural and synthetic) produced, of which, 65% is utilized directly in tire industry. (Roland et al. 2013). A modern car’s tire consists nowadays of about 40% SBR and 13% butadiene rubber (BR), the remaining 47% are mainly silica, oil, sulfur compounds, zinc and other additives and trace compounds (Kocher 2010).

Pure SBR materials have densities between 0.93 and 0.94 g/cm^3 (Patki et al. 2007), while car tire rubber has a density of about 1.2 g/cm^3 (Degaffe and Turner 2011). In comparison to natural rubber (NR), SBR sustains higher operational temperatures, 110 °C for SBR and 80 °C for NR. in addition, excellent abrasion, adhesion, oxidation and weathering resistances (Scholz and Gehringer 2021; Princi 2019).

2.2.3. Common shapes of MP

Previous studies on MP morphology identified many shape classes. Frias and Nash (2019) classified up to ten groups: pellets, fragments, fibers, films, ropes, filaments, sponges, foams, rubber, and microbeads. Yet a clear geometrical definition of the stated shapes is missing, and some shape groups appear to share the same geometrical meaning (e.g., ropes and filaments). In General, four shapes (**beads**, **fibers**, **fragments** and **films**) were cited in most studies (Rosal 2021).

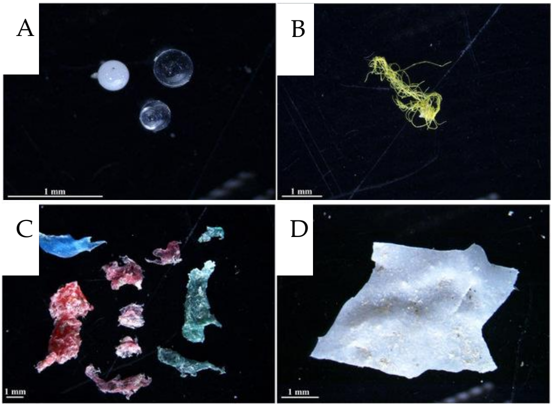

Figure 2-2 The most cited microplastic shapes (here in macro-size) as shown by D'Hont et al. (2021): A) Beads B) Fibers C) Fragments D) Films

Rosal (Rosal 2021) suggested a new classification system (Figure 2-3) that identifies all possible MP shapes within a 3-dimentional model. Accordingly, a particle with equally sized dimensions is a perfect sphere. While a particle with one dimension extremely larger than the other two dimensions is seen as a perfect rod or cylinder. Fragments can be described according to their location to one of the three perfect shapes in the model.

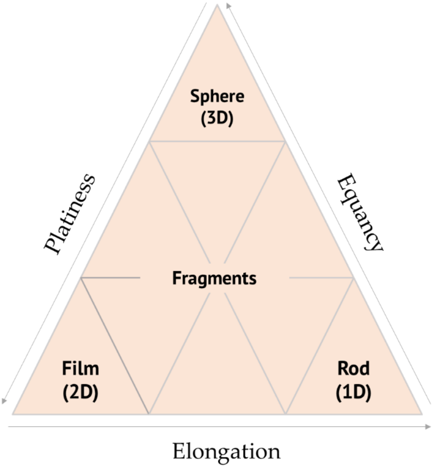

Figure 2-3 MP shapes vary within a 3-dimensional space (Rosal 2021), own representation

Kooi and Koelmans (2019) argued that environmental MP is too complex to be described with distinct shape classes, and introduced a continuous probability distribution that combined size, shape and density, to contribute to future fate modelling studies. This empirical statistical distribution suggests that fibers and fragments are the most abundant environmental MP.

Nonetheless, Schwarzer et al. (2022) and Lehtiniemi et al. (2018) suggested that size and polymer type are more decisive factors for environmental toxicology in marine environment, rather than shape.

2.2.4. Additives in plastic products

Additives are organic and inorganic trace substances that are added to polymers during or just after polymerization, to improve a physical property or protect against property deterioration during production or use phases. For instance, almost all thermoplastics are spiked with stabilizing agents during and after polymerization process (Drobny 2014). Table 2-2 summarizes common additives used in plastic industry and the purpose of using them.

Table 2-2 Overview of common additives used in plastic industry (Drobny 2014), own representation

Additive group	**Use**
Antioxidants	• Protect against aging and degradation and represent 0.05 – 1% of the resin.
UV absorbers	• Chemicals that hinder photodegradation by filtering the wavelength range 290 – 400 nm.
Flame retardants	• Help to reduce calorific value of plastic by absorbing heat (vapor formation) and formation of char
Colorants	• Organic dyes soluble in plastics, or organic/inorganic solid pigments incompatible with polymer material (0.01 – 0.1 μm)
Antistatic agents	• Chemicals that hinder the accumulation of electric charge on plastic surface, and thus hamper the buildup of dust and impurities.
Slip agents	• Surface coatings and lubricants that reduce friction coefficient

Anti-blocking	• Chemicals that reduce the adhesiveness of plastic sheets and films, help to avoid fine sheets from sticking to each other
Processing agents	• Additives improve the handling of plastics by reducing the viscosity of polymer melts
Fillers	• Active or inert materials that adjust volume, weight, cost, and some chemical properties of plastics
Plasticizers	• Agents that improve flexibility and processability of plastic melts

Therefore, additives are classified into protecting and enhancing agents (Ambrogi et al. 2017). On one hand, protecting additives, such as antioxidants and UV stabilizers, are designed to react with environmental predators and sacrifice itself to prolong the life of plastic. This reaction results in the migration of additives or the release of some of their by-products (Hahladakis et al. 2018). On the other hand, properties enhancing additives, such as slip agents and plasticizers, migrate during production phase and throughout life cycle of plastic products (Bejgarn et al. 2015). The potential effects of released additives and their by-products on human health are described in multiple publications. In this regard, the author suggests the works from (Campanale et al. 2020) and (Leslie et al. 2022) to be a reference for further detailed investigation on the topic.

2.3. Origins and transport pathways of urban waterborne MP

Urban areas saw rapid growth in size and density during the nineteenth century as migration from rural areas to industrial hubs surged (Newman 2007). By the end of 2021, more than 57% of world´s population lives and work in urban areas, this portion reaches almost 100% in some developed countries (e. g., Belgium) (Figure 2-4) (World Bank 2022b). The proximity to manufacturers and major transportation nodes, as well as being cultural and social hubs, made urban areas very attractive for labor force and wide range of economic activities (Griffith et al. 2012).

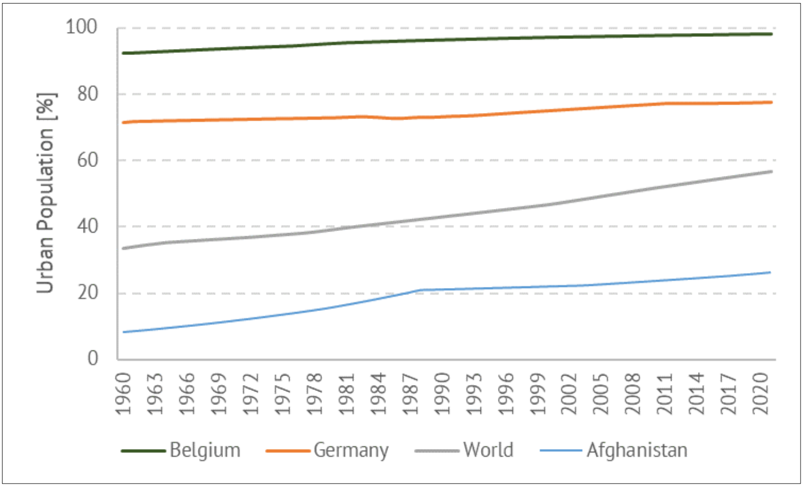

Figure 2-4 The development of urbanization levels worldwide from 1960 to 2021 (World Bank 2022b)

The rapid growth of urban areas added more stress on resources and intensified emissions into the surrounding environment. Overcrowded cities with traffic jams and littering issues are attributes of modern day cities (Malamis et al. 2016). Solid waste and wastewater management systems have accompanied this growth and also saw an increase in size and complexity to cope with the latter developments. Alongside food, water and energy, essential materials like plastics are utilized in numerous applications. One cannot, for example, imagine car and packaging industries in their current shape without the use of plastic and composite materials.

The definition in (2.1) classifies environmental MP into **primary** and **secondary** MP, but it does not distinguish between **indoor** and **outdoor** sources nor according to their potential **transport pathways** within an UDS. However, these extra classifications according to source are helpful in the field of urban drainage to better estimate the fate of MP and the efficiency of UDS in retaining them.

Examples for sources of primary MP are personal care products, synthetic fibers in textiles and pigments in paints (Turner 2021; Lassen et al. 2015; Boucher and Friot 2017). MP from these sources is intentionally produced to fulfill a physical (i.e., mechanical, or optical) requirement in a certain product. Sources of secondary MP are usually the degradation or fragmentation of larger plastic particles, e.g., photodegradation of plastic litter (refer to 2.2.1) and abrasion of road markers (Bertling et al. 2018;).

The classification of MP sources into indoor or outdoor serves as a tool to predict potential transport pathways MP will likely take on their way to a receiving environment (i.e., soil or water body) or a retention structure in the UDS. Indoor MP sources are located inside roofed structures, less prone to weathering conditions, have no contact to stormwater runoff, and their MP can only become waterborne in domestic or industrial sewage streams. In addition, indoor MP sources can release both primary and secondary MP. Outdoor MP sources are released in open areas and can be washed off from impervious surfaces and reach UDS. Similarly, both primary (e.g., pellet losses) and secondary MP (e.g., tire abrasion) are released from outdoor sources.

Besides waterborne MP, small plastic particles are transported by air, the so-called "airborne MP". Unlike waterborne MP with relatively predictable transport pathways, airborne MP can travel long distances from the source to receiving environments in form of dust, aerosols, and depositions (Habibi et al. 2022). Among others, factors, such as wind flow and direction, and particle characteristics determine the range and mobility pattern of airborne MP particles (Enyoh et al. 2019). According Dris et al. (Dris et al. 2017) indoor airborne MP are more abundant than outdoor ones, probably due to their proximity to sources like synthetic textiles. Accordingly, airborne MP are able to remobilize and accumulate on adjacent environmental compartments, such as soil, or on man-made outdoor surfaces (i.e., impervious urban surfaces). Unice et al. (Unice et al. 2019) estimate that around 61 % of tire wear particles (TWP) emissions are transported airborne into soil, while only 2 % remain suspended in the air. Figure 2-5 suggests a generic transport scheme of MP from both indoor and outdoor sources as waterborne and airborne MP. Although a portion of MP from urban areas are first transported airborne before they end up waterborne, the scope of this work is only waterborne MP within UDS.

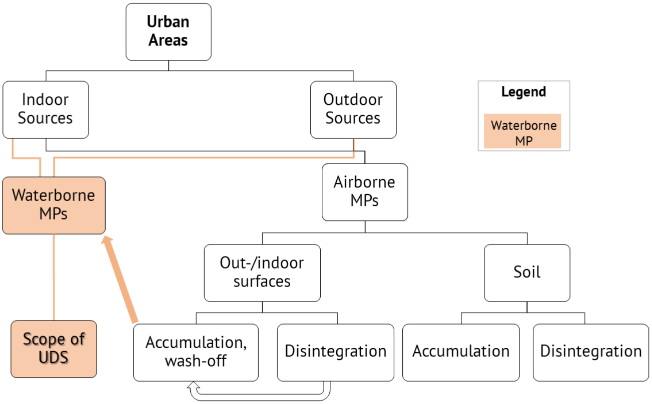

Figure 2-5 Potential transport pathways of MP within UDS (Unice et al. 2019; Bertling et al. 2018; Habibi et al. 2022), own interpretation and representation

In their study "Plastics in the Environment: Micro and Macroplastic, P.10-11", Bertling et al. (2018) predicted at least 58 potential MP sources from urban catchments, 35 of which have potential access to one or more wastewater streams in UDS and emit waterborne MP. According to own analysis and interpretation of the data (see **Error! Reference source not found.** in appendix), o utdoor sources are probably responsible for more than 80 % of all MP in urban areas (Figure 2-6). Considering waterborne MP only, the share of MP of outdoor sources increase to represent about 87 % of all waterborne MP.

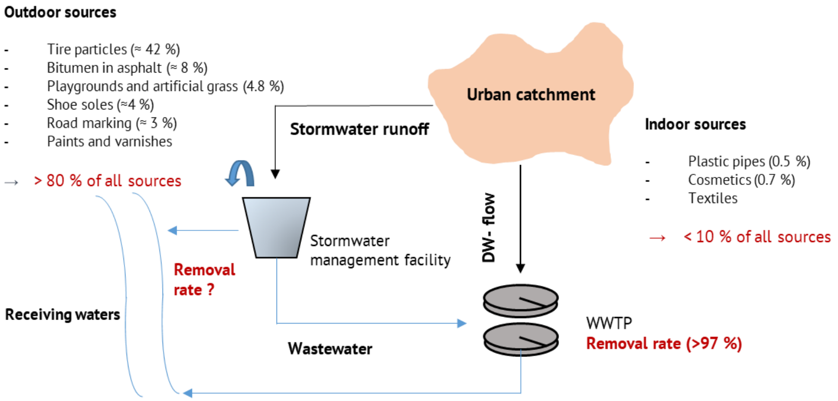

Figure 2-6 The proportion of MP from indoor vs. outdoor sources according to Bertling et al. (Bertling et al. 2018), own interpretation and representation

While the previous study failed to mention other major contributors to MP emissions like littering, the results shown earlier represent an important milestone towards creating a mass balance on MP emissions in urban areas and opened the door for designing relatable sampling strategies. In the following sub sections, relevant MP sources in urban areas (2.3.1) are discussed and explained.

2.3.1. Sources of MP in urban areas

Sources of MP in urban areas cover a wide range of human activities both indoor and outdoor. Starting from the early morning hygiene routines to driving a personal vehicle to work and not ending by washing synthetic clothes, MP is emitted into urban environment. However, the focus in the following sections is shed on some major sources of secondary MP (i.e., littering, transportation, construction works, synthetic textiles and urban synthetic surfaces) that will accompany us for the coming years, since new regulations are heading towards banning the intentional use of primary MP in industrial activities, see *"Upcoming initiative on microplastics"* (EC 2022).

2.3.1.1. Littering

Littering or unlawful disposal of solid waste into the environment is a global phenomenon that stresses human societies and leads to deterioration in life quality in surrounding urban areas. The littering problem surged after world war II with increasing consumption rates and the mass production of single use products, mainly of plastic materials (Bristol Waste 2021). The World Bank (World Bank 2022a) estimates that about 2.24 billion tons of solid waste were generated worldwide in 2020 (0.79 kg per capita equivalent/day). The waste generation rates are unfortunately increasing with over 90 % of which is being unproperly disposed. The organization Keep America Beautiful (Keep America Beautiful 2021) estimates that there are about 50 billion litter items discarded on American side roads and waterways. In Europe, the Clean Europe Network estimates that tax payers are charged with €1 billion annually to manage litter problem (ELPA 2022). In the state of Rhineland-Palatinate, where this research took place, the Ministry of Environment recorded the collection of 4,004 tons of litter in 2019 with specific per population equivalent emissions of about 0.97 kg/ca.a (MKUEM 2021). These numbers refer, however, to collected and disposed litter materials. Considering the unreported or undetected amounts, litter emissions are probably higher than the official numbers. Furthermore, one would expect the detection of plastic litter only after elongated residence time in a humid and/or temperate environmental compartment. Hence, detected aged litter in forests and urban roads are mostly made of non-degradable synthetic materials, mostly plastics.

A study on urban litter in Basel, Switzerland and Vienna, Austria showed that take-away and drinks packaging, as well as cigarette butts are the most common litter material to be spotted on streets (Heeb et al. 2016). Figure 2-7 shows numerous cigarette butts, containing cellulose acetates, captured from an effluent stream (treated) of a stormwater treatment plant in an industrial region in Freiburg, Germany. Due to their light weight similar to other plastic litter, cigarette butts are transported effortlessly along street runoff into UDS. Personal observations from the sampling site showed that cellulose acetate, the filter material, has begun to degrade and probably release smaller parts into the environment.

Figure 2-7 Partially degraded cigarette butts are found in the effluent of a storm water treatment plant in Freiburg, Germany (Own documentation, Abusafia 2016)

Other common litter items, such as coffee cups, wrappers and plastic bottles, are also expected to degrade into smaller particles and release its MP counterparts (Öborn et al. 2022). In addition, these litter items are capable of adsorbing other contaminants (e.g., PACs in road dust) during their residence time in environment and serve as pollution vectors (Golwala et al. 2021).

2.3.1.2. Transportation

The mobility sector is one of the essential backbones of the modern economy. The number of motorized vehicles for personal and commercial uses has been constantly increasing since the invention of the internal combustion motor. The number of personal and commercial vehicles reached in 2023 a record high of about 1.282 billion vehicles worldwide (Statista 2017), this number is estimated to reach 1.474 billion by the end of 2023 (Hedges & Company 2023). In Germany alone and by the end of 2021, 67 million vehicles were licensed with an ownership rate of 717 vehicles per 1000 inhabitants (KBA 2022).

Plastics and engineered plastics are basic components of modern vehicles' interior and exterior building parts. However, only the emissions from tire (ISO 2020) and brake materials are relevant in the scope of MP research. The vehicle related traffic emissions result from the mechanical friction of tire and brake materials with paved road surfaces (TWP) and speed band plates (brake wear). Among other factors, the rate and amount of TWP emissions are affected by motorway roughness and geometry, weather conditions, weight and suspension of vehicle, and tire material itself (EPA 2014).

While standardized procedures for sampling from street dust, soil, and air are available (ISO/TS 21396 2017; PD ISO/TS 20593:2017 2017), there is currently no established methodology for the systematic sampling and quantification of TWP in aquatic environment or in street runoff (Mattonai et al. 2022). This lack of standardization is reflected in the high variation of release amounts observed in the many studies in the field. However, a certain consent on the release parameter does exist, so that most studies report the emission values in mg TWP per driven km or mile [mg/km $_{\text{driven}}$]. Liu et al. (2022) monitored the loss in tire volume of 76 taxis in Rome and Athens over 22 months by measuring the loss in rubber depth every 3 months. The study analyzed the effect of vehicle and tire material types, as well as the driving behavior on TWP emission rates. For instance, the study found that winter tires release more particles compared to summer and all-year ones, and hybrid cars with higher instant torque tend to release more particles. Cunha-Lopes et al. (2022) conducted a monitoring campaign using online particle filters at two sites with varying traffic densities; a highly frequented tunnel and a less busy street near the tunnel area. The previous study showed that high traffic density in the tunnel was responsible for 10 to 20 times more particle pollution in the air compared to neighboring areas. Gaga et al. (2018) conducted a monitoring campaign at two locations before and after a highly frequented tunnel in Turkey and providing results comparable to the ones from Cunha-Lopes et al. Two sampling methods were employed in this study: active sampling, involving high-flow rate collection of various pollutants using specific filters and weighing before/after sampling, and passive sampling for BTEX[4] compounds using specialized samplers placed alongside active samplers during sampling periods and analyzed with GC-MS. While the previous studies were conducted under environmental conditions, Aatmeeyata et al. (2009) conducted a laboratory study on synthetic tires. The experimental set-up aimed to exclusively collect particles generated from the wear caused by rolling friction between a two-wheeler tire and a cylindrical concrete road simulating a road's rigid pavement. The results show low emission rates compared to other studies mentioned earlier. Table 2-3 summarizes some emission rates from studies that were carried out under varying boundary conditions and sampling methodologies.

Table 2-3 TWP emissions from different studies reflect the variation in release patterns following the boundary conditions of each case

Study	Description	No. samples	TWP emissions [mg/km driven]
(Liu et al. 2022)	Tracking the loss in tire 76 taxis in Rome and Athens with a measurement every three months	500	72 (hybrid cars) 53 (conventional cars) 160 (winter tires)
(Cunha-Lopes et al. 2022)	Sampling of street dust (tire and brake wear)	8-days continuous measurement	83 – 274
(Piscitello et al. 2021)	Different sources	-	5.4 – 330 (cars)
(Gaga et al. 2018)	Sampling of street dust at the inlet and outlet of rural tunnel, Turkey	20	96 ± 30
(Aatmeeyata et al. 2009)	Lab study on two and four wheelers with summer tires	8	3.5 (two wheelers) 6.4 (four wheelers)

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[4] Benzene, toluene, ethyl benzene, and xylenes (BTEX)

The core profile of tire material of modern passenger cars is made from synthetic rubbers (53.6 %); [SBR (40.9 %) and Butadiene Rubber (BR) (12.8 %)], silica as a filler material (34 %), plasticizer (oil) (4.3 %) and other additives and chemicals for vulcanization (≈ 8.1 %) (Degussa 2007) cited in (Kocher 2010). In contrary, the material of tread in trucks' tires consists of NR (30 %), synthetic rubber (5 %), halogenated butyl rubber (4 %) and other chemicals (37 %) (Continental 2020). Therefore, the detection of one or more tire components leads to the quantification of other materials under known traffic conditions in studied areas.

According to (VDI-Norm VDI 3782) (cited in (Kocher 2010)), 93-99 % of TWP are non-airborne particles (> 10 µm), which means that most of TWP are found in the micrometer range (1-1000 µm). The definition of MP in (2.1) included synthetic rubber materials ,mainly SBR, as a MP material and it will be referred to as marker for MP emissions from transportation sector along this research.

2.3.1.3. *Building and construction*

Plastic materials revolutionized the sector of building and construction due to their wide range of applications and cost advantages. For instance, they are deployed intensively in plumbing, electrical and insulation works as pipes and sheets. Plastic Europe (Plastics Europe 2021) estimates that about 10 million tons of plastics, mainly Polyolefins and PVC, are consumed by building and construction sector in Europe. Which makes this sector with 20 % share the second largest customer for plastics after packaging.

MP emissions are expected from buildings both during the construction and demolition phases, as well as along the life time of the structures (ISO 2020). Fitting and installation works of piping and insulation materials are responsible for the release of considerable amounts of MP (Bertling et al. 2018). In addition, the abrasion of pre-installed plastic materials, and probably more vulnerable ones due to aging, during demolition works is likewise a source of secondary MP. To the author's best understanding, there are currently no available methods for quantifying emissions originating from this source.

2.3.1.4. *Synthetic textiles*

The boom in the production of synthetic textiles was a result of advancements in the polymer industry. At a certain point in the 1960s, the cost of manufacturing synthetic fibers dropped heavily and made synthetic textiles economically competitive against natural counterparts. The global production of synthetic fibers increased since then to reach an annual high of 76.5 million tons in 2019 (≈ 62 % of all fibers in market), of which 82 % is the share of polyesters (Fernández 2021; EFG Ltd 2021). The popularity of synthetic fibers is linked largely to its low price and wide range of applications they are suitable for.

Synthetic fibers from textiles are released intensively in indoor environments (Dris et al. 2017) through washing, drying and utilizing synthetic fabrics in clothes and carpets (Periyasamy and Tehrani-Bagha 2022). Waterborne MP from synthetic textiles is released during washing cycles in households and industrial laundries. The amount of released MP (i.e., fibers) depend on parameters such as detergent type, pH of water and washing temperature (Periyasamy and Tehrani-Bagha 2022). According to Šaravanja et al. (2022), PET and PA represent 60 % of all global fabrics fibers. In addition, PET is the most detected synthetic microfiber (Gaylarde et al. 2021) with a size distribution within 100-800 µm, according to laboratory using different washing detergents and temperatures (Hernandez et al. 2017). Hann et al. (2018) reported in a study for the European Commission that 18,430 to 46,175 tons of textile fibers are released annually during different washing practices in Europe.

Under the umbrella of the research project RUSEKU, where most of this research took place, a research package focused on the MP release from synthetic fabrics. The team from HTW[5] Berlin tested a bundle of shirts and t-shirts (4 kg) made from PET and PA respectively, by conducting a consecutive 30 washing rounds using standard washing detergent (IEC-60456-reference detergent A) and a standard dose (67.8 g dry powder) (DIN EN 60456:2017-05). The results showed that MP was at highest level in early washing cycles (169 ppm per shirt at cycle 1) and the release decreased gradually afterwards (11 ppm per shirt at cycle 30). In addition, PET was dominant in all cycles with a fraction size ranging from 1 to 400 µm. (Braun and Altmann 2022)

2.3.1.5. Synthetic surfaces

Synthetic surfaces are utility surfaces made from polymeric materials that substitute natural ones. Examples of these surfaces are sport fields (i.e., artificial grass and infill materials), children's playgrounds and roof tops. It is estimated that in Europe alone a total area of 112 million m^2 of turf pitches are installed in European sport fields (e.g., football, rugby, and tennis) (KIMO International

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[5] University of Applied Sciences for Engineering and Economics, Berlin

2022). There are to date little field investigations on the actual release amounts of MP from sport pitches. Most estimations are backed by deployment rates in sport arenas provided by national and international sports associations such as FIFA and DFB of Germany (Hann et al. 2018). Hann et al. (2018) estimated in their report mentioned earlier in (2.3.1.5) that around 18,000 to 72,000 tons of MP are released in Europe from sport pitches alone, mainly SBR rubber. The European Chemicals Agency (ECHA) (2021, as cited in (Zuccaro et al. 2022) has gone for a smaller number of 16,000 tons annually. Bertling et al. (2018) projected a specific emission rate of 131 g/(ca.a) from football, hockey and horse-riding fields, as well as from domestic playgrounds.

The German Football Association (DFB 2022) recommended in a leaflet addressing football clubs in Germany a ten-step action plan to help minimize MP emissions from football pitches. The action plan includes measures during the design of the pitch (e.g., installing filters in stormwater gullies and grates at the entrance) and during maintenance works. Figure 2-8 shows displaced SBR infills after a snow melt event in Germany.

Figure 2-8 SBR particles are released from football fields after snow melt or storms (DFB 2022)

2.3.2. Transport pathways of MP in Urban Drainage Systems (UDSs)

Alongside the **source** itself (indoor or outdoor) of waterborne MP, the **layout** of the UDS (combined or separate) and **weather conditions** (dry or wet) play a significant role in determining the transport pathway they might take on their way to receiving waters. Figure 2-5 in 2.3 showed different possibilities for MP to turn into waterborne one. From that point on, the layout of the UDS decides whether waterborne MP from indoor sources is transported separately as dry weather flow in sewage canals regardless of weather conditions (separate UDS) or combined with outdoor sources in a under wet weather conditions (combined UDS). The following section describes the characteristics of dry and wet weather flows within the two mentioned layouts of a drainage system.

2.3.2.1. Dry weather flow

Dry weather flow is defined as the blend of **domestic**, **commercial** and **industrial** (e.g., food industry) wastewater discharges during dry weather, including **infiltration** water from groundwater table and wrongfully discharged **inflow** from urban surfaces (rain and non-rain related) (McHhee 1991). The German term *"Fremdwasser"* translates into *extraneous water and* combines both infiltration and inflow waters (DWA 2012). Domestic wastewater comprises all liquid discharges from households, including black (feces, urine and flushing water) and greywater (kitchen and toilet sinks, showers and bathtubs, and washing machine discharge) (DWA 2015).

Besides the unknown commercial and industrial MP inputs, the split stream greywater is probably the most interesting pathway for indoor MP during dry weather conditions. Greywater is the carrying medium for residuals of hygiene products and synthetic textiles. Detailed information about the split steam greywater is given in the coming sub-section.

Greywater

Greywater is categorized into light; showers, tubs, and domestic washing machines (Friedler and Hadari 2006) and dark greywater; laundry facilities, dishwashers and kitchen sinks (Birks and Hills 2007) as cited in (Ghaitidak and Yadav 2013).

With a daily yield of about 60 L in water-saving households (Sartorius 2007) or 75 % of the total wastewater yield in normal households (Oteng-Peprah et al. 2018) and low pollutant loads, greywater has a high reuse potential in many blue-green construction concepts. However, the quantities and qualities of greywater streams may vary heavily along different locations depending on the decentralization scheme and other local factors, such as lifestyle, abundance of water and water use patterns (Oteng-Peprah et al. 2018). In terms of transporting MP, greywater is a confirmed transport medium for MP from synthetic textiles and domestic hygiene products (Hernandez et al. 2017; Leslie 2015).

2.3.2.2. Wet weather flow

Wet weather flow is the conveyed liquid discharge flowing in sewer systems during wet weather conditions. In separate UDSs, the stormwater canal conveys urban runoff and infiltration water only. While in combined UDSs surface runoff is added to the dry weather flow already flowing in combined sewer. However, stormwater runoff represents the overwhelming proportion during runoff events (> 10 folds). The amount of wet weather flow from a catchment area depends, among others, on precipitation intensity, evapotranspiration potential, topography, infiltration potential and depressions in the area (McHhee 1991; Chin 2006).

Stormwater runoff, the largest portion of wet weather flow, is the prime medium when it comes to conveying outdoor MP into UDS. As shown in (2.3), considerable amounts of MP are probably released through littering and transportation activities, and from synthetic surfaces.

2.4. Sampling of wastewater and stormwater runoff

Sampling of wastewater and stormwater runoff is conducted to monitor a physical, biological, or chemical parameter in the medium, to determine its concentration, load or release pattern in a temporal or spatial context (Grupe and Selent 2018; Shelley 1977). According to the international norm on water quality (DIN EN ISO 5667-1), sampling strategies or programs should encompass and develop the following elements:

- Time of sampling during a day, a week, or a year.
- Duration
- Volume
- Frequency during the monitoring campaign and number of samples
- Sampling locations
- Equipment and methods.
- Quality assurance concept for the selected sampling method; including conservation precautions during transport and preparation in situ and in the laboratory.

In addition, the mentioned elements should be carefully documented in a clear manner using a standardized protocol that has been developed specifically for the sampling program.

Temporal variations in the occurrence of the monitored parameter determine the choice of sampling **time** in a day or a week. For instance, a parameter that experiences minimum to no concentration change during the day could be sampled at any hour indifferently. Likewise, a parameter with a stable daily release pattern could be sampled once a week only (e.g., using a 24h composite sample).

The **duration** of sampling is set according to the purpose of sampling. Sampling programs aiming at investigating the concentrations and loads at peak times tend to be short and concentrated, while others who examine the average concentrations or loads over longer periods are usually longer with fewer samples. In addition, the durability of the sample plays a role in choosing the right duration before collection for analysis. (Grupe and Selent 2018)

Sample **volume** is set according to multiple factors that compete among each other. High detection limits and low original concentrations of the monitored parameter drive the sample volume to upper limits, while long preparation times, for instance, force the planners to choose a smaller sample volume. Spatial and temporal representativity, equipment limitations, sample durability and flow fluctuations are other factors to be considered while planning a monitoring strategy.

Sampling **frequency** is influenced largely by the purpose of monitoring a particular parameter. Legal requirements on national or international levels are often the decisive factor to determine sampling frequency of a parameter listed as a priority substance (e.g., monitoring of Phosphorus (P) concentration emitted from WWTPs into critical receiving water). In Europe, the national guidelines under the umbrella of the framework 91/271/EWG (1993) determine the minimum monitoring frequency of wastewater parameters from direct disposal points.

The suitable sampling frequency of a certain parameter depends on the randomness of occurrence. Therefore, a statistical estimation is applied based on a pre-defined confidence interval (L), usually 10 % or 95% confidence level within a normal distribution or t-student distribution for n samples ≤ 30, and preliminary samplings (; Sullivan 2015). The preliminary samplings help to estimate a preliminary standard deviation of a sample (s), then a number of samples (n) is derived. Equations 1 to 3 describe the statistical method to estimate the number of samples n. The frequency is then set according to the duration time of monitoring campaign (Eq. 4). Since L is widely set to be 10%, n depends solely on s and the number of samples (Walpole et al. 2007)

$$s = \sqrt{\frac{\sum_{i=1}^{n}[x_i - x]^2}{n-1}} = \sqrt{\frac{1}{n-1}\left[\sum_{i=1}^{n} x_i^2 - \frac{1}{n}\left(\sum_{i=1}^{n} x_i\right)^2\right]} \tag{1}$$

$$k = 1.96 \tag{2}$$

$$L = \frac{2k\sigma}{\sqrt{n}} \tag{3}$$

$$F = {}^{n}/_{T} \tag{4}$$

Where:

s	is the standard deviation of samples
xi	parameter value of a sample
x	arithmetic average
k	statistical distribution constant, 1.96 for t-student distribution
σ	is the standard deviation of the population
L	is the confidence interval and
n	Number of samples needed
F	sampling frequency
T	duration of the monitoring campaign

The search for sampling **locations** begins by understanding the sources of the environmental pollutant and defining, accordingly, areas of interests and possible hot spots. Then preliminary screening is conducted to test the relevance and spatial representativity of the *"hot spots" (Grupe and Selent 2018).*

At this point of delineating the strategy, sufficient input is collected, and the choice of **equipment** is clearer. In addition to sample volume, duration and frequency, the equipment is expected not to cause any alteration to the tested parameter. Certain parameters are sensitive to light or temperature, others face the risk of contamination by the building parts of the equipment. The preference of manual or automatic sampling is set at this stage as well considering, among other factors, the location, flow regime and sample sensitivity.

The sampling of wastewater media is a sensitive process that is prone to multiple sources for errors and misinterpretations. Hence, **quality assurance** measures are essential pillars of any effective sampling strategy. The norm (DIN EN ISO 5667-14) gives a comprehensive approach for quality assurance during planning and conducting the sampling campaign (e.g., handling, preservation, equipment checkups, transport and preservation).

2.4.1. Sampling and monitoring of Total Solids (TS)

The goal of sampling for TS is the investigation of the mass distribution (horizontal or vertical) of non-soluble organic and inorganic particles in water media, as well as the determination of physical (e.g., PSD) and chemical composition of these particles. TS in water media are the sum of settleable, floating and suspended solids detected (DIN 38409-2 1987). The monitoring of TS normally requires the utilization of active sampling methods, typically using pumps and designated containers, followed by a solid-liquid separation process (i.e., filtration, sieving) and concluded by analysis step. In addition, the combination of sampling and solid-liquid separation is possible using mobile centrifuges (Albertson and Guidi 1969; Sørensen and Møller 2006). Due to high organic contents, the efficiency of solid-liquid separation and the effort required are challenging aspects when monitoring TS in wastewater media. Microscopic imaging shows that small particles are subject to misallocation during solid-liquid separation procedures (Abusafia 2017).

The German norm DIN 38 409 (1987) and the American EPA[6] method 160.2 (Keith 1996) both promote the filtration of TS samples as soon as possible to assure representative results from the samples. Table 2-4 describes the steps and the specifications of the apparatuses needed to determine the mass and concentrations [mg/L] of solids according to DIN 38 409 and EPA method 160.2.

Table 2-4 Comparison between the requirements of TS measurement in DIN 38 409 and EPA method 160.2

Step	Apparatus	DIN 38 409	EPA method 160.2
Filtration	• paper filtration • filter support	⌀ 55-70 mm (0.45 μm) according to filter size	(0.7, 1 or 1.5) 40-60 μm
Drying	• vacuum flask/pump • Drying oven • thermometer • desiccator	1-2 L flask 103-107° C For drying oven drying agent (e.g., silica gel)	- 103-105° C - no specifications
Weighing	• analytical scale	-	0.1 mg accuracy

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[6] The Environmental Protection Agency (EPA) of the United States

Based on the quantifications according to previous methods and using a sieve stack instead of paper filters, particle size distributions can be delineated by measuring the mass concentrations in the different size fractions. Chemical compositions analyses are then performed on the dried material harvested from paper filters or the sieves.

In addition, as part of the effort within the research project RUSEKU to develop new sampling devices and strategies, a new sedimentation box (SB) was developed by Umwelt-Geräte-Technik GmbH (UGT, Müncheberg) in cooperation with the German Environment Agency (UBA, Berlin) to sample weakly loaded water streams, such as surface waters and effluent of WWTP, on the long run.

2.4.2. Sampling of MP in UDS

The beginning of the last decade witnessed a rapid rise in the number of research articles that were trying to answer many questions regarding MP pollution in the environment. Researchers from wide range of research fields joined on board (refer to 1.2) utilizing, not surprisingly, their scientific background and forcing the point of view of their research disciple on the field of MP research. Marine biologists, toxicologists, civil and environmental engineers, and chemists worked independently or in hybrid teams in order to set definitions and standardized strategies for MP monitoring. Figure 2-9 depicts the increase of MP research articles on the scientific search engine Science-direct by inserting the keywords *microplastic* and *sampling* (2011-2022). However, the number of articles drops massively to less than 10 % when adding the keywords *urban* and *drainage.*

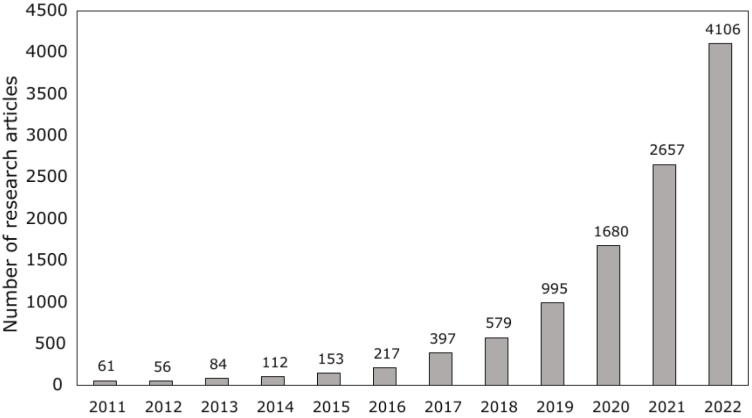

Figure 2-9 Number of research articles with the keywords "Microplastic" and "sampling" retrieved on the search engine sciencedirect.com (2011-2022) as of November 22nd, 2022

The lack of standardized sampling and detection methods (2.5) made the comparison of the results rather difficult. Furthermore, the lack of a clear definition that clearly outlines the size range and the exact chemical compositions of MP lowered the chances, even more, for a wide-range understanding of the spatial and temporal distributions of MP.

Since 2014, the vast majority of research projects on MP from UDS focused on sampling WWTP streams to evaluate the retention capacity and emissions into receiving waters. Table 2-5 gives a review on monitoring strategies of selected research articles on MP from WWTPs. The number of samples collected in each research work varied depending on the selected detection method or the finest mesh size in use for the analysis. Samples with low volume are normally taken manually as grab samples (Cabernard et al. 2016; Leslie et al. 2017), while automatic sampling methods (e.g., online pumping into a sieve stack, automatic samplers, mobile centrifuges) were deployed to collect composite samples with higher volumes from dozens of litters to hundreds of cubic meters (Mintenig et al. 2017; Hildebrandt et al. 2019; Carr and Thompson 2020; Wolff et al. 2021). Samples from the lightly-loaded effluent streams allowed both using fine sieves for the analysis and a larger volume (Murphy et al. 2016; Uurasjärvi et al. 2020; Carr et al. 2016; Mason et al. 2016; João P. G. L. Frias et al. 2018; Mintenig et al. 2017). The requirements of the different detection methods and their effect on the choice of sampling strategy are discussed in the next sub-section (2.5). In the study by **Carr et al. (2016)**, the emissions of MPs from seven WWTPs in California were investigated. Composite samples of treated wastewater were taken from the effluent canals and were subsequently subjected to filtration through a cascade of filters with the smallest mesh size set at 40 μm. The filtered materials were then concentrated using a lab centrifuge to maximize the quantity of material available for analysis using Raman Micro-spectroscopy. Notably, this investigation provided only counts of MPs per liter and lacked a comprehensive assessment of the mass balance for MP pollutant dispersion or emissions into the environment, making it difficult to compare with other studies.

Murphy et al. (2016) investigated the removal efficiency of a large WWTP serving 650,000 population equivalents (p.e.[7]). Water and solid samples (grease/grit) were collected at four treatment stages: Influent WWTP, effluent grit/grease chamber, Effluent primary settling tank, and effluent secondary settling tanks. The results indicated that, on average, 16 MP particles/L entered the WWTP, with only 0.25 MP particles/L exiting, resulting in a removal efficiency of 98.4%. The grit/grease chamber played a key role, removing 44% of MP particles, which were predominantly larger in the solid phase. However, the study's use of a 65 μm sieve size may have introduced bias in the size and shape of the particles in the samples. The counting method, coupled with FTIR testing, had limitations when quantifying MPs in complex matrices. Importantly, the study focused solely on MP counts for comparison, offering no data on MP densities or environmental emissions.

Mintenig et al. (2017) examined the presence of MP in the effluents of 12 WWTPs. A plastic-preserving enzymatic-oxidative procedure was applied, followed by density separation using a zinc chloride solution for sample purification. MP of sizes as small as 10 μm were identified using attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FT-IR) and focal plane array (FPA)-based transmission micro-FT-IR imaging. The predominant polymer type in both size categories was polyethylene (PE). The estimated quantities of MP particles and fibers released by the WWTPs annually ranged from 9 x 10^^{7} to 4 x 10^^{9}. Notably, one tertiary WWTP featured an additional post-filtration system, which reduced the total MP discharge by 97%. Moreover, an examination of sewage sludge from six WWTPs revealed the presence of MP, primarily PE. These findings suggest that WWTPs can be both sources and sinks of MP, playing a significant role in environmental MP pollution. While this

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[7] The abbreviation PE is common for population equivalents. However, the alternative abbreviation p.e. was adopted in this work to avoid confusion with PE for polyethylene.

study applied much sophisticated preparation, detection and quantification methods leading to lower uncertainty levels, the comparability of this study in form of mass balances of MP to other studies is yet limited.

Table 2-5 A review of different monitoring strategies from selected research works on MP from urban areas

Study	**Scope**					**Sieve(s)/Filter(s) pore size(s)**
	[n]	medium	Sample volume	Sampling method	Detection method	[μm]
(Magnusson and Norén 2014)	4	Effluent WWTP	2- 1000 L	Grab samples	Microscopic count	>300
(Baltic Marine 2014)	3	Effluent WWTP	50 L	Grab samples	Microscopic count	>20
(Carr et al. 2016)	2 x 7	Effluent WWTP	200 m^3	Composite samples, online filtration	Raman microspectroscopy	>45
(Mason et al. 2016)	17	Effluent WWTP	0.5 - 21 m^3	Composite samples, pump, online filtration	Microscopic count	>125
(Murphy et al. 2016)	14	Effluent WWTP	30 - 50 L	Grab samples	FTIR	65
(Sutton et al. 2016)	8	Effluent WWTP	-	2h composite samples	Microscopic count	125, 355
(Cabernard et al. 2016)	91	Various WWTP	2 - 5 L	Grab samples	Microscopic count	8
(Mintenig et al. 2017)	13	Effluent WWTP	1 m^3	Composite samples, pump, online filtration	ATR_FTIR	10, 500

(Ziajahromi et al. 2017)	6	Various treatment stages	3 - 200 L	1h composite samples	FTIR	25,100, 19, 500
(Leslie et al. 2017)	36	Influent/effluent WWTP	2 L	Grabs samples	Microscopic count, FTIR	10, 300, 5000
(Conley et al. 2019)	18	Influent/effluent WWTP	0.5 L Influent, 1.5-15.5 L Effluent	Grab samples	Microscopic count	43, 60, 178, >418
(Uurasjärvi et al. 2020)	168	Lake water	6 - 468 L	Composite samples, online filtration	FTIR	20, 100, 300, 333
(Wolff et al. 2021)	3	Effluent WWTP	1 - 2500 L	Composite samples	Raman microspectroscopy	10
(Bayo et al. 2021)	28	Influent/effluent WWTP	2 - 6 L	Grab samples	FTIR	> 0.45
(Picó et al. 2021)	9	Influent/Effluent WWTP	2.5 L	Grab samples	Microscopic count	50, 100, 250, 500, 1000, 5000

2.5. Detection methods for MP

Looking at the chronology of MP research field, the detection of MP particles in environmental samples (i.e., water, air, soil) has evolved immensely since early research works in the 2000s. Since then, a large number of detection procedures and methodologies based on varying working principals, tinged with different accuracies and detection limits (Rochman 2018). The heterogeneity and lack of standardization of the available detection methods made the comparison of the results and conclusions highly challenging (Löder and Gerdts 2015). While no single method is capable of capturing all physical and chemical characteristics at once, combining two or more methods is a possible approach to put to light a wider-range of MP characteristics (Primpke et al. 2020). The available detection methods are classified into three major groups: optical, spectroscopic, and thermal methods.

The first analytical methods included optical identification of plastic-like small objects in environmental samples according to color, shape, size, consistency and fluorescence behavior (Norén 2007). The latter method was carried out using either naked eye with a low identification limit of 1 mm (Zhang et al. 2015) or using a light microscope with a detection limit of 100 µm (Barrows et al. 2017), or 3 µm applying a dye staining method (Wiggin and Holland 2019). However, optical methods are able only to identify the number and size of “possible” plastic particles without giving information on the chemical composition or actual mass of these particles. Hence, a much-advanced technique was needed to determine polymer types and, if possible, the physical characteristics and mass of MP. Table 2-6 gives a summary of most frequently applied detection methods for MP.

In comparison to optical methods, spectroscopic methods possess the ability to confirm the occurrence of MP in environmental samples based on a uniqe reflection or absorption pattern of a light beam when focused on the sample (Braun et al. 2020a). The Fourier-Transform Infrared (**FTIR**) spectroscopy is a well established analtical method in the fields of chemistry and material science. Being a non-destructive method, tested samples have the chance to undergo other analytical methods and, thus, the results of FTIR analysis can be compared or adjusted accordingly (Litescu 2012). The basic working principal of FTIR method is the application of middle-frequency infrared radiation on a sample to stimulate the covalent bonds of an unkown material, and force these bonds into vibration. The spectrum yielded from the difference in energy due to absorbtion within sample is then compared to a reference spectrum without a sample to form a uniqe fingerprint-like spectrum of the studied matter (Primpke et al. 2020; Braun et al. 2020a). The collected spectra is compared with computer spectra database to identify the chemical composition of sample (e.g., polymer type) (Csoka and Djokovic 2011; Litescu 2012). For MP particles larger than 500 µm, the Attinuated Total Reflection FTIR (ATR-FTIR) method is usually applied without sample pretretment. Samples with MP particles smaller than 500 µm require a chemical digestion pre-treatment, to be later analysed using the µFTIR method (Bergmann et al. 2017). In addition, integrating the Focal Plane Array (FPA) method allows for a larger area-based detection, compared to point-based one (Löder and Gerdts 2015). Obbard (2006) and Corcoran et al. (2009) were the first scholars to apply the FTIR method to study MP pollution in an environmental sample, followed by Browne et al. (2010) and Frias et al. (2010). All previous studies exmined sand samples taken from shorelines of Singapore, United Kingdom, Portugal and the island of Hawaii.

Besides FTIR, the second most deployed spectroscopic method is the Raman Microspectroscopy (**RM**). In comparison to FTIR methods, RM detection limit for MP is lower, so that particles with a size of 300 nm can still be detected. RM is also a non-destructive detection method and uses a monochromatic laser source to stimulate chemical bonds and cause molecular vibrations. Due to energy loss, the frequency of irradiated laser beam shifts following a unique fingerprint of the studied material. The latter mechanisim allows for the identification of type, PSD, number and form of the MP particles in sample. A major drawback of RM method is its sensibility to noise from high florescente particles in sample (Löder and Gerdts 2015; Primpke et al. 2020; Pittroff et al. 2017).

Optical and spectroscopic detection provide valuble information on MP occurrence. However, a dircet quantification of the mass of MP particles is rather dificult. Thermal extraction methods with subsequent gas chromatography / mass spectroscopy are able to offer this significant piece of information about MP occurrence. The identification of MP masses in different environmental compartments and streams allows in return for generating pollutant transport models explains MP in a wider-scope. Two thermal extraction methods in particular are modified and tested to detect polymers and additives simaltanously, online pyrolysis-GC/MS (py-GC/MS) and TED-GC/MS. Both methods involve the application of heat on the sample to gradually release the pyrolysis products (pyrograms), which are then harvested, separeted and quantified using a GC/MS equipment (Primpke et al.

2020). In online py-GC/MS method, samples are heated inside a pyrolisis chamber with the presenece of an inert gas (e.g., Helium) to high tempretaures (500-700° C) and pyrograms are transported with the gas stream to the GC/MS unit (Rødland et al. 2021; Fischer and Scholz-Böttcher 2017). In TED-GC/MS method, samples are heated in a nitrogen environment to ca. 600° C and then a thermo adsorbtion of the pyrograms occurs in a thermo adsorption-desorption unit (Eisentraut et al. 2018; Duemichen et al. 2019). The detection and quantification is carried out by the connected GC/MS unit. While samples must be prepared before the injection in a py-GC/MS system, samples anlysed using TED-GC/MS are analysed without any prior preparation for samples larger than 20 mg. In addition, TED-GC/MS is capable of analysing large sample masses compared to py-GC/MS, which is limited to the the size of pyrolysis champer. Although thermal detection methods are destructive ones, the produced GC spectra can be analysed retroactively in case of an update of the detection library.

Other methods for MP detection are available in literature. Nevertheless, these methods will not be described in this chapter, as they hold limited relevance to the work. For more information I highly recommend the review works from Hidalgo-Ruz et al. (2012), Löder and Gerdts (2015) and Primke et al. (2020). For specific information on the thermal method TED-GC/MS, I recommend the review of the novel works from Eisentraut et al. (2018), Duemichen et al. (2019) and Goedecke et al. (2022). A detailed description of the application of TED-GC/MS method in this work will be included in detail in (3.1.6).

Table 2-6 Review of the detection methods for MP marking the attributed effort and limitations (Primpke et al. 2020; Braun et al. 2018)

	Method	**Sample preparation**	**Detection time**	**LOD**		**Limitations**
				Size	**Mass**	
			[min]	**[µm]**	**[µg]**	
Optical methods	Light optical microscopy	Chemical extraction	420	>100[1]	n/a	no chemical identification bias to particular MP colors researcher bias
	Dye staining	Chemical digestion (e.g., H_2O_2)	245	>3	n/a	Organic residuals can adsorb dye No mass quantification
Spectroscopy	FT-IR (µ, FPA, ATR)	Chemical digestion (e.g., H_2O_2)	60 - 120	>10	n/a	No measurements for particles <10 µm[2] Measurement noise due to water content No mass measurements
	Raman Microspectroscopy (RM)	Extraction/digestion of OM	60 - 580	>1 (0.3)	n/a	No mass measurements Partial destruction of particles due to laser beam Noise in spectra due to liquids, bio-films, and additives[3] Highly time consuming

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[1] Barrows et al. 2017.

[2] Cabernard et al. 2018.

[3] Lenz et al. 2015.

Thermo- GC-MS	Online py-GC-MS	Extraction/digestion of OM	72 - 216	-	0.3 (PP), 0.5 (PA6), 0.01 (PS)	Only a fraction of a sample can be analyzed. No direct analysis for environmental samples No information on PSD, shape, color, brightness, nor age Destructive method
	TED-GC-MS	No measures for samples >20mg	120[1]	-	0.3 (PP), 0.5 (PA6), 0.01 (PS) or 100 mg with MP 0.5-1 wt%	Pretreatment of samples <20 mg No information on PSD, shape, color, brightness, nor age Destructive method
Other methods	Scanning Electron Microscopy (SEM)	No measures	-	> 0.1	n/a	High investment costs Limited quantification capabilities
	Liquid chromatography UV[2]	No preparation for <50g samples	-	-	LOD = 31, LOQ = 121 (for PET)	High LOD and LOQ values No information on physical features

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[1] Altmann et al. 2019.

[2] Müller et al. 2020.

2.6. Interim conclusion

Microplastics cover a wide range of types, each with varying physical and chemical properties that influence their transport reach and toxicity. Presently, there is no standardized definition for MP in the context of urban drainage systems, resulting in a lack of comparability among studies. Meanwhile, a predominant focus of research pertains to particle sizes ranging from 1 to 5000 µm. Achieving a comprehensive understanding necessitates mass-based analyses to document input pathways and evaluate their significance. Nevertheless, a substantial proportion of earlier studies predominantly employ particle-count analyses. It is pertinent to underscore the specific advantages and disadvantages associated with such approaches when deemed necessary.

The sources of microplastics in urban environments are diverse, but several key factors stand out, including littering, transportation, synthetic surfaces, and textiles, due to the extensive exposure and contact with vector wastewater streams, which serve as pathways for the transport of MP. To better understand the sources and quantities of microplastics, it is important to study their transport pathways under different weather conditions, specifically dry and wet weather. This approach can provide valuable insights into the dynamics of MP pollution and help identify effective mitigation strategies. Very few studies of MP have captured MP from wastewater streams away from WWTP. For Instance, representative monitoring strategies for stormwater runoff, where autonomic sampling aggregates are utilized, are lacking. Thus, wholistic monitoring approaches are yet to be developed.

While existing sampling methods for solid particles can serve as a starting point, further development of methodologies specifically tailored for MP monitoring is essential. Standardized sampling and detection methods are crucial for facilitating accurate comparisons of research results. The lack of such standardization has posed challenges in analyzing and interpreting data from different studies. The elaborate dynamics associated with sampling under wet weather conditions have frequently been overlooked in prior studies, highlighting the necessity for a more comprehensive and representative approach of this particular transport pathway. In addition, previous studies have dealt with MP as a collective parameter overlooking the different polymer constituents and the changing particle size distributions.

In addition, the role of additives in microplastics and their stability and desorption potential in the urban environment remains insufficiently studied. Further research is needed to investigate the impacts of additives and their potential contributions to the overall environmental burden of microplastics.

In summary, the study of MP in urban environments is a complex and multidisciplinary field that requires collaboration among researchers and the development of standardized methodologies. Addressing the challenges related to definitions, sampling, and detection methods is crucial for advancing our understanding of MP pollution and its potential consequences for the environment and human health.

2.7. Research gap

Despite the growing concern over MP pollution in water bodies, several critical research gaps exist in understanding the full extent and dynamics of this issue. This section highlights the key areas where further investigation is needed to track waterborne MP in urban areas:

- The WWTP bias: research predominantly focuses on monitoring MP concentrations within WWTP and quantifying emissions in the effluent. However, there is a lack of measurements outside of treatment plants, thus treating catchment areas as black boxes. This approach fails to capture the full picture of MP sources, pathways, and sinks within the catchment, hindering the development of effective mitigation strategies.
- Lack of information on MP emissions from stormwater runoff and direct discharge: There is a dearth of knowledge regarding MP emissions from stormwater runoff and direct discharge into receiving waters. Current studies overlook plausible emission rates from urban stormwater streams occurring outside the WWTP context. Understanding the magnitude and composition of MP in these sources is crucial for implementing targeted pollution control measures.
- The effect of new treatment aggregates in WWTPs: many WWTPs are being equipped with treatment aggregates that remove organic micropollutants. However, limited data are available on the efficiency of these novel aggregates in removing MP.
- Absence of standards for sampling, sample preparation, and detection processes: The absence of standardized protocols for sampling, sample preparation, and detection of MP hampers the comparability and reliability of research findings. The lack of consistent methodologies

makes it challenging to draw accurate conclusions and compare results across different studies. Developing standardized protocols is essential for advancing research in this field.

- Treating MP as a collective parameter: The current approach often treats MP as a collective parameter without differentiation between types, intermediate sizes, and possible sources. However, different types of MP have varying physicochemical properties, toxicity, and transport behaviors, leading to differential impacts on ecosystems. Neglecting this differentiation limits our understanding of the ecological risks associated with specific types and sizes of MP.
- Limited methods for extending information to larger catchments or other catchment areas: Most existing studies focus on specific catchment areas or individual WWTPs, limiting the generalizability of their findings to larger catchments or other urban areas. There is a lack of research exploring methods to scale up the findings from smaller-scale studies and extend the understanding of MP dynamics to broader geographical contexts.
- Inadequate investigation into the fate of MP within the urban drainage system: The fate of MP within the complex urban drainage system, including its transport, retention, and transformation processes, remains poorly understood. Additionally, considering the paradigm shifts occurring in UDSs, such as green infrastructure implementation or retrofitting of existing systems. There is therefore a need to investigate how these changes may influence the fate and distribution of MP.
- Overlooking the role of additives in MP as trace elements utilizing chemical characteristics, such as solubility, and thus the easy of sampling.

Addressing these research gaps is crucial for developing effective management strategies to mitigate MP pollution. Future research should focus on expanding our knowledge beyond WWTP, developing standardized protocols, differentiating between MP types and sizes, scaling up findings, designing accurate models and investigating the fate of MP within evolving UDSs.

3 Materials and Methods

The materials and methods described in this chapter were applied and optimized at three essential stages during this work. The first stage (I) involved preliminary analyses on candidate wastewater streams in the studied catchment, the selection of sampling locations and designing the sampling parameters as part of a comprehensive monitoring strategy.

Stage II incorporated the actual implementation of preliminary monitoring strategy along two main sampling campaigns of dry and wet weather wastewater streams. The main sampling campaigns can be further divided into sub-groups according to sampling location involved.

Stage III dealt with the curation and analysis of sampling metadata (i.e., precipitation, flow, catchment characteristics), quantification methods of MP based on emissions extrapolation and derivation of specific emission values, and correlation tests of MP emissions with standard wastewater parameters and event characteristics. In addition, the methodology for conducting an uncertainty analysis of sampling and sampling results is described.

Table 3-1 Overview of sampling strategies and motivation of each sampling location

Location	Catchment / Source	Sample type	Sampling Volume [L]	Goal/Motivation
Influent of WWTP (L1)	City 210,000 [p.e.]	24h composite samples	25	MP characterization (particle size distribution (PSD), type, and concentrations). Quantifying of per population equivalent emission rate (g/p.e.*a). Removal efficiency of different MP
Effluent of WWTP (L2)	City 210,000 [p.e.]	4h composite samples	1000	
SRT in combined drainage system (L3)	Residential district 5000 [p.e.]	12h-composite sample	22-25	MP characterization (PSD, type, and concentrations) Comparison of per population equivalent

(dry weather)				emission rate ((g/(p.e.*a))) to one at WWTP with industrial influence Comparison between emissions during dry and wet weathers.
SRT in combined drainage system (L3) (wet weather)	Residential district 5000 [p.e.] and (67 ha)	Composite samples, LVS	1000	Designing and adjusting sampling strategy using Large Volume Samplers (LVS). MP characterization (PSD, type, and concentrations). Quantification of MP emissions from catchment area (g/(ha_b*a)) (ha_b: impervious area). Comparison between wet weather emissions of two catchment areas different in size and land use.
SRT in separate system (L4)	Residential district (17 ha)	Composite samples, LVS	1000	
Reinighof (GW) (L5.1)	Off-grid residential compound	Grab samples	10-22	MP characterization (PSD, type, and concentrations) in greywater. Quantifying of per population equivalent emission rate (g/p.e.*a).
L5.2 Birkenfeld Campus (GW)	Student dormitory	Composite 24h sample	20	

3.1. Development of monitoring strategies

3.1.1. Sampling goals

The first goal of sampling for waterborne MP was to **cover relevant wastewater streams** in UDS along their transport pathways and at sampling locations that allow for a meaningful interpretation of the results. In other words, a selected sampling location should represent a well-known catchment area, including size, land use, anthropogenic activity, drainage scheme and layout, and storage capacity of retention structures.

MP particles in environmental media occur in very low concentrations in the range of 10^{-6}-10^{-3} mg/L, and in different shapes and sizes. Moreover, the available detection methods, whether thermal or spectroscopic methods, have high detection limits and require concentrated samples in solid phase to deliver reliable results. For example, the thermal method TED-GC/MS has a low detection limit when used for detecting MP in dried sediment samples. Thus, sampling activities aimed at **harvesting and accumulating an adequate amount of MP** material for analysis.

Sampling procedures and materials were designed to **minimize contamination** of environmental samples from surrounding environments. As a general rule, only plastic-free materials were utilized during sampling, storage, and preparation steps. Stainless-steel and glass containers (1-1100 L) were used to collect and store raw samples at different project stages. Building parts of pumps and fittings that have been in contact with samples are made of stainless-steel. An exception for this rule was made for PVC building parts, since they are not part of analysis pool and do not affect the analysis results. In addition, the research team abstained from wearing textiles made from synthetic materials.

Since the development of monitoring strategies was a goal in this work, **testing and improving the materials** adopted for sampling were also a central topic during all research stages. Besides samples protocol, the research team used field and laboratory diaries to document all kinds of technical observations surrounding sampling, and the behavior of technical materials when confronted with different wastewater materials and volumes. The section (3.2), for example, includes observations on sieving behaviors of two sieve-cascade types, that were originally documented in the field diary book.

Finally, sampling was assigned the task of **tracking and quantifying the occurrence of MP** within specific size fractions. This new knowledge on amount, type and sizes of MP is designated for the study of pollutant fate scenarios, creating pollutant mass balances and models, and for guiding new avoidance policies in the near future.

3.1.2. Sampling locations

The sampling locations in this work were selected to provide plurality to the results. In other words, the dynamics of MP emissions within the UDS as a result of changing weather conditions (**dry** or **wet**), layout (**combined** or **separate**) and size of the catchment served were considered to capture possible variations and discuss the relevance of a specific variable on MP emissions. In addition, sampling locations covered potential "hotspots" such as greywater streams and combined wastewater discharges from an industrial area. Figure 3-1 shows a generic allocation of all sampling **L**ocations (**L1 - L6**) marked with yellow stars. Locations **L1** and **L2** were located at the WWTP Kaiserslautern in Kaiserslautern, location **L3** was the effluent canal of a SRT in combined system, **L4** in the influent canal of an STR in separate system and, **L5.1** and **L5.2** represented greywater streams. A detailed description of the sampling locations and the characteristic of their wastewater is provided in the following sections.

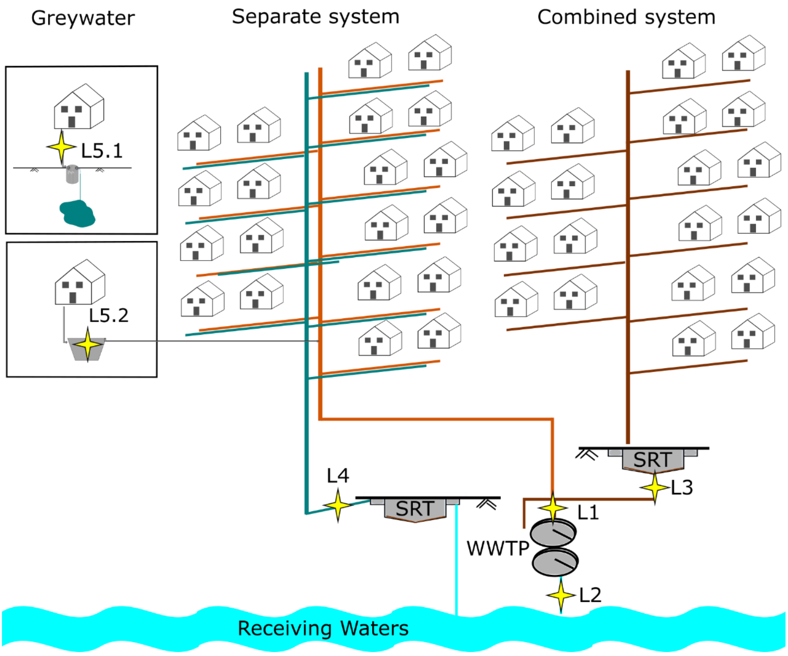

Figure 3-1 Generic illustration of all sampling locations in this work

3.1.2.1. Central municipal wastewater treatment plant of Kaiserslautern (L1 and L2)

The municipal WWTP of Kaiserslautern (49°27'33.786''N,7°44'33''E) has a nominal capacity of 210,000 population equivalents [p.e.] and treats domestic and industrial wastewater from the UDS of the city and other neighboring districts with a total served area of ca. 3500 ha. The treated wastewater flows through maturation ponds into the bordering river Lauter. Under dry weather conditions, considering the flow measurements of days with 0 mm total precipitation on the actual day and previous one, around 49,000 ± 7542 m³/d or 570 l/s (median = 47,210 m³/d) of wastewater volume reaches the WWTP. Figure 3-2 shows the daily flow variations of influent wastewater entering the WWTP during the period from January 2018 to December 2020. Figure 3-3 shows the daily variations of dry weather days only (n=126).

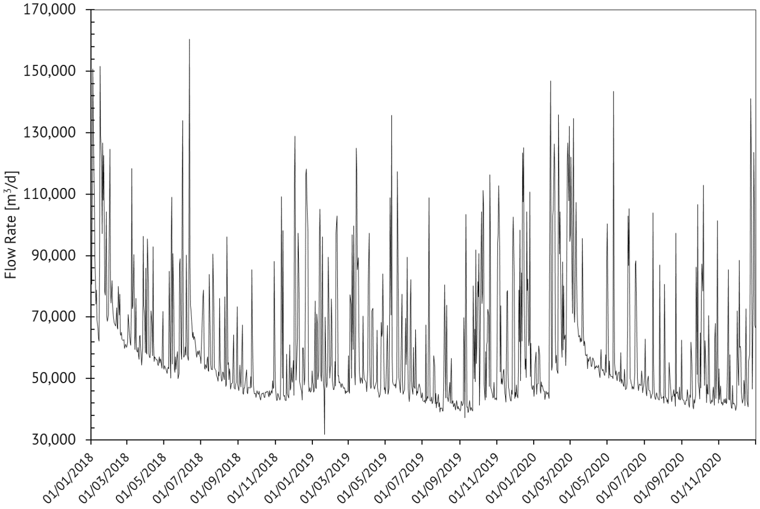

Figure 3-2 Daily flow in the influent of the WWTP Kaiserslautern (2018-2020) (Stadtentwässerung Kaiserslautern 2021), own representation

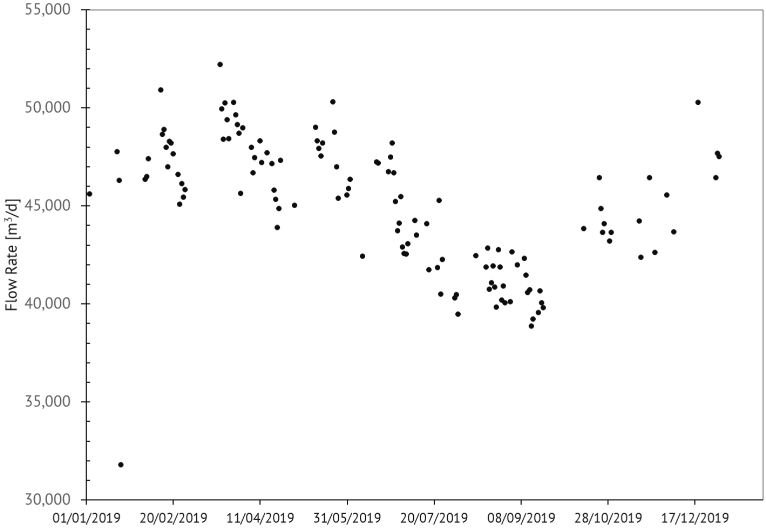

Figure 3-3 Daily flow in the influent of the WWTP Kaiserslautern of dry weather days, 0 mm precipitation at measurement day and previous day in 2019 (n=126) (2021), own representation

Around 80% of the drained area is served by a combined sewer system, while the rest, ca. 20%, is served by a separate one. The entire sewer system has a total length of about 520 km and consists mainly of brick or concrete sewerage (ca. 87 %[13]). Only 4% of the public sewer system is made of plastic materials; PVC 3.2%, High-density PE (PEHD) / PE 0.5%, and PP 0.1%. In contrast to the public network, domestic sewer pipes are made from plastic materials, usually PVC or PP.

Initial trials of an automatic sampler (ASP Station 2000, Endress+Hauser) in the influent canal of the WWTP to gain 24h-composite samples were unsuccessful due to repeated clogging of the main suction pipe by coarse impurities in wastewater. Consequently, further trials were conducted in the effluent channel of mechanical screening. This location was then selected to represent the influent of the WWTP, thanks to successful sampling trials. However, the flow regime after screens is less turbulent compared to the point upstream. Therefore, three grab samples were taken from three different water levels, 30 cm below surface, 30 cm above bed level and at a point in the middle of inflow

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[13] Based on length and not nominal diameter

channel to sand traps (h ≈ 2 m). The comparable settling velocities of the solid fractions 500, 100 and 50µm from the three water levels gave a green light for proceeding with sampling program at this location (L1) in the effluent of four screening units with 3mm Ø mesh size. Sampling at L1 enabled the investigation of dry weather MP emissions released from the large catchment area of the WWTP.

In addition to the sampling location L1, a second sampling location (L2) in the effluent canal of the secondary settling tanks (Figure 3-4) was selected to assess the removal efficiency of the WWTP in terms of MP types and size fractions.

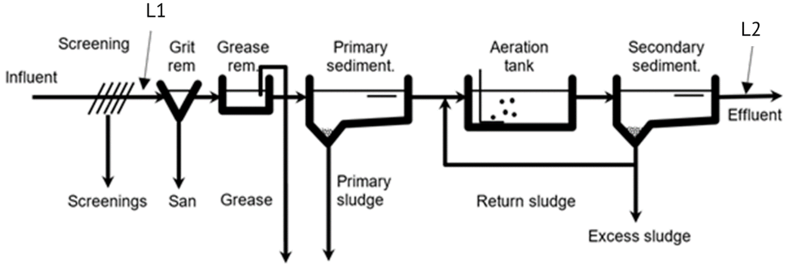

Figure 3-4 Sampling locations L1 and L2 shown in a simplified scheme of a WWTP mechanical, biological, and secondary treatment phases

3.1.2.2. Stormwater retention tank (SRT) in combined drainage system (L3)

The sampling at the treatment plant delivers general information about the MP emissions and polymer types from the served catchment area. However, for a catchment area of 3,500 ha, it is not possible to derive conclusions and estimations regarding the sources and release patterns of the many MP types that are detected. Other factors that contribute to this problem rather than the size of catchment area, are the presence of many retention structures in the combined sewer system and the release from commercial and industrial zones in the catchment. These many structures may act as sinks or release spots for MP that have been emitted earlier. In addition, high rates of base flow recorded at the outlet of the catchment area may heavily alter the estimations of specific MP emissions (per population equivalent/household). Therefore, a smaller catchment area in a combined sewer system at the edge of the drainage system was chosen to sample dry weather flow, and since the optimal location was the outflow of a large SRT, combined sewer flows during wet weather conditions (combined stormwater runoff) from the exact catchment area can be later sampled and the results compared with the ones during dry weather conditions.

The sampling location L3 is found in the effluent canal (DN 800) of a large SRT (14,000 m^3) (49°25'37.8"N 7°44'53.6"E) serving a sub-catchment area with combined drainage system (refer to Figure 3-5). The sub-catchment has a *total area* of 67.22 ha [A_T] and an *effective impervious area* of 34.8 ha [A_{EIA}] and is located in the farthest southwestern part of the catchment serving the WWTP Kaiserslautern.

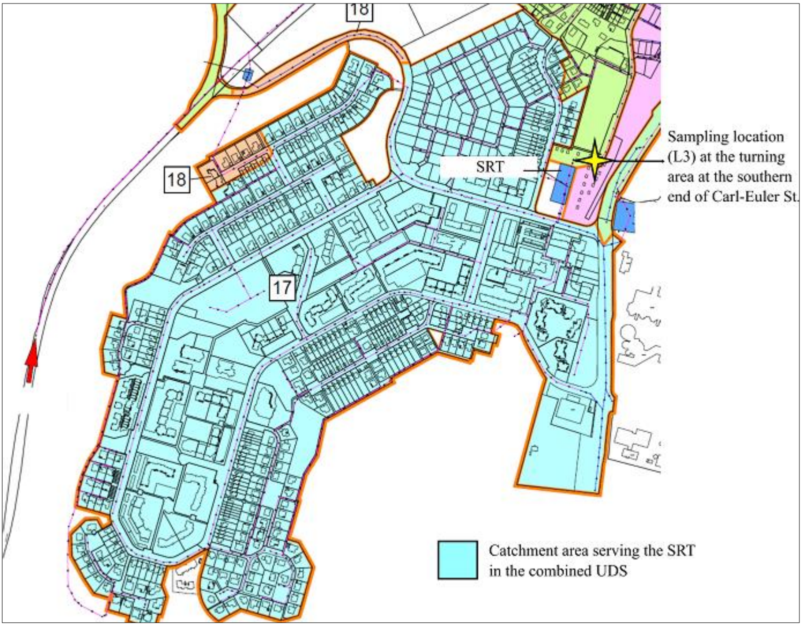

Figure 3-5 The catchment area serving the SRT in combined UDS (Stadtentwässerung Kaiserslautern 2021)

The sub-catchment area shown in Figure 3-5 is located at the edge of the UDS of Kaiserslautern, hence only combined discharges from the very sub-catchment were expected to be recorded at L3. Likewise, the base flow recorded at L3 is likely originating from the sub-catchment itself since the entire sub-catchment is scattered at the crown of a hill (Figure A 1 in appendix). In comparison to the entire catchment of the UDS, the small catchment is contained and easier to analyze in detail. For instance, the number of inhabitants (5000 p.e.), land use, traffic densities and base flow estimations are available. This in return allows more accurate interpretations of specific MP emissions and potential MP sources. The traffic densities on the two main streets Theodor-Heuss-Straße and

Trippstadter Straße were as high as 4200 (Lenz 2020) and 6300 vehicle/d (MWVLW-RLP 2022) respectively.

Under dry weather conditions, the SRT diverts the combined flow through a half-circle flume into the effluent channel. Thus, no retention of solids is expected over SRT floor. As soon as the water level in the flume rises as a result of a storm event, combined flow is spread gradually over the SRT floor and both retention of combined runoff and sedimentation of solids are likely to occur.

During the period from May to November 2019 and in coordination with the drainage authority of Kaiserslautern, a flow measurement campaign was conducted at L3 using a W.A.S UFO-Ex (Ultrasonic Flow Observer, Typ /S) at a measuring rate of 5 minutes. Based on this measurement campaign and adopting the definition of a dry weather day as the day with 0 mm precipitation following a day with the same condition, diurnal dry weather flow pattern from 68 eligible days during this period could be generated accompanied by water level and velocity profiles. (refer to Figure 3-6, Figure 3-7 and Figure A 17 in appendix 8.3). On average, around 711 ± 62 m^3/d of wastewater volume was recorded at L3 during dry weather days (n=68). Additionally, applying the nightly minimum concept suggested by DWA (2012), the base flow amounts for 1.29 L/s or 111 m^3/d.

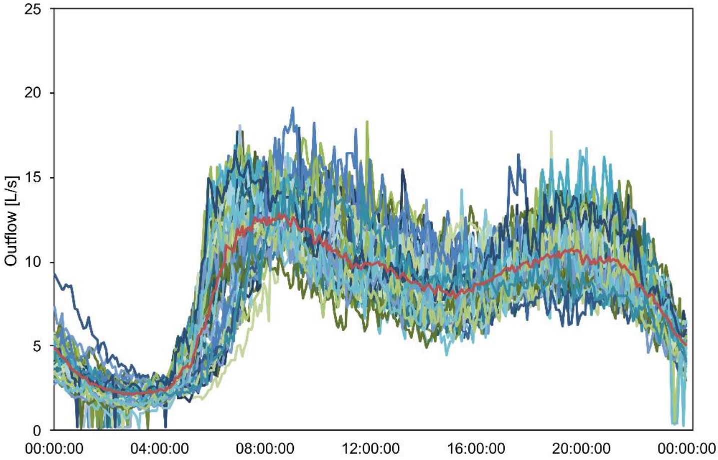

Figure 3-6 Diurnal dry weather flow pattern at the effluent canal of SRT in combined system (n=68), red line in the middle represents the average value

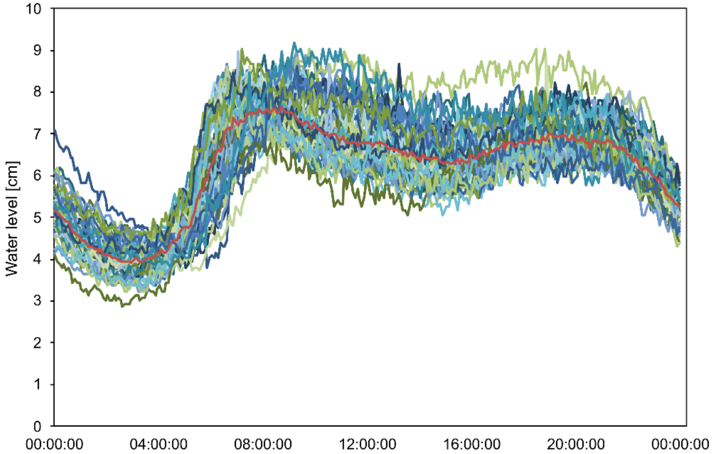

Figure 3-7 Diurnal water level pattern under dry weather conditions at the effluent canal of SRT in combined system (n=68), red line in the middle represents the average value

The mentioned flow measurement campaign also provided information on the generated runoff from the catchment and the catchment response to different precipitation heights and intensities. Figure 3-8 shows the daily combined flow from the catchment for all days from May to December 2019 and the precipitation heights recorded at the DWD weather station 2486 located about 450m away from the sampling location L3. The precipitation data from this weather station will be the foundation for the runoff analysis during the monitoring campaign under wet weather conditions in (3.3.2.3).

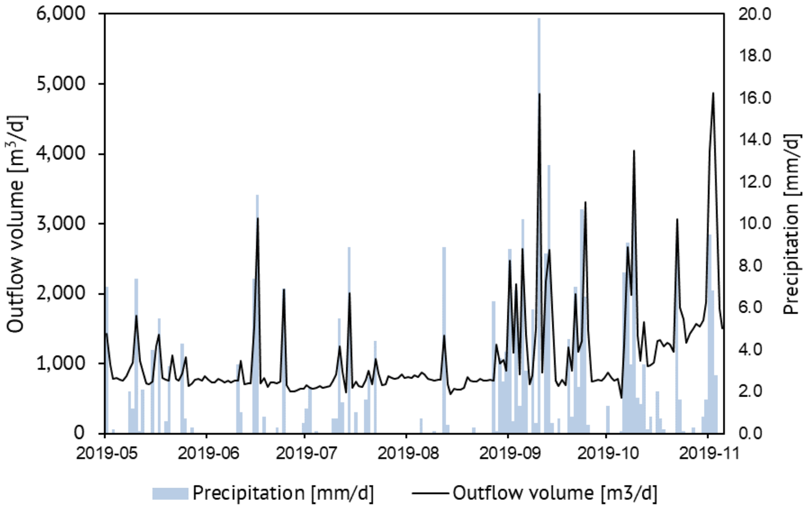

Figure 3-8 The diurnal effluent volumes at L3 for all days during the measurement campaign from May to December 2019 vs. precipitation data retrieved from the DWD weather station 2486 in Kaiserslautern (DWD 2022)

3.1.2.3. Stormwater Retention Tank (SRT) in separate drainage system (L4)

The sampling location L4 is located in the outlet point of a small catchment area with a separate drainage system in a residential district in southeast Kaiserslautern (Figure 3-9). The sampling and flow measurements activities took place in the influent canal (Ø 800 mm) of an SRT (4,700 m^3) (49°25'00.2"N 7°41'44.7"E), see detailed schematic drawing in appendix (Figure A 2). Since only stormwater runoff was expected at the location, a comparison between MP emissions from separate and combined system (L3) is achievable. The relatively small catchment has a total area of 16.93 ha [A_T] with an effective impervious area of 6.67 ha [A_{EIA}]. All public sewer conduits are made of reinforced concrete and have a total length of about 3.5 km. The traffic density in the area is not recorded, but very low traffic was observed during sampling activities. Information about the number of residents and private drains is not available. The slope profile of the longest flow path in the catchment is shown in appendix Figure A 3.

The STR at the sampling location is an underground structure with a fenced green roof on top. The walkable roof favors flexible housing methods of sampling equipment since traffic and pedestrians are not in direct contact with the structure. In addition, an adjacent municipal electrical enclosure is capable of supplying three-phase electrical power to a potential sampling plant.

Figure 3-9 A satellite image of the small catchment area in separate system showing the SRT and sampling location L4 (Google Earth 2019)

At the beginning of the research activities at L4, no historical flow data on precipitation records were available. However, the hydrological response of the catchment to various classes of precipitation events was needed to design a monitoring campaign in the future. Thus, flow meter sensors (refer to sampling concept in 3.3.2.1) were installed at a point 2000 mm away from the tip of the SRT inside the influent canal (DIN 800). The short flow measurement campaign from December 2019 to March 2020 gave an initial picture of the hydrological response of the catchment due to precipitation events with light (0.7 mm/h) to moderate (3.8 mm/h) intensity (Figure 3-10). In addition, the hydraulic response of the effluent canal was also recorded so that a maximum flow rate of 274 L/s was recorded as a response to the precipitation event with the highest intensity.

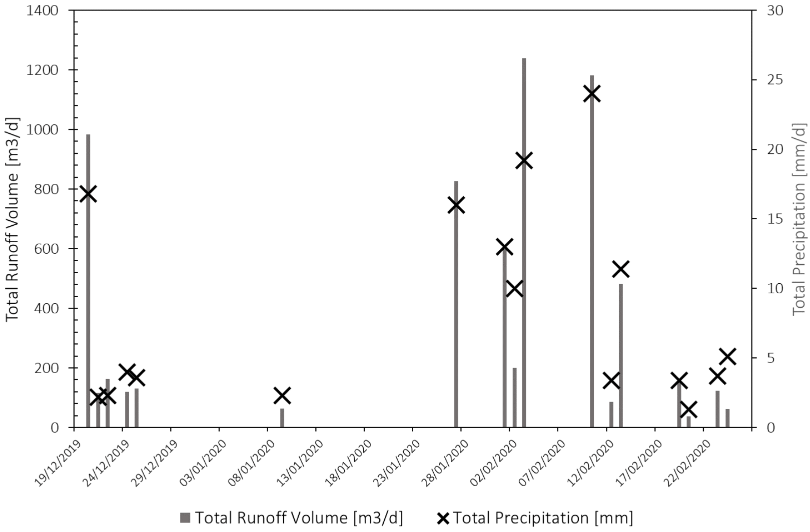

Figure 3-10 The hydrological response of the catchment area in separate system at L4 in terms of daily stormwater runoff compared to total precipitation of the same day (Precipitation data (wetterkontor.de 2022))

3.1.2.4. Greywater sampling locations

In Germany, the collection and reuse of greywater is limited to a small number of facilities, such as research institutes, hotels, and few residential compounds. Therefore, the search for a representative sampling location was rather challenging. In total, two sampling locations with heterogenous characteristics were found for this study.

Split wastewater system at rural settlement Reinighof (L5)

The first greywater sampling location (L5) lies in a small sustainable lifestyle project Reinighof of (8-20) inhabitants near Bruchweiler-Bärenbach in Südwestpfalz district. The produced greywater from this compound originates from kitchen sink, washing machine and showers, and is collected and discharged into a 3-chamber sump pit before it is further treated in a constructed wetland. A portion of the treated greywater is then reused for irrigation, and the rest is drained into an evaporation pond. Since the collected greywater in the settling tank is mixed eventually with greywater from previous day and does not represent real-time yields, the goal of sampling at this location was limited to identifying the type of microplastics released and its dominant size fractions. However, since the sampling took place mainly during the pandemic time in 2020/21, the exact number of residents during sampling was not always given and estimation had to be made (students were asked to register their presence in a specific log made for this purpose).

Split wastewater system at a student dormitory (L6)

The second greywater sampling location is located in dormitory at the Umwelt-Campus Birkenfeld of the Hochschule Trier. The dormitory building is equipped with separate sewer system for greywater and blackwater, where each stream is collected and stored separately for future treatment and reuse. In addition, the building has a maximum occupant capacity of 72 students and greywater yield ranging from 1.71 m^3/d (during semester time) and 1.04 m^3/d (during lecture-free time) originating mainly from bathtubs, kitchen and washing sinks (no washing machines). However, not all residents were connected to the drainage system and there were partial COVID-19 restrictions at the time, which made occupancy uncertain. In addition, the kitchens were only partially connected.

3.1.3. Requirements and important criteria for the selection of sampling equipment

The sampling equipment deployed in this work is diverse and was chosen according to the nature and needs of each sampling location and wastewater type. In general, the different equipment had to fulfill three major requirements to be eligible for use during sampling activities. First of all, the equipment must guarantee the **representativity** of samples taken within the wastewater stream. Secondly, single components should be **free of plastic** materials that might contaminate the samples and/or interfere with the results of the thermal analysis. Finally, the equipment should run as **autonomously** as possible to avoid random errors or bias resulting from manual sampling methods or human intervention, and to facilitate tracking systematic errors.

Wastewater streams transport heterogeneous matter, from dense minerals, such as sand, to light organic materials. Hence, finding the optimum location with sufficient homogeneity levels of all constituents is utterly challenging. The settling velocity of suspended solids from different water levels in a wastewater stream is a practical measure to test the mixing rate and choose a representative suction depth. However, high mixing rates due to shooting flow velocities might lead to a decrease in relative sampling velocity and shift the sampling into non-isokinetic phase. Isokinetic sampling means that the velocity of sampling should be similar or close to the one of the sampled media in pipe or canal (Tyree and Allen 2004). According to Nelson and Benedict (1951), no significant representativity errors in sediments concentrations are expected as far as the sampling velocity remains between 80 - 200 % of the flow velocity.

In order to fulfill the second requirement of avoiding equipment made from plastic materials, alternatives made from glass, stainless-steel or silicon were preferred. An exemption was made for PVC elements in accordance with Braun et al. (2020a) where non-detected plastic materials are tolerated.

Automatic sampling methods provide a great help for identifying and quantifying systematic errors during sampling. For instance, the sample volume of manual sampling is prone to personal bias based on visual reading capabilities of measurement instruments. In addition, the input signals that trigger automatic sampling can be traced and documented with high accuracy. Hence, a larger room for calibrating sampling methods is available. Automatic sampling methods were preferred in this work for all wastewater streams and primary tested. In case the automatic sampling method was impossible to implement, semi-automatic methods using real-time environmental measurements were deployed.

Conventional automatic samplers are reliable instruments for wastewater sampling. However, very large sample volumes (>>50 L) are needed in the case of MP sampling. Hence, novel upscaled automatic sampling setups were developed in this work to mimic the function and reliability of conventional samplers but to deliver large sample volumes up to 1100 L. The upscaled automatic samplers consist of three main components: i) measurement apparatuses, ii) control units and iii) Large Volume Samplers (LVS) with capacities ranging from 100 to 1100 L. LVSs allow for long-term and event-based monitoring of specific pollutants in terms of event mean concentrations (EMC) and provide adequate amounts of particulate matter for analysis and suitable for deriving reliable particle size distributions (PSD) of solids in sample (Nickel and Fuchs 2021). The description and function of these components will be discussed in the following sections.

3.1.4. Sampling frequency

The method for choosing a suitable sampling frequency depends on an earlier knowledge of MP occurrence patterns and the degree of fluctuations expected on daily basis (refer to 2.4). However, this pre-knowledge that should help in determining sampling frequency for the chosen wastewater streams and locations will be an outcome of this work. Based on the statistical method in 2.4 and the results of the monitoring campaigns, suggestions on sampling frequencies for certain locations and MP types will be given in section 4.1.4. I will solely discuss the methodology applied for defining the type and number of samples taken in the following passages.

When choosing the sample type for all dry weather samples, a basic assumption was adopted at the WWTP and in the sewer network. Namely, there is a daily occurrence pattern for MP concentrations and only volume-proportional 24h composite samples are capable of capturing its magnitude. Moreover, the daily fluctuations in MP concentrations on a daily basis are considered to be absolute random events. Hence, the number of 24h samples (n) during a monitoring campaign is selected randomly at first for later to be adjusted according to the method in 2.4. Besides the narrow window for sampling under strict dry weather conditions, other factors lead to a further reduction of sample number per location and wastewater stream. One can summarize these factors in the following:

- The effort linked to sampling and sample preparation both in situ and in the laboratory.
- The time for sampling and sample preparation was estimated to take three to four days at the beginning.
- The time and costs assigned the analytical method at the *Bundesanstalt für Materialforschung und -prüfung* (BAM) laboratory were very high, namely, two hours of running the automatic setup and 800 € per analyzed sample. Therefore, the allowed number of samples assigned for the whole project was limited and needed to be allocated carefully[14].
- Considering that many locations were sampled during this work, the quota of continuously flowing dry weather streams was put to a minimum to allow for further wet weather sampling.

The approach for selecting sampling frequency of wet weather streams was completely different due to random occurring nature of storm events with

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[14] All thermal MP analysis with TED-GC/MS in this work were performed at the Bundesanstalt für Materialforschung und -prüfung (BAM) by laboratory team of department 6

varying MP accumulation levels. Theoretically speaking, all runoff events that could have been captured during the project time were target for sampling.

3.1.5. Sample preparation and handling

Following each sampling event, samples were collected and prepared within 48h after the end of the event. In addition, a special sampling protocol was developed for all samples in shadow of the norm DWA- A 704 to systematically document all sampling information (see Figure A 5 in appendix 8.2.2). Depending on the size of each sample, some samples were first sieved in situ with the sieve sizes 1000, 500, 100 and 50 µm, and then transported to the laboratory for further preparation steps. However, a universal handling method (Figure 3-11) was developed to deal with the different types of samples from the different wastewater streams.

Samples were mixed either manually, for volumes smaller than 30 L using aluminum sticks in a stainless-steel container, or using a mobile mixing device (Atika RL 1000, max. 1000 rpm) for sample volumes larger than 30 L. Afterwards, a homogeneous sub-sample of 500-1000 ml was taken for the wastewater matrix analyses (SS >0.45 µm, COD). The remaining sample volume was wet sieved using a sieve-cascade of four Sieves (1000, 500, 100 and 50 µm, Retsch, Germany); for dry weather samples Ø200 mm sieves and for stormwater runoff samples Ø400 mm sieves, then a sub-sample of the filtrate 1-2 L was vacuum filtered using Combisart® stainless steel filtration system connected to a vacuum pump (Microsart® e.jet (Sartorius AG, Göttingen, Germany) and 5 µm stainless-steel weaves (Ø5 mm, GKD - Gebr. Kufferath AG, Düren, Germany). To minimize the drying time in the coming step, the volume of each wet fraction did not exceed 300 ml. Then, samples were sterilized in (VARIOKLAV 75 S, HP Labortechnik GmbH) with slow-cooling program and dried in Teflon® plates at 105 °C in a compartment drier. To avoid cross-contamination, all samples are preserved and transported in plastic-free instruments (Teflon or glass). Each dry sample was then divided into three portions; for MP analysis, Loss on ignition (LoI) analysis and a third portion was saved for potential future analysis (e.g., MP particles morphology, heavy metals in samples).

The fraction with the size of 50-5µm from the rainwater retention basin was filtered by BAM manually. Therefore, a stainless-steel vacuum apparatus (Whatman plc, Maidstone, England) was used to filtrate the samples with a volume of 2L. Filters with a mesh size of 5µm and 50 mm in diameter (GKD –

Gebr. Kufferath AG, Düren, Germany) collected the solid residue. For further analysis, the filter cake was dried overnight in the oven at a temperature of 50°C.

Sample preparation method was continuously developed to minimize cross-contamination errors, as well as to avoid filter cake build-up during samples wet sieving. For samples of high suspended solids and organic contents, sieves were washed back and cleaned after 3-4 L feed.

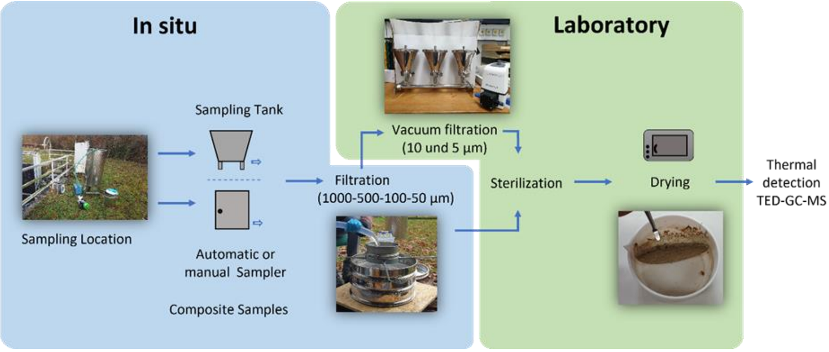


Figure 3-11 Universal scheme of sampling and sample preparation for all samples (partial editing, Christian Scheid 2021)

3.1.5.1. *Objective and application areas of the sieve cascades*

The main objective of using sieve cascades is the efficient mechanical separation of sediments and suspended solids from the environmental medium; either in form of liquid/solid separation as in wastewater samples or solid/solid separation as in soil samples.

Environmental media are heterogenous matrices of organic and inorganic constituents of different origins and residence times within the wastewater media. During the filtration process, particles of varying sizes are forced through the cascade as well as through already retained particles, thus, the higher the amount retained on the filter material, the higher the chance that smaller particles are misallocated and retained at a larger filter or sieve. A common concern when operating a sieve cascade is the build-up of what so called *filter cake* because of large amounts of filtered material accumulating in the filter. An objective of efficient filtration is then the avoidance of filter-cake formation by extracting the filtered material early enough, or if needed washing the cascade using sample filtrate or distilled water. While previous concerns may apply to solid/liquid separation only, other concerns are related to solid/solid separation processes (dry sieving). Due to mechanical thrust during dry sieving some larger particles may break-down into smaller ones and alter the original size distribution in the sample. Another concern is the formation of dust, especially when sieving particle sizes < 100µm (Braun et al. 2020a).

Regardless of the type of filtration, wet or dry, or the type of phase separation, avoiding cross-contamination from surrounding environment and measures regarding the location, used materials and equipment are highly recommended.

3.1.5.2. Description of the sieve cascades: technical structure and mode of operation

A sieve cascade is a column of vertically stacked sieves or filter weaves in a descending manner, where the sieve with the largest mesh size is placed on top. Depending on the type of environmental samples that are being prepared, there are two sieving methods available, dry, and wet sieving. During the sampling in the urban drainage system of Kaiserslautern, only wet sieving was applied for wastewater and stormwater samples.

Using stainless-steel sieves with 5cm spacing, the environmental samples are poured into the cascade gradually; the following sieve and mech sizes were deployed for the different sample types:

- Sieves of Ø 200mm, 5 cm height with mech sizes 50, 100, 500, 1000, 3000 and 5000 µm (most common sieves in wastewater laboratories) (refer to Figure 3-12 right)
- Sieves of Ø 400mm, 5 cm height with mech sizes 50, 100, 500 µm (refer to Figure 3-12 left)
- For very small fractions, 5 and 10 µm filter weaves and vacuum filtration

In addition, filtrate was always collected in stainless-steel containers to be homogeneously sampled and vacuum filtered.

Figure 3-12 Sieve cascade of Ø 400mm sieves (left) and sieve cascade of Ø 200mm sieves

3.1.6. Polymer determination using TED-GC/MS

The determination of polymer mass contents, with MP as the main component, was conducted using TED-GC/MS at BAM in Berlin. The sample underwent heating up to 600 °C in a thermobalance, with a constant nitrogen flow, to extract characteristic pyrolysis products of the polymer. These products were then collected on a solid phase adsorber and automatically transferred to a GC/MS system. Following remobilization and cryo-focusing, the pyrolysis products were separated by the GC column and detected using a mass spectrometer. The analytical method employed was described by Eisentraut et al. (2018), Duemichen et al. (2019), Altmann et al. (2019), and Braun et al. (2020a). Specifically, the screening method was used to identify PE, PP, PS, PET, PA6, acrylate, and SBR. The limits of detection ranged from 0.08 µg for PS and SBR to 2.2 µg for PE, relative to the absolute sample weight in a crucible. The limit of quantification was twice the limit of detection. In each analytical run, a sub-sample weighing approximately 10 mg was analyzed using TED-GC/MS. To identify the polymers, specific degradation products were utilized, including 1,14-pentadecadiene and 1,14-hexadecadiene (m/z = 55) for PE, 2,4-diphenyl-1-butene (m/z = 208) for PS, 4,6,8-tetramethylundec-10-ene (m/z = 111) for PP, ethylbenzoate (m/z = 150) and benzoic acid (m/z = 105) for PET, caprolactam (m/z = 113) for PA6, acrylate (m/z = 69) for PMMA, and 3-phenylcyclohexene (m/z = 104) for SBR. Polymer quantification was achieved through one-point calibration with the addition of pristine polymers. Quality assessment involved the mandatory use of an internal standard of deuterated polystyrene, as well as conducting a blind value measurement before each environmental sample measurement to ensure no carryover of pyrolysis products from previous measurements and, consequently, avoid false positive results (Altmann et al. 2023; Abusafia et al. 2023). Figure 3-13 depicts the TED-GC/MS equipment located in the department 6.6 (Physics and Chemical Analysis of Polymers) at BAM laboratory.

Figure 3-13 Entire TED-GC/MS setup with automatic sampler (upper right) and reusable filter crucibles (lower right) at BAM (Braun et al. 2020b)

3.1.6.1. *Quantification of the concentrations of waterborne MP*

The thermal detection with TED-GC/MS was conducted on each size fraction individually, and for each size fraction, detected polymers were measured as weight fraction of total solids within respective size faction in μg/mg. Then, mean concentration in sample was calculated as a sum of concentrations of all detected MP according to sample volumes (Eq. 5, 6 and 7).

$$C_{m,total} = \sum_{x=1}^{k} C_{m,MP,x} \tag{5}$$

$$C_{m,x} = C_{m,x,y1(\mu m)} + \cdots + C_{m,x,yn(\mu m)} \tag{6}$$

$$C_{m,x,y} = \frac{m_{x,y} + m_{s,y}}{V_s} \tag{7}$$

Where:

$C_{m,\ total}$ mean concentration of all detected MP in sample in [μg/L]

$C_{m,x}$	mean concentration of MP x in sample in [µg/L]
$C_{m,x,y}$	mean concentration of MP x in size fraction y (µm) in [µg/L]
$m_{x,y}$	mass concentration of MP x in analyzed subsample of size fraction y (µm) in [µg/mg]
$m_{s,y}$	total mass of sediments of size fraction y (µm) in [µg]
V_s	sample volume in [L]

3.1.7. Wastewater standard parameters

As a preliminary step before designing the monitoring campaigns, candidate wastewater streams were sampled, and standard parameters were analyzed. The quality parameters COD, TS and LoI are valuable metrics to estimate the proper sample volume from each wastewater stream, and to select the suitable sample preparation equipment. In addition, the solid and organic contents in the medium determine the degree of difficulty to be expected during sample preparation. For MP detection methods where, organic digestion is required (not in this work), other quality parameters (e.g., Dissolved Organic Carbon (DOC)) might be needed to select the sample preparation practice.

COD was measured using a fast cuvette test kit (LCK 514) for concentration range 100-2000 mg/L from © Hach (HACH LANGE GMBH 2019). This range was adopted for all samples based on own testing at the beginning of sampling campaigns. Sub-samples of 500-1000 mL were extracted from homogenized samples and 2 mL of which were pipetted into test cuvettes before they were heated for 15 min at 170° C using DR Lange HT200s (© Hach Company). Cuvettes were then cooled down to room temperature and concentrations were determined using the photometer DR5000, also from © Hach. The results were reported in [mg/L] and since no dilution steps were adopted; the resulted concentration represented an average value of the homogeneous sample during the sampling time frame (e.g., 2h, 24h, runoff duration).

TS larger than 0.45 µm and loss on ignition (LoI) were measured according to the German standard DIN 38409 for determination of filterable matter and the residue after ignition (refer to 2.4.1). TS values were reported in [mg/L] and also represented homogeneous sample during the sampling timeframe. In case of estimating the Total Solids (SS) content for size fractions in the sample, the term TS (e.g., $TS_{100\text{-}500\ \mu m}$) in [mg/L] is adopted. LoI estimations in [%] reflected the organic content within TS.

The analytical methods described earlier in this section were adopted also during the main monitoring campaigns in this work. So that for samples that were analyzed for MP content, standard wastewater parameters were conducted.

3.2. Preliminary tests for the development of the sampling strategy using sieve cascades in sample preparation

Sample preparation for MP analysis is a time-consuming task that demands careful attention. As suspended solids are concentrated from substantial volumes, there is a relatively high chance of inaccuracies or misallocation of size fractions occurring. To streamline the process without compromising quality standards, it becomes crucial to establish comprehensive guidelines for sample preparation. These guidelines would serve as a roadmap, enabling investigators to expedite the process while maintaining the utmost accuracy and precision in identifying and analyzing microplastics.

3.2.1. Boundary conditions for the application of sieve cascades in samples preparation

Sieve cascades can be deployed both in laboratory and in field to avoid transporting large sample volumes. However, the amounts of prepared samples in field are affected by factors, such as filtration time, sampling location and weather conditions, thus, for environmental media with low TS concentrations only 1-2 m^3 can be manually filtered at once. On the other hand, environmental media with high organic content and TS concentrations, feasible sample volumes could not exceed 50L at most.

Within the urban drainage system, the characteristics of wastewater streams vary significantly, so that each wastewater stream is filtered and fractionated using specific approach. However, one can sort out these streams into three main categories.

I) Wastewater samples with high TS and (COD) contents, such as influent streams to WWTP, combined wastewater flow under dry weather conditions or in some cases dark greywater.

II) Wastewater streams with high TS contents and low to moderate (COD) contents, such as stormwater runoff from separate and combined sewer systems,

III) Treated wastewater samples with low TS contents < 15 mg/l, such as effluent streams of WWTP.

TS and COD values are deciding factors for choosing the volumes to be feasibly filtered from each category (Table 3-2):

Table 3-2 Suggested sampling volumes for the 3 categories of wastewater streams

Category	TS [mg/l]	COD [mg/l]	Sample Volume [L]
I	223 ± 62	530 ± 200	20-50
II	280 ± 49	197 ± 51	max. 1000
III	<15	20 ± 3	1000-2000

Wastewater samples of the above-mentioned categories showed different size distribution schemes, however, the size fractions 100-500µm and 50-100µm showed the higher sediment contents respectively. According to the results from ca. 59 samples and the observations from sample preparation by the research team, the sieves were back-washed multiple times during the process to avoid the build-up of filter cake. For example, the sieves 100µm and 50µm required at least one cycle of back-washing after every 5l sample of category I poured into the cascade, while the larger sieves needed one cycle after 10l. The following Table 3-3 shows the estimated number of back-washing cycles for each wastewater category and sieve size.

Table 3-3 Back-washing cycle for different wastewater streams and sieve sizes after pouring x volume of sample

Category	Mesh size [µm]					Ø Sieve
	5 [ml]	50 [L]	100 [L]	500 [L]	1000 [L]	[mm]
I	500	5 L	5 l	10 l	10 l	200
II	2000	50, or 50% sieve area covered	50, or 50% sieve area covered	100	100	400
III	10000	500	500	500	500	200

3.2.2. Application times and sampling effort

3.2.2.1. Category I: samples from influent WWTP

The preparation of environmental samples of category I is very demanding and time-consuming, both in field and laboratory. The occurrence of Organic Matter (OM) in high concentrations and the many large impurities, such as toilet paper, challenge the filtration process immensely. Consequently, sample volumes were limited to 20-50l, and the samples were stirred continuously during the process of filtration and back-washing. On average, samples required at least 2h filtration time including intensive multiple back-washing cycles depending on sample properties.

3.2.2.2. *Category II: samples from wet weather flow*

For wet weather flow, sampling parameters were set in a way to cover events of up to that occur in the area based on historical data and with a maximum sample volume of 1000l. However, average actual sample volumes for sampling point at the stormwater retention tank (SRT) in separate system was 435 ± 332 m^3 (using peristaltic pump) and for the sampling point in combined system 840 ± 306 m^3 (using submerged pump). The first two runoff samples (July and August 2020) were filtered using a conventional Ø 200 mm sieve cascade, then, a new Ø 400 mm cascade was deployed for the rest of samples to accelerate the filtration process in field.

Since an optimal flow rate to operate the sieve cascades with differing sample properties was unknown at the beginning, the cascade’s behavior under different flow rates (valve openings) was noted intensively and documented in a special diary. Based on the documented optimal valve openings and actual filtration times, a flow rate range of 10-15 l/min (Figure 3-14) was found to be optimum to avoid fast filter cake build-up, as well as to avoid spillage and loss of sample. To assure quality filtration throughout the process, samples were stirred continuously using a mobile mixer with a mixing rat of max. 1000 rpm. Under the above-mentioned conditions, filtration time is expected to last for ca. 2h in situ.

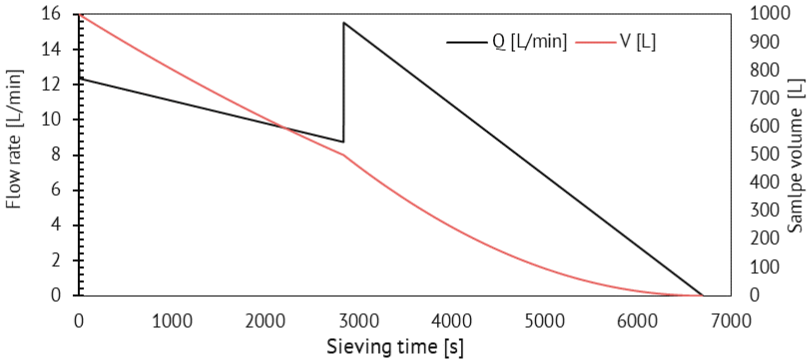


Figure 3-14 Sieving time for wet weather flow samples in combined system with 150-250 mg/L FS content

3.2.2.3. Category III: samples from effluent of WWTP

Samples with very low solids content may be the easiest to process using sieve cascades considering the low chance for filter cake build-up or clogging by large impurities. However, due to the large sample volumes, the operating times increase significantly. The samples from the effluent of the treatment plant with TS-contents <15 mg/l were filtered in situ using a ø 200mm sieve cascade and the sieve material were then transported to the laboratory for further analysis. The flow rates based on valve openings and cascade's capacity were noted and documented in a special diary and a range of 7-12 l/min was found to be optimal for the operation. With this setup and with ø 200mm sieves , samples required on average 2.5 h to be fully filtered.

Based on the experience achieved during the operation of larger sieves (ø 400mm) for samples of category II, a theoretical projection was set to predict the time-saving potential when these sieves were deployed for samples of category III. The projection shows (refer to Figure 3-15) that at least 60% timesaving is expected when doubling the size of sieves used in the sieve cascade. So, for a 1000 L effluent sample with TS-content of 10 mg/l a filtration time of < 1h 15min is expected.

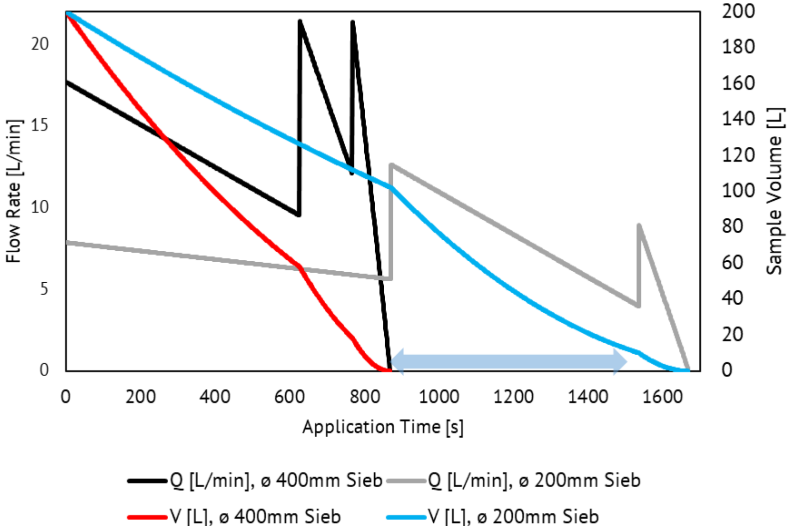


Figure 3-15 Filtration time using ø 400mm instead of ø 200mm sieve cascades

3.2.3. Interim conclusion

This section provides guidelines and recommendations for the proper handling and preparation of samples in the context of sieving and filtration processes. These guidelines aim to ensure accurate and reliable results by addressing various factors such as sample mixing, sieve washing, sample volumes, filtration equipment, and separation quality. By following these guidelines, researchers and practitioners can optimize their sampling procedures and enhance the effectiveness of their sieving and filtration methods, particularly in the context of MP monitoring. These recommendations cover aspects such as sample preparation, sieving techniques, suitable sieve sizes, flow rates, and the use of mechanical mixing and automated filtration. Implementing these suggestions will help achieve representative and dependable outcomes in sample analysis and research endeavors.

- Sieves should be washed properly with distilled water before use to remove contaminants and to reduce the electrostatic resistance of the weave material.
- Samples should be mixed properly before and during sieving.
- To reduce the effect of filter cake before the backwashing (emptying) cycle, filtrate can be used to wash the sieve cascade.

- Samples should be transported and wet sieved on the same day and mechanical mixing for at least 15 min till fully homogenized is recommended.
- 1000 L stormwater runoff sample volume is too much, considering the requirements of detection methods. Instead, 100-500 L sample volume is sufficient to assure representative microplastic monitoring.
- For samples larger than 100 L, larger sieves > ø 400mm are recommended for sieve cascades to reduce the filtration time considerably.
- For large samples with high TS-contents, flow rates should not exceed 20 L/min to guarantee good separation quality.
- Large samples need mechanical mixing, mobile mixing devices can be useful.
- Automated filtration for very low concentration samples is feasible, knowing that almost no backwashing was needed for sample volumes up to 2 m^3.

3.3. Monitoring campaigns

The monitoring campaigns were designed in alignment with the objectives of this work explained earlier in 1.3. Hence, the goal was to consider and screen all key wastewater streams within the UDS that might be relevant to the transport of waterborne MPs. The monitoring campaigns were classified into two main phases and stretched over the time period from September 2018 till August 2021.

During **Phase I** (09.2018 – 07.2020), all sampling locations were identified, and preliminary sampling and sample preparation approaches were introduced for dry and wet weather streams. Subsequently, all sampling locations (except L4) were sampled under dry weather conditions. In parallel to the previous activities and by the end of this phase in summer 2020, the two fully automatic stormwater sampling plants were designed and built to sample stormwater runoff in combined and separate systems. During **Phase II** (08.2020 - 09.2021), the two sampling plants for stormwater runoff at L3 and L4 were tested, adjusted, and operated in order to capture multiple runoff events. Table 3-1 reviews all sampling locations of this work including the adopted strategies, scope, and the motivation behind sampling.

3.3.1. Monitoring of dry weather streams

The monitoring of dry weather streams took place during phase I of this work prior to the one of wet weather streams. The reason behind was simply the fact that necessary experience and equipment in this field of monitoring were available at this early stage. Also, to earn some time that is needed to develop the sampling concept of stormwater runoff. Dry weather streams were monitored at six different locations (L1, L2, L3, L4, L5.1 and L5.2) in the catchment: starting at the WWTP Kaiserslautern (L1 and L2) and within the catchment itself at L3. Greywater sampling (L5.1 and L5.2) took place at remote locations outside the city catchment since no suitable ones were found within.

3.3.1.1. Sampling of dry weather flow at WWTP and quantification of MP emissions

Dry weather influent of the WWTP Kaiserslautern (L1)

Considering its importance for the entire urban drainage system, the first sampling activities (as part of Phase I) were conducted at the WWTP Kaiserslautern to quantify the emitted MP loads as well as to investigate the removal efficiency of the plant.

Figure 3-16 The automatic sampler ASP Station 2000 used for sampling the inflow of the WWTP Kaiserslautern

Under dry weather conditions, the stationary automatic sampler (ASP Station 2000, Endress+Hauser) was deployed to sample the outflow of the screening units at a suction depth of around 40 cm below water surface using a Ø 19 mm suction hose of about 2.5 m. Samples were taken time-proportionally (100 ml shot every 6min) and preserved in 24 glass bottles at 4 °C, hence each bottle represented one sampling-hour. With a total volume of around 24 L (24h-composite sample). Samples were then transported to the laboratory of the TUK, where they were volume-proportionally mixed into a 24h composite sample according to a $Q/Q_{max/min}$ ration, and a daily flow pattern with Q_{max} assumed at 08:00 and Q_{min} at 03:00. Afterwards, composite samples were prepared for analysis according to the generic method displayed in section 3.1.5.

Dry weather effluent of the WWTP Kaiserslautern (L2)

MP in the effluent of WWTPs occurs in low concentrations of about 10^{-3}-10^{1} mg/L (Hinzmann et al. 2022). Hence, sampling of large amounts of effluent water is needed to extract enough suspended particulate matter for polymer detection using TED-GC/MS (Eisentraut et al. 2018; Duemichen et al. 2019).

While concentrations of suspended solids under dry weather conditions in the influent of WWTP might fluctuate heavily according to release patterns in the catchment within a day, the concentrations in the effluent are less sensitive to these diurnal fluctuations due to continues mixing in several treatment steps. According to DIN EN ISO 5667-1, the time of sampling is not relevant because the fluctuations are related to the functionality of WWTP itself. In addition, WWTPs are designed to minimize such fluctuations. In other words, we have a case of unpredictable fluctuations due to WWTP specific treatment behavior. Hence, 4h composite samples were taken from the effluent stream, usually from 10:00 to 14:00, of secondary settlings tanks to evaluate the removal efficiency of the treatment processes and characterize MP emissions in term of PSD and polymer type.

The sampling of the effluent stream was carried out in the effluent canal of secondary settling clarifiers using a stainless-steel garden pump (flora-best 1100 W) and, due to the low concentration of total solids in the effluent (2-10 mg/L), a relatively large sampling stainless-steel tank of 200 L, which was filled and emptied (samples were sieved spontaneously) multiple times during the course of 4h sampling. According to the estimation of WWTP operators, the total residence time of wastewater in the treatment plant is 36 h. However, dry weather conditions could not be guaranteed for long periods, thus, an intended 36h lag between sampling in the influent stream and the effluent one could not be maintained. To avoid transporting large water volumes to the laboratory, the samples were initially sieved using a sieve cascade (1000-500, 500-100, 100-50 µm) in-situ. Then, a sub-sample of 10-20 L was vacuum filtered with a 5 µm stainless-steel weave. Further sample preparation steps were conducted in the laboratory according to the method described earlier in 3.1.5.

In analogy to measurements in influent of the WWTP (3.1.2.1), median daily flow of $Q\ T_{aM}$ (median) = 47,819 m^3/d was adopted to calculate per population equivalents yearly emissions into receiving waters using equation 11 (chapter 3.4.2.1). The removal efficiency of WWTP for total MP, specific MP types or size fractions were derived by comparing the concentrations in influent and effluent resulted from equations 5, 6 and 7 (chapter 3.1.6.1) respectively.

Integral sampling using Sedimentation Boxes (SBs)

The objective of the long-term sampling, in addition to gaining knowledge about MP removal efficiency at the WWTP, was to compare the results of conventional sampling practices. The use of SB allowed for integrative long-term sampling of particulate matter in surface water streams or effluent of WWTPs by forcing the flow through zigzag-shaped path against baffle plates attached to the ceiling and bottom of the SB, and due to the sudden reduction of flow velocity in the SB (Kittner et al. 2022).

In the beginning of February 2019, an early version of the SBs (UGT GmbH, Germany) (Figure 3-17 left) was installed in February 2019 in the effluent canal of secondary clarifiers for about 13 days. Then the box was removed from the effluent canal for further analysis. The obtained sample (38.8 L) was subsequently homogenized and prepared as shown in (3.1.5).

Figure 3-17 left: an early version of SBs was submerged into the effluent channel entirely. Right: Third version of SBs was fed through a by-pass flow without being submerged fully in the effluent canal

The previous sampling campaign was accomplished as part of phase I. However, the producing company of SBs released a modified version with a single-feed opening to be operated through a by-pass flow outside of the effluent canal. In addition, and at the same time when the modified SB was released, a pilot plant for the elimination of OMPs in the effluent of the secondary clarifiers of WWTP Kaiserslautern was already in operation by colleagues from the same institute as the author (Wasser Infrastruktur Ressourcen, WIR). The plant (Figure 3-18) consists, among others, of an ozonation plant with a subsequent Granulated Activated Carbon (GAC) filter.

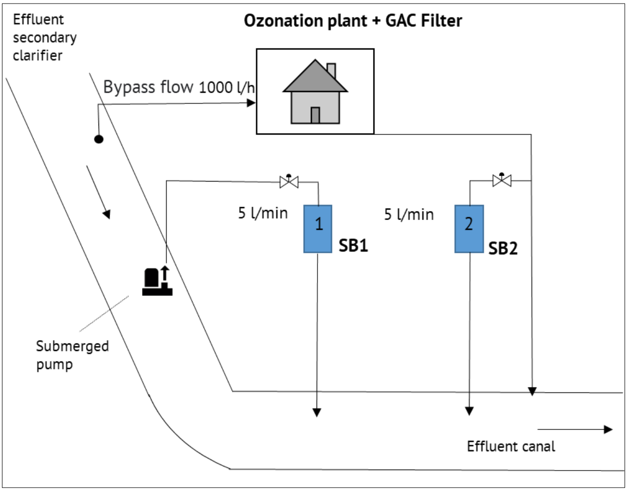


Figure 3-18 Parallel and simultaneous sampling of effluent of secondary clarifiers and GAC-Filter using two SBs

The particulate nature of MP favors the mechanical removal by filtration or floatation (Baresel et al. 2019) and Large-scale GAC-filters in operation at WWTP demonstrate high removal potential of TS (81-87 %) (Benstöm et al. 2014). Besides the mechanical removal of MP, the surface adsorption capabilities of the negatively charged GAC particles can be effective in removing MP in the presence of Organic Matter (OM) coating (Ramirez Arenas et al. 2021). Moreover, the ozonation of MP particles with OM coating prior to GAC-filtration can lead to further reduction in the surface charge of these particles (Chandrakanth and Amy 1996), and thus enhance their adsorbability. Hence, this opportunity was used to gain initial insights into MP removal capabilities of such novel treatment combination.

The ozonation plant and GAC-filter were operated continuously with a flow rate of 1000 L/h (or 16.6 L/min), therefore a 3/4" gate valve was installed between the GAC-filter and SB_2 (Figure 3-18) to regulate the flow to 5 L/min as recommended by SB manufacturer. A submerged pump (FlatOne 6000 INOX, T.I.P. GmbH) was installed in the effluent canal of the secondary clarifiers to feed SB_1. Similarly, a 3/4" gate valve was installed between the pump and SB_1 to regulate the flow to 5 L/min. (Kolisch et al. 2022)

The initial sampling strategy was set to feed both SBs continuously for a period of 14 days. However, due to multiple pump clogging, the sampling was not performed continuously during the two weeks. Instead, the operation times of the ozonation plant were recorded to calculate the flow amounts and to estimate average polymer concentrations during the studied intervals. Therefore, average concentrations of polymers are applied to compare emissions and removal rates, and not the absolute loads of polymers.

During the time from April 14th till May 25th, 2021, two sampling cycles were executed for 15 and 14 days respectively. During the first sampling cycle, about 110 m^3 from the effluent of secondary clarifier and 115 m^3 from the effluent of Ozonation plant /GAC-filter were sampled by SB_1 and SB_2. During the second cycle, about 127 m^3 by SB1 and only 75 m^3 by SB_2.

The samples inside the SBs (≈ 46 L each) were prepared similar as above according to the process described in 3.1.5). The results of the thermal analysis were given for each detected polymer in μg polymer/μg dry sieve residue in sample. The average concentration of MP during sampling cycle was then calculated using equations 5, 6 and 7.

3.3.1.2. Sampling at SRT in combined drainage system (L3) and quantification of MP emissions

At an early stage of sampling, an attempt to automatically sample dry weather flow using a peristaltic pump failed due to repetitive clogging in the suction pipe. Consequently, 24-h composite sampling was not practical in the long run. Instead, a manual sampling approach was developed to replace 24-h sampling. This approach assumes that residential areas tend to have reproducible dry weather flow patterns. Based on long-term flow measurements from May till December 2019, a flow pattern could be identified with two flow peaks starting at around 06:30 and 18:00, and two recessions at around 14:00 and 03:00 (refer to Figure 3-19). According to nightly minimum method (BW) (LUBW 2007), minimum flow at 03:00 is nearly equal to base flow in the catchment. Hence, the sampling at this time window was not performed. Only three grab samples per day were taken at 06:30 (≈10 L), at 14:00 (≈ 5 L) and at 18:30 (≈ 10 L) to represent the whole day. In total, six samples were taken using this method at the described location (refer to Figure 3-20).

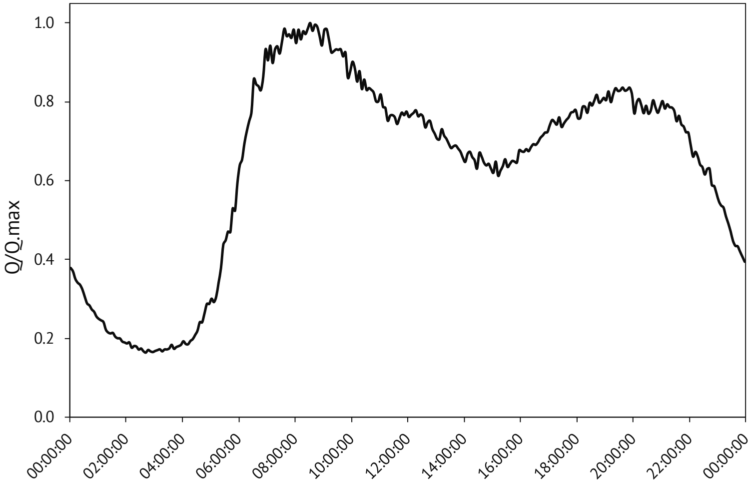


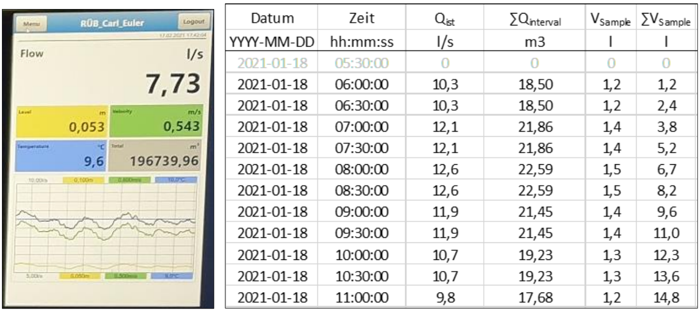
Figure 3-19 Daily Q/Qmax factor of dry weather flow from May to December 2019 at L3

Figure 3-20 Sampling location at L3 in the effluent canal of SRT in combined system under dry weather conditions

The previous approach, however, does not capture sudden changes during the peak flow time from 06:30 till 18:30, but assumes a linear change in released MP amounts. To overcome this disadvantage, a modified approach was introduced to mimic automatic sampling devices; flow-proportionally and sample the whole duration from 06:30 till 18:30 in a 30-min-sequence.

The modified approach was developed to estimate the sub-sample volume every 30 min based on dry weather flow pattern mentioned earlier real-time flow measurements at the sampling site and aiming at a total sample volume of around 30 L. In total, two samples were taken in this manner.

The previous modified approach was developed to estimate the sub-sample volume every 30 min based on dry weather flow pattern mentioned earlier (Figure 3-19), real-time flow measurements at the sampling site and aiming at a total daily sample volume of around 30 L. The sampled volume was set to ensure sufficient sediment amount for the thermal analysis (a minimum of 50 mg per sediment size fraction) and to reduce the sample preparation time. The previous long-term flow measurements showed that, on average, 472 m^3 of dry weather flow is recorded from 06:30 to 18:30. Hence, for each 16 m^3 of dry weather flow, 1 L sample was taken (Equation 8). Before each sampling activity, the real-time flow was retrieved and equation 9 was used to calculate representative sub-sample volumes for the time interval. The actual composite sample volume (V_{sample}) is calculated using equation 10.



Datum	Zeit	Q_{ist}	$\Sigma Q_{interval}$	V_{Sample}	ΣV_{Sample}
YYYY-MM-DD	hh:mm:ss	l/s	m3	l	l
2021-01-18	05:30:00	0	0	0	0
2021-01-18	06:00:00	10,3	18,50	1,2	1,2
2021-01-18	06:30:00	10,3	18,50	1,2	2,4
2021-01-18	07:00:00	12,1	21,86	1,4	3,8
2021-01-18	07:30:00	12,1	21,86	1,4	5,2
2021-01-18	08:00:00	12,6	22,59	1,5	6,7
2021-01-18	08:30:00	12,6	22,59	1,5	8,2
2021-01-18	09:00:00	11,9	21,45	1,4	9,6
2021-01-18	09:30:00	11,9	21,45	1,4	11,0
2021-01-18	10:00:00	10,7	19,23	1,3	12,3
2021-01-18	10:30:00	10,7	19,23	1,3	13,6
2021-01-18	11:00:00	9,8	17,68	1,2	14,8

Figure 3-21 Left: real-time flow measurement at L3, right: table used to estimate the sampling volume of each 30-cycle based on real-time flow measurement and flow pattern showed in Figure 3-19

$$\frac{V_{S.ref}}{Q_{d.ref}} = \frac{30\ L}{472\ m^3} = 6.36\ \times 10^{-5} \tag{8}$$

$$V_i = \left(Q_{RT,i} \times t_i\right) \times \frac{V_{S.ref}}{Q_{d.ref}} \tag{9}$$

$$V_{sample} = \sum_{i\,=\,06:30}^{18:30} V_i \tag{10}$$

Where:

$V_{S.ref}$	targeted daily sample volume [L] from 06:30 till 18:30
$Q_{d.ref}$	reference median dry weather flow for the time interval from 06:30 to 18:30 based on long-term flow measurements [m^3]
V_i	sample volume representing the time interval I [L]
$Q_{RT,i}$	$Q_{RT,i:}$ real-time flow measurement at the sampling point [L/s]
t_i	time interval between each sampling [sec]
V_{sample}	summation of all sub samples representing the day [L]

The extrapolation of average daily MP concentration into per population equivalent yearly loads ($B_{MP,a}$) [g/p.e.*a] was conducted using equation 11 based on median daily flow values under dry weather conditions from May till December 2019, with $Q_{T,aM}$ (median) = 714 ± 62 m^3/d (n=68). The number of p.e. (5000) was retrieved from own estimations of WWTP operators (Stadtentwässerung Kaiserslautern 2021).

3.3.1.3. Sampling of greywater streams and quantification of MP emissions

Reinighof (L5.1)

Since the sump pit (Figure 3-22) was the only possibility to sample the entire greywater stream, sampling was limited to this point. The disadvantage is, however, that there is constant mixing of greywater of different ages in the collection tank, so that continuous sampling was not meaningful. Therefore, sampling was limited to single samples (grab samples) in order to obtain information on the type and size distributions of the accumulating microplastic. For this purpose, three grab samples of about 15 liters were taken and analyzed from August to October 2018.

Figure 3-22 Collection and settling tank of greywater at L5.1 Reinighof on 19.19.2018

Birkenfeld (L5.2)

The daily yield of greywater was collected in two storage tanks with a volume of 1 m^3 each, which made it possible to capture 24h composite samples of about 20-30 L. The greywater volume harvested was measured using an ultrasound contactless level measurement sensor (P3 NIVUS GmbH) mounted at the top of the IBC container. In total and during the period from April 2020 till April 2021, six 24h composite samples were taken at the sampling location L5.2 (Figure 3-23), fractionated, and analyzed for their MP content.

Figure 3-23 Greywater collection tanks at the sampling location L5.2 dormitory Birkenfeld

3.3.2. Monitoring of wet weather streams

The actual monitoring activities of wet weather streams took place during phase II (08.2020 - 09.2021). However, the planning and conceptualization of this monitoring campaign started early during phase I. At this early stage, the author set guidelines to shape a generic sampling concept that might be adjusted and deployed at various sampling locations with different wet weather flow conditions and qualities (refer to 3.3.2.1).

The first sampling plant for wet weather flow in separate system (L4) was designed by the author and assembled in April 2020 by the engineers of the central electronics workshop of the University of Kaiserslautern. The test trials of the plant had been delayed till summer 2020 due to the lockdown measures at the begging of the COVID19 pandemic. However, the sampling plant was then operational by the end of July 2020 and the first runoff events could be sampled by then. Based on the experience gathered while assembling and operating the first sampling plant, the second sampling plant for wet weather flow in combined system (L3) was assembled in February 2021 considering few adjustments for the new location and the different wet weather flow quality expected.

3.3.2.1. Sampling concept and quantification of MP emissions

With a total storage volume of about 410,000 m^3 stretched over almost 150 stormwater retention structures, the UDS of Kaiserslautern manages huge quantities of wet weather flow generated from its 3,500-ha catchment area.

In order to study MP emissions from outdoor sources, which are transported during wet weather with stormwater runoff, two stormwater retention tanks in combined and separate systems were selected as sampling location to study the wet weather flow generated from the two catchment areas. The boundary conditions of the two catchment areas were acquired and studied forehand to develop a suitable sampling strategy. The following data were essential to perform that:

- The size of the catchment area, including the size of impervious areas within.
- Previous flow measurements at the sampling location.
- The response coefficients of the catchment area to previous rain events.
- Land use; paved areas, roofs, and playgrounds.
- Type and length of sewer network.

- Traffic density (if available).

The two stormwater retention tanks in separate (L4) and combined (L3) systems manage two distinct wastewater flows; combined flow with dry weather component and separate stormwater runoff generated from catchment areas with different size and traffic density (refer to 3.1.2.1. and 3.1.2.2). Since representative sampling of wet weather flows impose capturing entire or multiple runoff events with as much solids as possible, LVSs were deployed at the two sampling locations over two sampling campaigns. For MP monitoring , entire sample volumes were to be homogenized and prepared (100 – 1,100 L).

The main element in a sampling system using LVSs is the control unit. Therefore, to maintain the goals of representative wet weather flow sampling, the control unit was designed to respond automatically to runoff events, and operational parameters were set to fulfill the following aspects:

- Controlled and fully automatic sequence of sampling.
- Event-dynamic sampling, which accounts for the temporal variability of stormwater runoff.
- Consideration of catchment-specific lag times after the end of rainfall event.
- Sampling as many runoff events as possible to assure event diversity.
- Volume-proportional sampling as composite sample, for obtaining up to 1000 L sample volume.
- The timestamp of flow measurement and control unit must always be synchronized to allow for the derivation of accurate sampling hydrographs.

At both sampling locations, flow measurement systems (NivuFlow 750, NIVUS GmbH, Eppingen, Germany) were installed in the inlet canal of the STR in separate system (Figure 3-24) and outlet canal of combined system (Figure 3-25). The two flow measurement systems provided redundant water level measurements using an ultrasonic sensor placed on top and piezo-resistive pressure sensor placed on canal bed, and an ultrasonic velocity measurement sensor integrated with the piezo-resistive sensor.

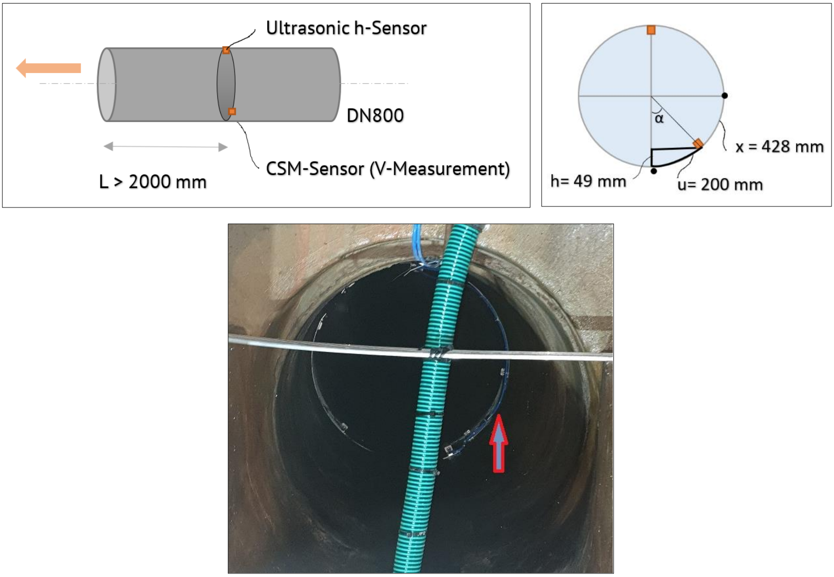


Figure 3-24 Flow measurement using NivuFlow 750 at L4 in the influent canal (⌀ 800 mm) of the SRT in separate system with location of the ultrasound water level sensor hanging from the ceiling and pressure unit at the lower right part of the canal

Figure 3-25 Flow measurement using NivuFlow 750 at L3 (combined sewer system) in the effluent canal (⌀800 mm) of the SRT in combined system similar to the measurement at L4. The ultrasound water level sensor hanging from the ceiling and pressure unit at the lower left side (viewer perspective). The sensor on the right is a particle quantification sensor (under development)

The ultrasonic velocity sensor is designed primarily to operate in a slightly to heavily polluted fluid media. Moreover, it detects the velocity at a certain height by comparing the interval lag between transmission and reception of sound echoes for a specific particle in the medium and at different heights (up to 16 velocity windows) (NIVUS GmbH 2016). In order to avoid clogging at the sampling location due to bulky objects in wastewater stream, the piezo-resistive pressure sensor was placed on the right side of canal bed.

The data loggers, after continuous data aggregation, send digital switching signals volume-proportionally to a Programmable Logic Controller (PLC) (Siemens LOGO). In parallel, an external rain sensor (REGME, B+B Thermo-Technik GmbH, Donaueschingen, Germany) was used to sense precipitation in the sampling area using heated electrical contacts to vaporize remaining water drops from previous events. In the case of rain, it sends a signal to the control unit to activate the entire control unit. The electrical wiring and the protocols of the Programmable Logic Controller (PLC) are shown in detail in appendix 8.2.3 Figure A 6 till Figure A 14.

The sampling itself is controlled by a setup for the sampling pump adapted to the boundary conditions of the respective sampling location. In separate system (L4) a peristaltic pump (Ponndorf P-Classic 35, Kassel, Germany) (Figure 3-26) and in combined system (L3) a submersible pump (Ebara Optima, Gambellara/Vicenza, Italy) (Figure 3-27).

Figure 3-26 The equipment of stormwater sampling plant in separate system at L4. Left: main sampling tank and a smaller tank used for sample preparation. Right: programmable control unit, flow measurement data logger and peristaltic sampling pump

Figure 3-27 The equipment of stormwater sampling plant in combined system at L3. Left: sampling tank, surveillance camera and programmable control unit

The sampling cycles last between 8 to 20 seconds per switching signal and are executed either until the end of the runoff event or until the maximum level in the stainless-steel collection tank (approx. 1,100 L) is reached. Figure 3-28 shows the detailed sampling algorithm and parameterizations that were adopted by the control unit. The electrical wiring schemes of the control unit as well as all communication protocols are shown in appendix 8.2.3.

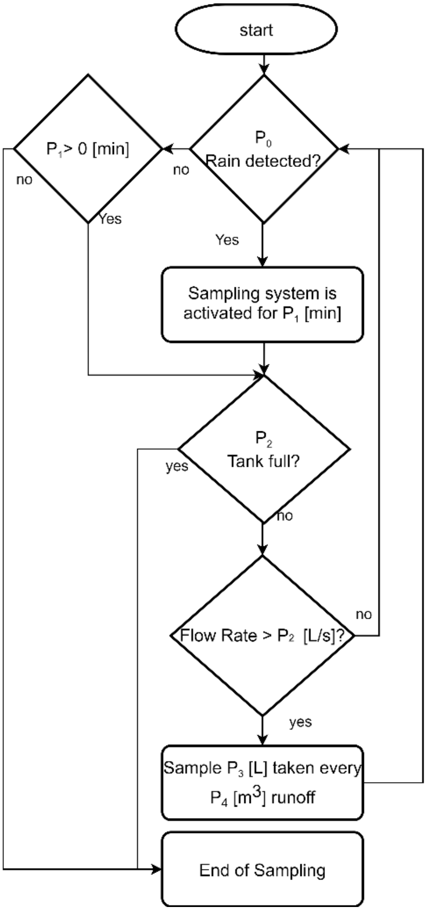


Figure 3-28 Sampling algorithm of the automated sampling concept for stormwater runoff with parameterization

Where:

P0	Weather condition test [rain = 1, no rain = 0]
P1	Sampling window after end of rain event [variable, set at 60 min]
P2	Capacity of sampling tank [full = 1 (at V = 1120 L), not full = 0]
P3	Real-time flow measurement [L/s] measured every 1 min
P4	Sub-sample volume [L]
P5	Sampling duration [15-30 s]
P6	Volume-proportion of stormwater runoff for sampling [m3]

A drawback of using an LVS-system is the lack of time allocation of sampling cycles (Nickel and Fuchs 2021). Therefore, the sampling areas were monitored continuously using a security camera (blink mini, LLC) equipped with a motion detector to capture every sampling cycle and to test the effectiveness of sampling parameters. Hence, the exact sampling cycles were located and validated within runoff hydrographs. The volume of sample was measured using the known geometry of LVS and an average of four free-board measurements above water level. Further sample preparation steps are described in (3.3).

3.3.2.2. The Sampling plant at the SRT in separate system (L4)

The parameters [P_0 - P_6] mentioned earlier in the previous section described broadly the capacities of the control unit regardless of sampling location. While the parameters P_0 to P_3 had fixed values, the parameters P_4 to P_6 had to be adjusted and tested for each location explicitly. To do that, fictional parameterization scenarios (arrangements) with different setups were tested using long-term flow measurements in terms of event duration and total runoff volume. The scenarios varied in terms of sampling duration [P_5], sampling rate [P_4] and volume-proportion for triggering the digital sampling signal [P_6]. In total, twelve scenarios were tested against all runoff events from December 2019 to February 2020 [n=24] to see whether the entire event could have been theoretically captured and how often would the pump start during a certain sampling event. Furthermore, the sampling rate must guarantee near-isokinetic sampling conditions where sampling velocity in the sampling hose is about 80 to 200 % of the actual flow velocity. The scenario analysis was essential to capture common effective runoffs which are characteristic of the catchment area, avoid partial sampling of runoff events and protect the sampling pump from continuous operation. Table 3-4 shows the twelve parametrization scenarios in terms of P_4 - P_6 and the maximum runoff volume that can be sampled before the sampling tank reaches its full capacity.

Table 3-4 Summary of the twelve parametrization scenarios for the sampling location L4 under wet weather conditions

	Sampling rate [P_4]	Sampling duration [P_5]	Volume-proportion [P_6]	Number of sub-samples	Max. runoff sampled
	[L/s]	[s]	[m^3]	[-]	[m^3]
Scenario 1	0.75	15	5	89	445
Scenario 2	0.75	15	20	89	1780
Scenario 3	0.75	30	5	44	220
Scenario 4	0.75	25	10	53	530
Scenario 5	0.75	45	5	30	150
Scenario 6	0.75	45	20	30	600
Scenario 7	1	15	5	67	335
Scenario 8	1	20	20	50	1000
Scenario 9	1	30	5	33	165
Scenario 10	1	30	20	33	660
Scenario 11	1	45	5	22	110
Scenario 12	1	45	20	22	440

The potential of each scenario in capturing each runoff event was then tested against previous flow measurement data from December 2019 till June 2020 using NivuFlow Mobile 750, and a coverage rate in [%] was calculated. The coverage rate is categorized into red (< 100 %), green (100 - 300 %) and blue (> 300 %). For instance, scenarios 2, 4 and 8 indicated potential coverage rate greater than 100 %. However, scenarios 2 and 4 showed a low sampling rate of 0.75 L/s which translates into very low or non-isokinetic sampling velocity of about 0.382 m/s, considering an average runoff velocity of 0.85 m/s. In addition, scenario 2 is forcing the sampling pump to start very often which can cause mechanical stress or that sampling signals jam in the control unit. Finally, parametrization scenario 8 was picked to be the default setup for the sampling campaign. Table 3-5 shows the coverage rate of all paremetrization scenarios.

Table 3-6 Event coverage rates of the 12 parametrization scenarios for 24 different runoff events at L4

Event date	**Runoff volume [m^3]**	**Coverage rate [%] of parametrization scenarios 1-12**											
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
20/12/2019	983	45	181	22	54	15	61	34	102	17	67	11	45
21/12/2019	116	384	1534	190	457	129	517	289	862	142	569	95	379
22/12/2019	73	610	2438	301	726	205	822	459	1370	226	904	151	603
22/12/2019	90	494	1978	244	589	167	667	372	1111	183	733	122	489
24/12/2019	70	636	2543	314	757	214	857	479	1429	236	943	157	629
24/12/2019	50	890	3560	440	1060	300	1200	670	2000	330	1320	220	880
25/12/2019	131	340	1359	168	405	115	458	256	763	126	504	84	336
09/01/2020	64	695	2781	344	828	234	938	523	1563	258	1031	172	688
27/01/2020	411	108	433	54	129	36	146	82	243	40	161	27	107
27/01/2020	416	107	428	53	127	36	144	81	240	40	159	26	106
01/02/2020	455	98	391	48	116	33	132	74	220	36	145	24	97
01/02/2020	144	309	1236	153	368	104	417	233	694	115	458	76	306
02/02/2020	200	223	890	110	265	75	300	168	500	83	330	55	220
03/02/2020	227	196	784	97	233	66	264	148	441	73	291	48	194
03/02/2020	1013	44	176	22	52	15	59	33	99	16	65	11	43
10/02/2020	673	66	264	33	79	22	89	50	149	25	98	16	65
10/02/2020	508	88	350	43	104	30	118	66	197	32	130	22	87
12/02/2020	86	517	2070	256	616	174	698	390	1163	192	767	128	512
13/02/2020	482	92	369	46	110	31	124	70	207	34	137	23	91
19/02/2020	151	295	1179	146	351	99	397	222	662	109	437	73	291
19/02/2020	19	2342	9368	1158	2789	789	3158	1763	5263	868	3474	579	2316
20/02/2020	37	1203	4811	595	1432	405	1622	905	2703	446	1784	297	1189
23/02/2020	123	362	1447	179	431	122	488	272	813	134	537	89	358
24/02/2020	61	730	2918	361	869	246	984	549	1639	270	1082	180	721

3.3.2.3. The sampling plant at the SRT in combined system (L3)

In order to adjust the sampling parameters, a scenario analysis and a coverage test were conducted in analogy to the ones in 3.2.2.2. In particular, the parameters P_5 and P_6 were adjusted to reflect the differences between the two sampling locations in terms of catchment size and pump characteristics. Table 3-7 shows four parametrization arrangements and the favored scenario (2) which guarantees a representative sampling of runoff events up to 2160 m^3. Since the sampling pump at L3 is equipped with a suction sieve with 40 opening of Ø10 mm each, the sampling rate was set at a maximum value of 2.3 L/s to maintain near-isokinetic sampling velocities (refer to 3.1.3) of about 0.8 m/s at all times. A low near-isokinetic sampling velocities (<80%) was recorded briefly during peak flow but was tolerated since first flush was already over at this stage.

Table 3-7 Summary of the parametrization scenarios for the sampling location L3 under wet weather conditions

	Sampling rate [P_4]	Sampling duration [P_5]	Volume-proportion [P_6]	Number of sub-samples	Max. runoff sampled
	[L/s]	[s]	[m³]	[-]	[m³]
Scenario 1	2.3	8	20	54	1080
Scenario 2	2.3	8	40	54	2160
Scenario 3	2.3	10	20	43	860
Scenario 4	2.3	10	40	43	1720

In summary, Table 3-8 shows the final parametrization setups at both sampling locations in separate and combined systems along with other boundary conditions of sampling.

Table 3-8 Parametrization arrangements of the two wet weather flow sampling plants at L4 and L3

Parameter	Sampling setup plant at L4 in separate system	Sampling setup plant at L3 in combined system
P_0 [0,1]	Variable	variable
P_1 [min]	45	60
P_2 [0,1]	Variable	variable
P_3 [L/s]	variable	variable
P_4 [L]	≈ 40	35-80
P_5 [s]	20	8 - 15
P_6 [m³]	20	20-40
Other boundary conditions		
Time increment flow measurement [min]	1	1
Max. pumping rate [L/s]	1.3	2.3
Volume sampling tank [L]	1120	1120

3.4. Data curation and analysis

Throughout this work, a collection of diverse datasets was used to prepare for and run the monitoring campaigns, and to extract findings and trends from the results. For instance, flow data was essential to all work steps since we are primarily dealing with waterborne solid micropollutants. In this section, I will describe the methods and procedures that were applied to prepare datasets chronologically from all sampling locations. Subsequently, I will explain the methods and assumptions utilized to extrapolate MP emissions over the entire study area on a yearly basis. Finally, the correlation tests according to Pearson between MP concentrations and other wastewater parameters (COD, TS and LoI) in the samples are explained, as well as the correlations between MP concentration and stormwater runoff characteristics.

3.4.1. Flow data

Flow data utilized in this work was gained either by retrieving historical data from the operators of the drainage systems or by direct measurements conducted by the author. Flow values measured in *L/s* were obtained by applying the continuity equation at a known cross-section of a pipe or duct given average water level and velocity within a time interval. An exception to this statement applies to the greywater flow measurement at L5.2 (Birkenfeld), where only one water level sensor was mounted to record the difference in the greywater level (amount) in the collection tank. As a rule of thumb and since sudden flow changes are not expected, dry weather flow data was recorded in a 5-minute sequence to preserve the life of batteries and extend measurement duration. In case of sudden flow increase (e.g., beginning of a runoff event), flow meters in this work were set to switch to a 1-minute sequence to increase the sensitivity and reliability of sampling control unit and to be able to delineate representative runoff hydrographs.

3.4.1.1. Flow data at WWTP L1 and L2

The flow data at the WWTP Kaiserslautern of Kaiserslautern was obtained from the operators in two forms, 5-min datasets of sampling days to delineate daily flow patterns and to volume-proportionally mix the 24 samples that were taken time-proportionally into representative 24h composite samples (refer to above), and three-years daily flow summations from 2018 to 2020 to be used for yearly MP load estimations.

The long-term daily flow measurements were classified into dry and wet weather readings. Only median flow values were considered for yearly MP load estimations. Figure A 15 and Figure A 16 in appendix 8.3 shows the aggregation of all daily flow data at L1 from 2018 to 2020.

3.4.1.2. Effluent of SRT in combined sewer system at L3

The flow data in the effluent of SRT at L3 was both retrieved from the operator of the sewer system for the period before sampling (2019) and measured directly by the author using NIVUFlow Mobile 750 (2020-2021) to actively control sampling. Both datasets provided water levels and velocities in 5-min sequence during dry weather and 1-min sequence during wet weather. The change in recording sequence from 5-min to 1-min mode occurred automatically after a water level of 100 mm was reached, and was set back to 5-min mode once the water level dropped to any value below 100 mm.

In order to perform a dry/wet weather allocation, the sliding minimum method from DWA (ATV-DVWK-A 198) was applied instead to classify the daily flow into dry and wet weather flows. According to ATV-DVKW-A 198, the minimum daily flow value $Q_{d,min}$ of the ten days before and ten days after the actual measurement day is considered (21 days including the actual day). This $Q_{d,min}$ is then multiplied by a factor of 1.20 as $Q_{d,min20}$ to cover the range of fluctuations of the daily dry weather flow assuming a constant amount of extraneous water. Ultimately, any daily flow value greater than $Q_{d,min20}$ was then considered as a wet weather value.

In summary and for the period from May 2019 to December 2019, a median daily dry weather flow of 714 m^3/d (n=68, S=62 m^3) was calculated using an excel command. The median daily dry weather flow was the base for MP load extrapolations and the followed per population equivalent estimations of MP emissions. In addition to flow measurements, a maximum **water level** of about 120 mm was observed during dry weather conditions. This piece of information was very important when choosing the sampling height during wet weather to avoid clogging due to large objects in the flow and to avoid dry operation of the future sampling pump.

For **wet weather days**, an additional analysis on flow velocities was performed to define **isokinetic sampling** range. As mentioned above in 3.1.3, the sampling velocity adjusted using sampling pump's frequency inverter should remain at all stages between 80 % and 200 % of the real-time flow velocity. Figure 3-29 shows the 5-min flow velocity during wet weather for the time period from May to December 2019, with possible isokinetic sampling range assuming a constant sampling velocity of 0.8 m/s.

With the data curation steps described above, the sampling campaigns during dry and wet weather conditions were feasible. However, further curation steps on own flow data from 2020 to 2021 had to be performed to allow for MP load estimations and for possible correlation tests. The following metrics were needed:

- Runoff volumes of sampled events, as well as the entire yearly events to allow for MP load estimations.
- Estimation of dry weather hours prior to event
- Duration of runoff event.
- Precipitation duration.
- Precipitation height per runoff event.
- Maximum and average flow rates per event.
- Volume of runoff events.

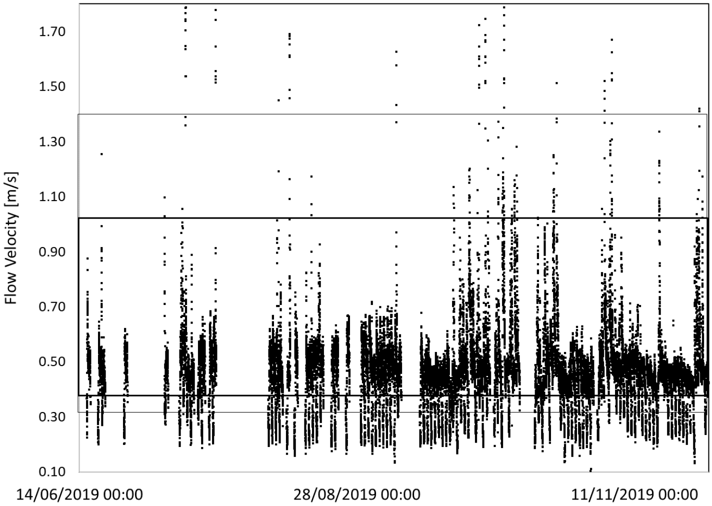


Figure 3-29 Possible isokinetic sampling range during wet weather from May to December 2019 assuming a constant sampling velocity of 0.8 m/s (inner rectangle), and near-isokinetic sampling range (60-220%) (outer rectangle)

For that, a **Python code** was written by Dr.-Ing. Amin Bakhshipour of WIR to cure and cluster flow data. Commencing with the import and organization of flow and precipitation data from the DWD weather station 2486 Kaiserslautern in CSV format (DWD 2022), the Python code utilized the Pandas library to generate data frames and arrays, while concurrently identifying and eliminating outliers and erroneous data points, and mitigating noise and anomalies through statistical filtering and smoothing methods. Subsequently, desired metrics such as dry weather hours and precipitation duration were extracted. During the data preprocessing phase, flow measurement and rain precipitation data were loaded, followed by the identification of dry and wet weather flow patterns based on wastewater level criteria (below 120 mm) and consecutive periods of dry weather flow defined by a 3-hour period with 0 mm precipitation. This was succeeded by rain event clustering to identify distinct rain occurrences and cluster precipitation heights per event, along with clustering runoff amounts per rain event. Further steps included measuring average and maximum flow for each period, determining the time taken to reach maximum flow for each runoff event, and ultimately outputting, cleaning, and clustering the processed data, with clusters visualized alongside pertinent statistics for comprehensive analysis. Finally, the code output runoff metrics is shown in Table A 2.

3.4.1.3. Influent of SRT in separate sewer system at L4

The flow data from the influent of SRT in separate sewer at L4 was recorded by the author using a NIVUFlow mobile 750 in a 5-min sequence during dry weather and 1-min after a water level of 50 mm is reached. The flow data was then cleaned from outliers and errors using excel tools. Finally, since the influent canal ran dry during dry weather flow and no wastewater component was mixed with the stormwater runoff, a simple **linear interpolation and aggregation** process was run on excel to cluster and extract the runoff volumes of all runoff events during the time period from 2020 to 2021. The output data was later used to estimate MP emissions from the separate catchment area.

3.4.2. Extrapolation of MP emissions

3.4.2.1. Specific dry weather emissions per population equivalent

The extrapolation of average daily MP concentration into specific yearly loads per population equivalent ($B_{MP,a}$) [g/p.e.*a] was conducted based on yearly median daily flow estimations under dry weather conditions ($Q_{DW,m,0mm}$) (eq. 11), i.e., < 0.0 mm precipitation. The number of p.e. was retrieved from own estimations of WWTP operators (Stadtentwässerung Kaiserslautern 2021). The accuracy of $B_{MP,a}$ value is dependent on the size of the catchment and number of p.e. considered.

$$B_{MP,a,ca,dw} = \frac{C_{m,total} \times [Q_{DW,m,0mm} \times 365]}{p.\text{e.}} \tag{11}$$

3.4.2.2. *Specific wet weather emissions per unit drained area*

For stormwater runoff, the number of p.e. is indirectly affecting the magnitude of MP released from the catchment. In other words, the population density in a catchment area can affect the load of MP released but is by far not the dominant factor as in the case of dry weather emissions. In this case, other factors such as traffic density, distance from commercial centers, type of settlement or size of industrial areas also play a role in the amount of MP released. Furthermore, the MP emissions under wet weather conditions were measured at two sub-catchments within the UDS representing only 3.6 % of the entire catchment area. Therefore, for runoff emissions, the specific emission estimation per effective drained impervious area (A_{EIA}) and sub-catchment $B_{MP(L3,L4)}$ [g/ha] is measured (refer to eq. 12).

$$B_{MP,ha,ww\ (\text{L3,L4})} = \frac{C_{m,total} \times Q_R}{A_{EIA}} \tag{12}$$

In order to extend the emission rates from the sub-catchments level into the entire catchment of the WWTP, the author suggested two approaches. A simplified approach, where the specific MP loads are multiplied by total effective drained area, and a second alternative approach where the following considerations were proposed:

- Seasonal factor for MP emissions excluding tire abrasion components
    - factor of 1 for summer emissions due to longer sunshine hours and intensified disintegration effect of MP from littering sources and increased outdoor activities in the catchment.
    - factor of 0.9 for spring and autumn seasons
    - factor of 0.7 for winter
- No seasonal factor for tire abrasion component (SBR). Although summer tires are releasing slightly less emissions, winter tires consists of larger portion of natural rubber, which is by definition (refer to 2.1) not a MP component (Thomas Kroher 2021)

Thus, one can estimate the yearly MP emissions from the sub-catchment at L3 or L4 by applying equation 12 for the four seasons (Eq. 13) and adding the SBR component to the sum in equation 14:

$$\begin{aligned} B_{MP-SBR,ha,R.a(L3,L4)} \\ &= B_{MP-SBR,ha,R.\text{summer}} + B_{MP-SBR,ha,\text{R.winter}} \\ &+ B_{MP-SBR,ha,R.\text{spring}} + B_{MP-SBR,ha,R.autumn} \end{aligned} \tag{13}$$

$$B_{MP,ha,R.a(L3,L4)} = B_{MP-SBR,ha,a} + B_{SBR,ha,a} \tag{14}$$

Once the yearly load of MP from the stormwater runoff of the smaller catchments (L3,L4) is calculated, three attributes of the studied sub-catchments were selected to compare these catchments with rest of sub-catchments within the UDS of Kaiserslautern (64 sub-catchments in total). These attributes are:

- Population density compared to studied sub-catchments, factor range of 0.1 – 2 (F_1), assuming that it mainly affects SBR emissions.
- The traffic density in and around the sub-catchment, factor range of 0.8 – 1.2 (F_2) in comparison to a traffic density of 4200 vehicle/d at L3 and ≈ 500 vehicle/d at L4. Hence, a factor of 1 is set to traffic density of around 4200 vehicle/d at the center of the catchment, 0.8 at density less than 1500 vehicle/d and 1.2 at density larger than 7500 vehicle/d, assuming that traffic density mainly affects SBR emissions. The classification of sub-catchments in this work was performed according to a rough spatial interpolation (Triangulated Irregular Network (TIN)) based on traffic density data of seven junctions in the catchment provided by LBM RLP (2015). This approach is over simplified and is probably underestimating SBR emissions at one point and overestimating them at another, but it is a tool to shed some light on this important parameter. For a reliable traffic density estimation, more complex analyses (e.g., Ant Colony Optimization Algorithm) are needed.
- Location of the sub-catchment within the UDS, i.e., distance from city center or pedestrian areas, factor range of 1 – 1.2 (F_3) [1: Catchment at the edge of UDS, 1.1: catchment outside city center, 1.2: catchment in city center], assuming that it mainly affects MP emissions without SBR.

The size of A_{EIA} and the effective fraction of all 64 sub-catchments that build up the entire UDS in Kaiserslautern, as well as the population density, were retrieved from the input data of a hydrological-hydrodynamic deterministic pollutant load calculation model (Scheid 2022; Schmitt 2004). The factor (F_2) for each sub-catchment was then calculated by dividing the population density by the population density at L3. In addition, geographically known sub-catchments were plotted as polygons using QGIS (version 3.30.2) supported by an open street map to test the factor allocation regarding land use, distance from commercial centers and densely commuted roads in the city (refer to Figure A 18 in appendix 8.5.1). Geographically unknown sub-catchments (not its A_{EIA}) were given a factor of 1.

According to the assumptions above, total yearly wet weather MP emissions from the entire UDS can be estimated using equation 15, where the author chooses to apply the factors 1 and 2 on traffic related emissions only and factor 3 on non-traffic related emissions:

$$B_{MP,a,R.total} = \frac{\sum_{n=1}^{63}\left[\left(\left(B_{SBR,ha,a} \times F_1 \times F_2\right) + \left(B_{MP-SBR,ha,a} \times F_3\right)\right) \times A_{EIA}\right]}{A_{EIA.total}} \quad (15)$$

3.4.3. Correlations of MP concentrations to wastewater parameters using Pearson correlation test[15]

The Pearson correlation test is a statistical method used to measure the strength of the relationship between two continuous variables. In the case of MP concentrations in wastewater and wastewater matrix parameters, this test can be used to determine whether there is a correlation between the two variables and the direction of that correlation (positive or negative).

The Pearson correlation coefficient (r) (eq. 16) is a value that ranges between -1 and +1, where a value of -1 indicates a perfect negative correlation, a value of +1 indicates a perfect positive correlation, and a value of 0 indicates no correlation. The closer the absolute value of r is to 1, the stronger the correlation between the two variables. To perform a Pearson correlation test, data on both MP concentrations and wastewater matrix parameters must be collected. The data can then be plotted on a scatter plot, with MP concentrations on one axis and the wastewater matrix parameter on the other axis. The scatter plot will show the distribution of data points and give an idea of the relationship between the two variables. Once the data has been plotted, the Pearson correlation coefficient was calculated using a excel tools. The resulting value of (r) can then be interpreted to determine the strength and direction of the correlation between the two variables.

$$r = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}} \quad (16)$$

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[15] This section was partially written with the help of the artificial-intelligence (AI) tool ChatGPT 4.0 for experimental purposes.

where:

r	Pearson Coefficient
n	Number of readings
x and y	are the two variables being correlated

This formula calculates the covariance between the two variables, which measures how much the two variables vary together, and divides it by the product of the standard deviations of the two variables, which measures how much each variable varies on its own. For example, if the calculated r value is +0.8, this indicates a strong positive correlation between microplastic concentrations and the wastewater matrix parameter. This means that as the concentration of MP in the wastewater increases the concentration of the wastewater matrix parameter also tends to increase. On the other hand, if the calculated r value is -0.3, this indicates a weak negative correlation between the two variables, meaning that as the concentration of MP in the wastewater increases, the concentration of the wastewater matrix parameter tends to decrease. Overall, the Pearson correlation test provides a useful tool for analyzing the relationship between MP concentrations in wastewater and wastewater matrix parameters and can help to identify potential sources and pathways of MP pollution in the environment.

Regarding MP emissions, the author has sought potential correlation between MP emissions and three parameters that reflect the organic and particulate characteristics of MP. Specifically, COD, TS, and loss on ignition were chosen for Pearson testing with MP.

4 Results and Discussion

In this chapter, I present the findings from comprehensive MP monitoring campaigns conducted in diverse locations within the UDS of the city of Kaiserslautern, including WWTP, combined dry weather flow of a small catchment at the edge of the larger catchment, greywater (not from Kaiserslautern) flow, and stormwater runoff from separate and combined sewer systems. A detailed account of all samples captured during this work is shown in Table A 3 in appendix. The findings below are divided into three groups, lessons learned from handling complex and large volume samples, description, quantification and classification of MP emissions and reflections on the fate of MP emissions transported in a large UDS.

Each sampling location offers a unique perspective on the distribution, composition, and fate of MP in UDS. The WWTPs represent critical points of interest as they serve as primary hubs for the treatment and discharge of wastewater. Effluents from WWTPs contain a wide range of micropollutants, including MP, which can potentially enter aquatic ecosystems. Investigating MP concentrations and characteristics in WWTPs can provide insights into the efficiency of treatment processes and the potential for microplastic release into receiving waters.

The dry weather flow of a small catchment reflects the composite input from residential, commercial, and industrial areas. This monitoring location enables more accurate assessment of MP loads originating from various sources, including household activities, urban infrastructure, and local industries. Understanding the distribution patterns and types of MP in this catchment can help identify hotspots and prioritize targeted interventions.

Greywater flows have been identified as potential sources of MP pollution due to the presence of personal care products, synthetic fibers, and other household sources of MP. By examining the characteristics, we can gain insights into the contribution of household activities to the overall MP burden in UDS.

Stormwater runoff from separate and combined sewer systems is of particular interest due to its direct connection to surface waters during rainfall events. This type of runoff carries a wide range of MP, from urban surfaces, roadways, and drainage networks. Investigating the occurrence and composition of MP in stormwater runoff can provide valuable information on the transport mechanisms, accumulation zones, and potential impacts on downstream ecosystems.

For each location, a yearly emission value per population equivalent or drained area is derived from the direct measurements and according to the methodologies described extensively in 3.4.2.

4.1. Microplastic occurrence in urban drainage systems

This section aims to describe and analyze the results obtained from monitoring campaigns under dry and wet weather conditions (**Phase I and II**) which were described earlier in (3.2), focusing on particle size distributions and polymer types. Additionally, a comparison between dry weather and wet weather conditions, as well as separate and combined wet weather emissions, will be presented. Furthermore, the findings of correlation tests will be discussed, highlighting their significance in identifying relationships between MP concentrations and the concentration of TS, COD and LoI. The lessons learned from running these campaigns will also be investigated, shedding light on the valuable insights gained from this research. Finally, this section will describe the advantage of the applied monitoring strategies, emphasizing why they outperform alternative approaches.

4.1.1. Occurrence in dry weather streams

After receiving the raw results from the BAM laboratory in Berlin, which included concentrations [µg/mg] per size fraction and polymer type referring to original sample volume, the aggregated results from the Phase I monitoring campaign of dry weather streams were analyzed. Subsequently, the data curation methods outlined in section (3.4) were deployed to extend the emissions for larger catchment areas and calculate yearly specific values.

4.1.1.1. WWTP Kaiserslautern at L1 and L2

Influent of WWTP behind screens

During the period from November 2018 till March 2019, five 24h composite samples were taken, four of these samples were thermally analyzed in the laboratory of the BAM to characterize MP emissions in terms of PSD and polymer type from the entire catchment area of WWTP. The results shows that PE is dominant in the total load (86%) and in the sizes from 50-100, 100-500 and 500-1000 µm with an average concentration of 244 µg/L. (Figure 4-1). No similar dominance was spotted in the size fraction 5-50 µm but also without any considerable relevance in the overall PE occurrence. In contrast, the remaining MP represent only 14 % of the total load. In Europe, about 30% of all plastic products utilized in domestic, commercial, and industrial branches are made of PE-HD or low density PE (PE-LD) compounds (Plastics Europe 2021). PE-compounds are mainly found in pipe materials, packaging materials, reusable bags, trays and containers (Plastics Europe 2021), products that are used intensively and have direct access to dry weather flow from households and commercial/industrial areas.

PP is also used extensively as a packaging material in urban areas. However, it represents only 6.6 % of overall MP load detected. Hence, mechanical, and thermal stabilities of both PP and PE might play a role in its degradation and release potentials. In the case of PS with the lowest share of 3%, the consumption rates in urban areas seem to be consistent with its release counterparts.

SBR, a main component in tire materials and mainly stormwater-borne, was remarkably detected in dry weather influent of the WWTP (5.8 %). Here plays, perhaps, the large size of the catchment area, some hotspots (e.g., tire workshops) as well as the presence of many retention-structures a significant role in holding and releasing “old” SBR that was washed off during previous runoff events.

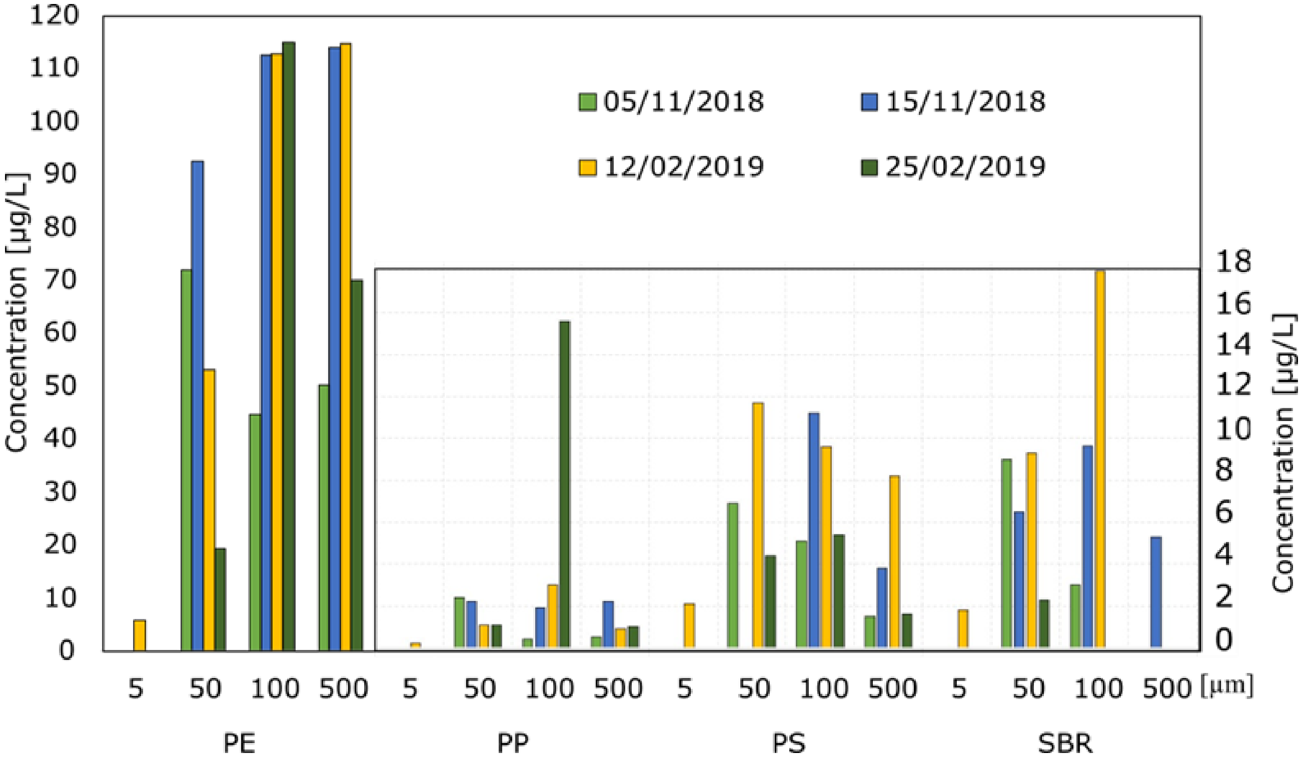

Figure 4-1 Polymer concentrations in different sieve fractions in the influent of WWTP (L1, n =4)

The approximate MP loads in the influent of the WWTP during dry weather conditions are calculated using equation 11 and shown in Table 4-1

Table 4-1 Estimated yearly microplastic loads based on concentrations of all fractions in 24h-composite samples (n=4) and the median dry weather flow of the years 2018-2020 in inflow of WWTP behind screens (L1)

Population equivalents	210,000	p.e.[16]
Median daily dry weather influent (3 year data)	47,819	m^3/d
Daily polymer concentration	286	µg/L
Total annual polymer load (n=4)	4,996[17]	kg/a
Per population equivalent annual polymer load	23.8	(g/(p.e.*a))
Per population equivalent annual PE load	20.1	(g/(p.e.*a))
Per population equivalent annual PP load	1.6	(g/(p.e.*a))
Per population equivalent annual PS load	0.7	(g/(p.e.*a))
Per population equivalent annual SBR load	1.4	(g/(p.e.*a))

Effluent of secondary settling tanks of the WWTP

The MP emissions in the effluent of the secondary settling tanks at the WWTP Kaiserslautern were monitored by deploying two different sampling setups. A conventional sampling using LVS and long-term integral sampling methods (refer to 3.3.1.1). While conventional sampling method was performed four times in 2019, integral long-term sampling was performed at three different occasions to compare the results with the conventional sampling and to test the treatment capacity of a pilot plant for removing organic micropollutants in the effluent of the secondary settling tanks.

Conventional sampling using LVS

The results of this sampling campaign (Figure 4-2) show that a drastic reduction of MP concentrations occurred within the WWTP. So that the average daily concentration of all size fractions in the effluent of WWTP is only 11 µg/L. Table 4-2 gives a rough projection of yearly MP emissions of approx. 189 kg/a or a

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[16] Not to confuse it with Polyethylene, PE

[17] The yearly MP resulting from considering the exact volumes of sampling day and the median daily influent of 2019 is 4,727 kg/a, i.e., only 1.6 % deviation from the load based on the 3-year daily dry weather median influent and average MP concentration (n=4). See Table A 4 in appendix 8.4.1

yearly p.e. load of 0.94 (g/(p.e.*a)). These results suggest an overall elimination rate of about 96 % of all MP entering the WWTP. However, sampling at the inflow of WWTP (L1) was carried out behind screens (Ø3 mm) (refer to 3.3.1.1). Hence, the actual removal rate is rather higher than 96 %. The specific emission rate per population equivalent is consistent with the ones from Simon et al. (2018) and Conley et al. (2019) where emission rates of 0.56 and 0.34 - 0.68 (g/(p.e.*a)) respectively were suggested. Similarly, an average WWTP removal rate of 97.26 ± 1.87% was estimated by Murphy et al. (2016), Cabernard et al. (2016), Minteng et al. (2017), Talvitie et al. (2017), Gies et al. (2018), Simon et al. (2018), Breitbarth and Urban (2018) and Carr and Thompson (2020), with varying detection methods and lowest fraction size considered. Table 4-3 shows the removal rates of MP at different WWTPs where the lowest sieve size varies from 10 µm to 1000 µm, and the detection method is mostly particle counting. The highest removal rates were reported from visual counting practices and with large sieve-size samplings.

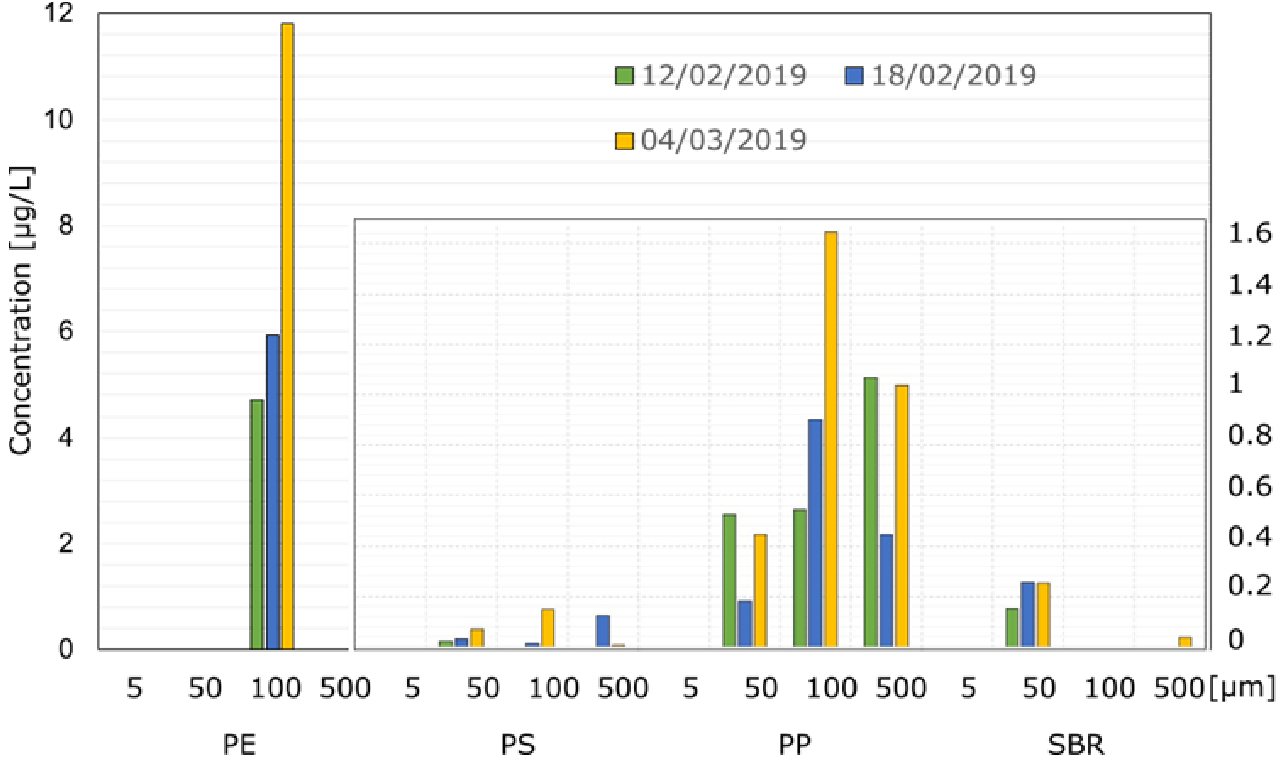

Figure 4-2 Polymer concentrations in size fractions (5-1000 µm) in the effluent of WWTP, 4h composite samples (L2, n=3)

In view of the different polymer types, PE was still dominant with a high share of about 77 % of all detected polymers or 147 kg/a. However, mainly the size fraction 100-500 µm is yet present, while smaller fractions <100 µm are not detected. PP and PS showed no considerable change in PSD with slightly higher removal rate for PS. The traces of SBR found in influent at L1 of WWTP were efficiently removed, with the fractions greater than 100 µm completely eliminated. To the best of author's knowledge, no previous studies investigated the changes in PSD of MP polymers before and after treatment in a municipal WWTP.

Similar to Table 4-1, Table 4-2 gives an estimation to yearly MP emissions from the effluent of secondary settling tanks by deploying equation 11 to calculate the yearly specific MP load.

Table 4-2 Estimated yearly microplastic loads in effluent of WWTP (L2) based on concentrations of all size fractions in 4h-composite samples (n=3)

Daily polymer concentration	11	µg/L
Total annual polymer load (n=3)	189	kg/a
Per population equivalent annual polymer load	0.94	(g/(p.e.*a))
Per population equivalent annual PE load	0.73	(g/(p.e.*a))
Per population equivalent annual PP load	0.19	(g/(p.e.*a))
Per population equivalent annual PS load	0.01	(g/(p.e.*a))
Per population equivalent annual SBR load	0.01	(g/(p.e.*a))

Table 4-3 Removal rates of MP at different WWTPs worldwide with heterogenous sampling and detection methods

WWTP	Removal rate [%]	Detection Method	Remarks
Vancouver, Kanada (Gies et al. 2018)	99	visual separation then FT-IR	Particle count
10 WWTP in Denmark (Simon et al. 2018)	98.3	enzymic digestion then FT-IR	10 µm filter
Four WWTPs in Northern Hesse, Germany (Breitbarth and Urban 2018)	96	1mm particle counting	1mm net in effluent stream. Particle count in influent WWTP. Large plant showed highest removal rate of 99.5 %

12 WWTPs in Lower Saxony, Germany (Mintenig et al. 2017)	97	enzymic digestion then FT-IR	10 µm, only large WWTPs of grade 5 (Germany, >100k p.e.)
One WWTP in Scotland (Murphy et al. 2016)	95% -99%	chemical digestion with H2O and FT-IR	-
8 WWTPs in Southern California(Carr et al. 2016)	99	visual	45 µm sieve size
Sweden (Magnusson and Norén 2014)	98	visual	~ 98% removal rate for MP >300 µm und ~ 85% for > 20 µm.

Integral sampling using SBs

At the beginning of February 2019, an early version of the sedimentation boxes (SB), with direct feeding through openings in flow direction, was deployed for about 13 days. Then the box was removed from the effluent canal for further analysis. The obtained sample (38.8 L) was subsequently homogenized in the laboratory and a sub-sample of approximately 6 L was wet sieved (refer to 3.1.5).

The results from the previous sampling showed that only three polymers could be captured in the SB, namely PP, PS, and natural rubber. Due to noise signals during thermal analyses, PE could not be correctly detected, therefore, the results here do not include PE-content. The highest content of which was polypropylene with a total mass of about 107 mg/13.days. In total, considering an average flow rate of 700 l/s, an average MP concentration of 0.15 µg/L is expected to be recorded. In comparison to the results from conventional sampling campaign (10,9 µg without PE/l), the SB indicated much low microplastic emissions.

In May and June 2021, a modified version of the SBs was again deployed to sample the effluent of secondary settling tanks. In addition, a second box was deployed in parallel to sample the effluent of a pilot treatment plant for micropollutants' removal using ozone unit and activated coal filter. The results of the two sampling cycles show that the average MP concentrations in the effluent of secondary settling tanks are as low as 373 µg/m^3 (cycle 1) and 167 μg/m³ (cycle 2). When passing through the combined ozonation plant/GAC-filter, 99% and 92% (Figure 4-3) of MP particles are further removed to concentrations of about 3.5 μg/m³ and 14 μg/m³, respectively (Figure 4-4).

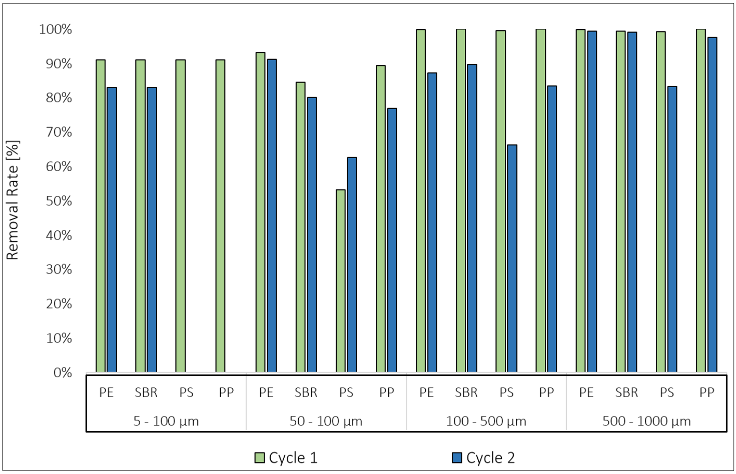

Figure 4-3 Removal rates of MP in the effluent of a pilot plant for the removal of organic micropollutants using ozonation and GAC filter aggregates

PE was the most abundant polymer representing on average for both cycles 93 % and 87 % of the total concentration before and after combined removal, PP with 3.5 % and 6 %, and SBR with 3 % and 6 % respectively (Figure 4-4). Considering a PSD before the combined removal of MP, particles within the size fraction (100 - 500 μm) were the most abundant representing 54 % of all polymers followed by the size fraction (500 - 1000 μm) and (50 – 100 μm) representing 24 % and 22 % each. However, the PSD after the combined removal shows a different picture. Here the size fraction (50 – 100 μm) turns to be the most abundant representing 67 % of all polymers followed the fraction (100 – 500 μm) with only 30 % representation. Nevertheless, both size fractions ended up with comparable concentrations of about 4.2 μg/m³ each. This shift in PSD was also observed in TS content after the combined removal. The size fraction (100 – 500 μm) loses the lion share to size fraction (50 – 100 μm) (Figure A 30).

The removal of MP particles in the micropollutant plant occurs mainly in the GAC filter. However, in comparison to Benstöm et al. (2014) with a setup of GAC filter only, higher removal rates of solid particles (5-1000 μm) of more than 99 %, compared to 81-87 %, were noted with the combined removal of ozonation and GAC filtration. This tendency is likely referred to the prior reduction of surface charge of particles due to ozonation. In addition, the removal rates of MP in this study (90-96 %) are comparable to the results from Kim and Park (2021) with electro coagulation step prior to GAC filtration. This notion suggests that a pretreatment step using ozonation can lead to enhanced removal rates inside GAC-filters.

The small MP size fraction (5 – 50 µm) was hardly detected before and after the combined removal. This can be related to a drawback in the sampling method where 30-100% of this size fraction can be captured depending on the flow rate into SB. However, the use of the same flow rates in the two SBs is theoretically neutralizing this drawback and keeps the removal rate of this size fraction yet relevant. Further investigations on the small MP particles (<50 µm) to determine the dominant removal mechanism (adsorption vs. filtration) with this setup of ozonation and GAC-filter.

The further removal of MP at treatment plants using the mentioned setup can be seen as an added value to the original purpose of removing OMP. Considering an average MP removal rate of ≈ 96% of the whole effluent stream from secondary clarifiers, and an expected annual MP emission of about 0.94 (g/(p.e.*a)), the combined removal of MP and OMP can reduce the specific annual emission to about 0.042 (g/(p.e.*a)).

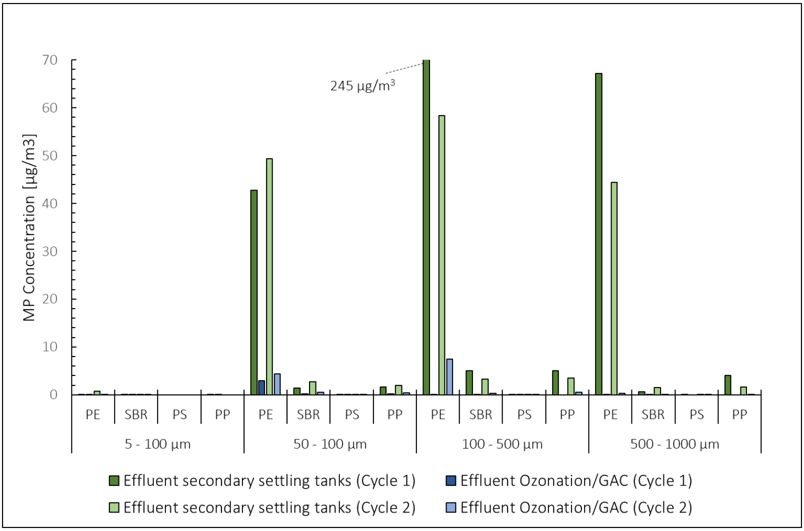

Figure 4-4 Comparison between MP concentrations in the effluent of secondary settling tanks and in the effluent of pilot plant for the removal of organic micropollutants along cycles 1 and 2

4.1.1.2. Dry weather flow at L3

During this work, two sampling approaches were adopted to sample the dry weather effluent of the combined system (refer to 3.3.1.2). In total, eight samples were taken using approach I and II, six samples with approach I (three grab samples per day) and two with approach II (volume-proportional/24 grab samples over 12 h).

The results in Figure 4-5 suggest an average daily concentration of 794 µg/L in this wastewater stream. High average concentrations of PE with 717 µg/L (all size fractions) and low concentrations of PS and PP with about 26 µg/L and 50 µg/L were detected. In addition, the size fraction 100-500 µm showed the highest concentrations in all detected polymers, while the size fraction 50-100 µm came in all polymers second in rank. The sampling location at L3 (combined sewer) is the closest to sources of MP. Hence, the particle size distribution (PSD) shown in Figure 4-5 is the closest representation of the actual MP occurrence under dry weather conditions.

In contrast to dry weather samples from the influent of the WWTP, SBR remained undetected (not existing or below detection limit). In addition, about 51 % of polymers were detected in the size fraction 100-500 µm, while only 22 % were detected in the same size fraction in the influent of the WWTP (L1) at the end of the catchment area. This suggests that changes in PSD are expected to occur during the residence and transport of MP particles in sewage network due to the extensive interaction with sewage particles, especially organic content, and also low flow velocities at some locations. Table 4-4 shows the changes of PSD of MP along its journey from near the source at L3 along the entrance of the WWTP (L1) and finally at the effluent of the same WWTP (L2). Remarkably, the normally distributed PSD-curve near the MP source at L3 becomes flattened at L1.

Table 4-4 Particle size distribution of MP within the investigated size fractions of 5-50 µm, 50-100 µm, 100-500 µm, and 500-1000 µm, along with the corresponding mass percentages in the dry sediments of three wastewater streams at L1, L2, and L3 under dry weather conditions

Location	**Distribution of microplastics in samples**			
	5-50 µm	50-100 µm	100-500 µm	500-1000 µm
Dry-Weather flow (L3)	4.4%	33.0%	50.9%	11.7%
Influent WWTP (L1)	19.0%	29.9%	21.6%	29.4%

Effluent WWTP (L2)	0.0%	5.9%	77.8%	16.3%
	Mass percentage within dry sediments			
Dry-Weather flow (L3)	0.24%	0.96%	0.71%	0.35%
Influent WWTP (L1)	0.46%	1.29%	0.41%	1.15%
Effluent WWTP (L2)	0.0%	0.4%	4.9%	3.6%

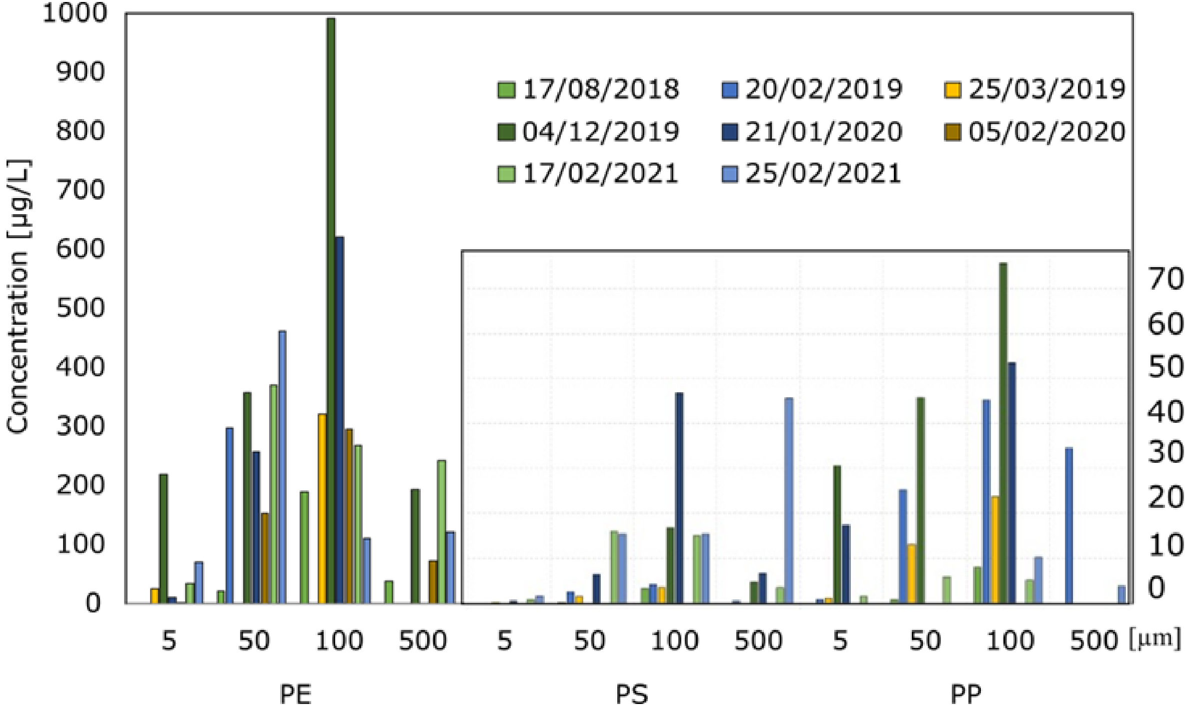

Figure 4-5 Polymer concentrations in dry weather flow of SRT in combined system at L3, Approach I (n=6) from August 2018 till February 2020, Approach II (n=2) on 17th and 25th of February 2021

Based on daily flow measurements at the sampling location, the daily dry weather volumes (see Table A 5 in Appendix 0) on sampling days were summed and used to estimate yearly per-capita MP emissions from the sub-catchment in combined system at L3 (Table 4-5). With an average MP concentration of 855 µg/l from approach 1 (n=6) and an average of 908 µg/l from approach 2 (n=2), the results from the two sampling approaches are comparable to one another. With such, more samples can be retrieved with less effort. However, reliable flow measurements and accurate dry weather flow analysis are necessary to guarantee representative sampling to derive reliable results. Extending these results to yearly loads per population equivalents, an average MP load of 31.3 g/(p.e.*a) is expected. In addition, both in combined sewer system at L3 and in the influent of the WWTP, PE constitutes the lion's share of MP yield and , therefore, a promising reference polymer for total MP yield.

Table 4-5 Dry weather polymer emissions from sub-catchment area in combined system (L3 during DW)

Population equivalents	5000	p.e.
Average daily polymer concentration	794	µg/L
Mean per p.e. polymer load, approach 1 (n = 6)	30.5	(g/(p.e.*a))
Mean per p.e. polymer load, approach 2 (n = 2)	33.4	(g/(p.e.*a))
Mean per population equivalent polymer load (n=8)	31.3	(g/(p.e.*a))
Per population equivalent annual PE load	28.28	(g/(p.e.*a))
Per population equivalent annual PP load	1.98	(g/(p.e.*a))
Per population equivalent annual PS load	1.04	(g/(p.e.*a))

In comparison to per-capita MP loads of the whole catchment area, higher values appear at the sub-catchment area upstream the WWTP; (30.54 (g/(p.e.*a)) with sampling approach I and 33.41 (g/(p.e.*a)) with approach II, or an average of 31.3 (g/(p.e.*a)) at L3 and 23 (g/(p.e.*a)) at L1 (Table 4-6). However, these values maintain a comparable order of magnitude considering the uncertainties involved with flow measurements at both locations and with actual p.e. number, as well as analytical uncertainties. In addition, sampling behind the screens plays here a potential role in underestimating actual MP loads entering the WWTP.

Table 4-6 Summary of estimated yearly MP loads in influent and effluent of WWTP (L1 and L2) and at the small catchment (L3) under dry weather conditions based on concentrations of all size fractions

	L1 (n=4)	**L2 (n=3)**	**L3 (n=8)**	
Average daily concentrations of polymers	286	11	794	[μg/L]
Total annual polymers load	4996	189	n.a	[kg/a]
Annual polymer loads	23.8	0.94	30.1	(g/(p.e.*a))
Average PE loads	20.1	0.73	27.2	(g/(p.e.*a))
Average PP emissions	1.6	0.19	1.9	(g/(p.e.*a))
Average PS emissions	0.7	0.01	1	(g/(p.e.*a))
Average SBR emissions	1.4	0.01	[-]	(g/(p.e.*a))

4.1.1.3. Greywater emissions at L5.1 and L5.2

The results from the first sampling location (Reinighof) showed that only PE and PP are detected and fairly distributed to size fractions, as well as traces from PS (Figure 4-6). After discussing the results with the residents of the compound it was clear that PP is likely released from sewers, which are made solely from this material. Natural rubber (NR) is a biodegradable material used in gloves, toys, and clothes. No reliable specific MP emissions per p.e. could be calculated due to missing information of greywater flow rates and number of residents at the time of sampling.

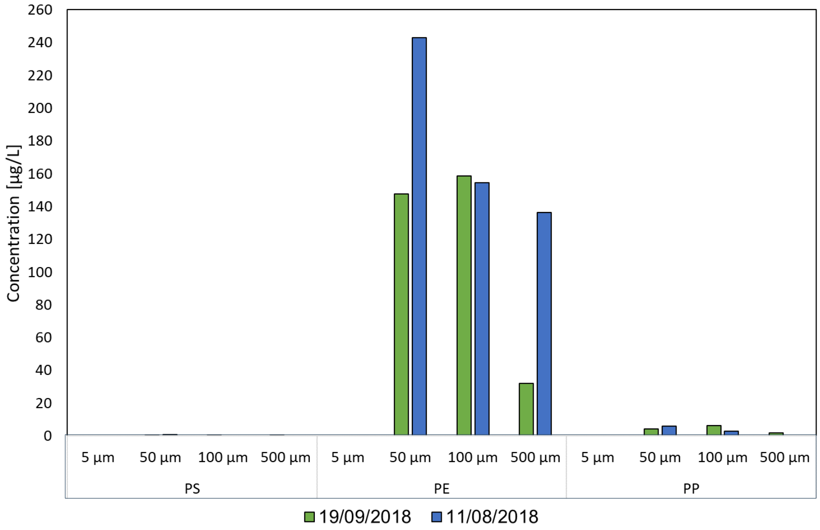

Figure 4-6 MP analysis at Reinighof in 2018 revealed that PE, PP and PS are released from the settlement

At the second greywater sampling location in the dormitory at the Umwelt-Campus Birkenfeld of the Hochschule Trier, the results in Figure 4-7 show that only PE is present in significant amounts in the greywater samples (greywater without washing machine and only partly kitchens connected) from L5.2, especially in the size fractions from 50 µm to 500 µm. PP and PS were detected only in small amounts. From these results, an annual MP emission load of about 5 (g/(p.e.*a)) can be derived as a rough estimation of greywater accumulation. In comparison to the yearly emissions from dry weather flow (refer to Table 4-6) of 30 (g/(p.e.*a)), the load from greywater is relatively low. The exceptionally low specific MP emission may be attributed to the lack of a washing machine in the building. Furthermore, the kitchens are only partially linked, and the students likely engage in minimal cooking activities, resulting in different behavior compared to an average household. For instance, entries such as cutting up fruit nets might be infrequent. Additionally, as the location is primarily residential within a university setting, there are no contributions from small businesses.

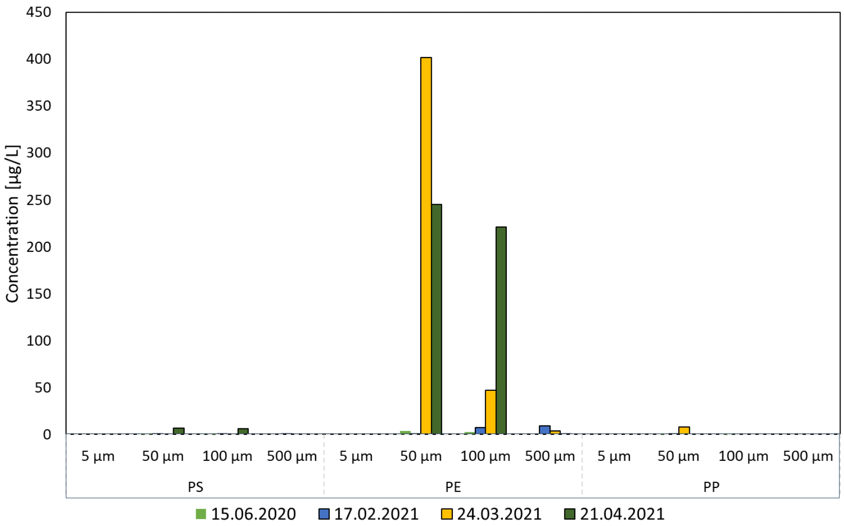

Figure 4-7 Results of MP analysis of greywater samples at Umwelt-Campus Birkenfeld (L 5.2, n=4)

4.1.2. Occurrence in wet weather streams

After receiving the raw results of the monitoring campaign of wet weather streams (**phase II**) from the BAM laboratory in Berlin, which included concentrations [µg/L] per size fraction and polymer type referring to original sample volume, the aggregated results were analyzed. Subsequently, the data curation methods outlined in section (3.4.2) were deployed to extend the emissions for larger catchment areas and calculate yearly specific values.

4.1.2.1. Sampling campaign in separate sewer system at L4 (2020/2021)

The SRT in separate system was the first location to test novel sampling system described in (3.3.2.1). During the period from July 2020 to April 2021, nine runoff events were sampled and analyzed for their MP content.

The thermal detection revealed that PE is the most abundant polymer in stormwater runoff (Figure 4-8) followed by SBR. PE concentrations occurred in all samples with a minimum average concentration of **44 µg/L** (0 - 138 µg/L, n=9) in the size fraction **50-100 µm** and a high average concentration of **249 µg/L** (13 - 628 µg/L, n=9) in the size fraction **100-500 µm** . In contrast, SBR loads showed a strong positive correlation with the number of dry weather days prior to rain event, with a Pearson coefficient of $r = 0.8205$ (Table 4-7), with a minimum average concentration of **9 µg/L** (1 - 84 µg/L, n=9) in the size fraction **500-1000 µm** and a high average concentration of **88 µg/L** (0.4 - 524 µg/L, n=9) in the size fraction **100-500 µm** (Figure 4-8). In addition, both, PE and SBR, were abundant the most in the size fraction of 100-500 µm, counting for 58 % and 45 % of the total polymer load respectively. This can be seen consistent to the findings of a study on tire particles abundance which found that the median value of size distributions of tire abrasion from urban areas is 140 µm (Venghaus et al. 2021).

While PE and SBR were the most abundant polymers in runoff samples, PS and PP represented only 2.3 % and 2.4 % of all MP load. In addition, polymers in the size fraction 100-500 µm counted for 55 % of total polymer load. The rest was distributed in the remaining size fractions as follows; 5-50 µm (12 %), 50-100 µm (17 %) and 500-1000 µm (18 %).

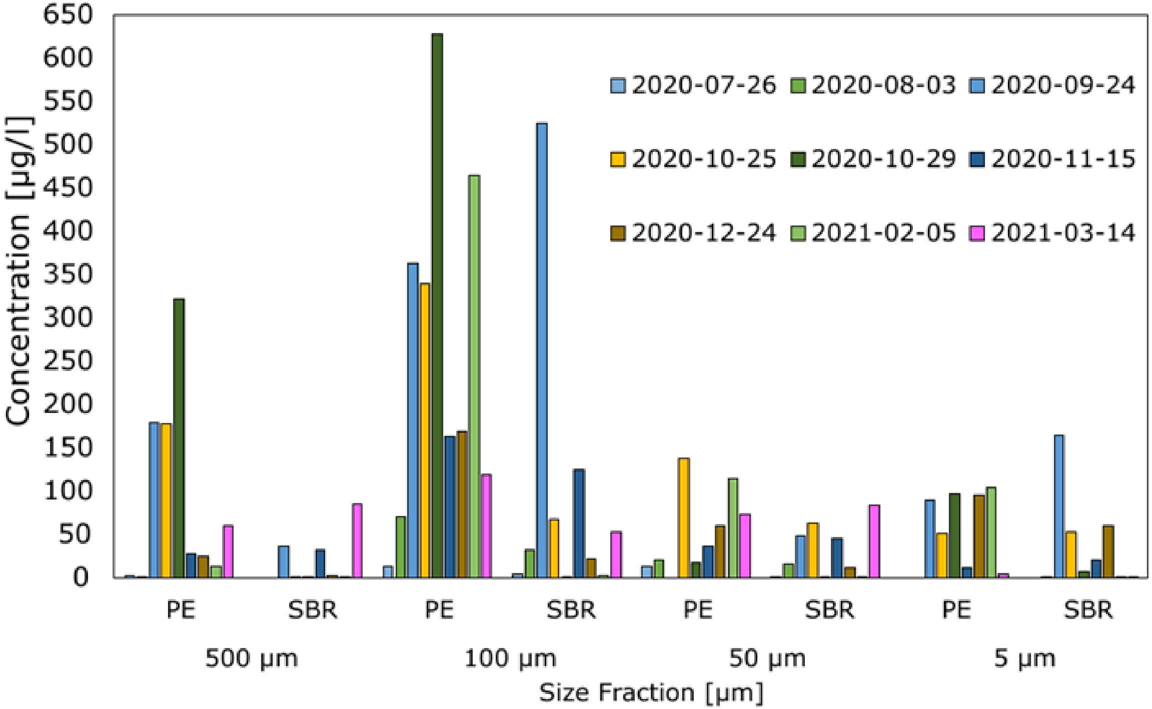

Figure 4-8 Concentrations of PE and SBR in stormwater runoff in separate system (L4, n = 9)

Table 4-7 MP loads in stormwater runoff events with focus on PE and SBR (L4, n = 9), (SBR compared to dry weather days before rain with $r_{Pearson}$= 0.8205)

Sampling date	MP load	Runoff Volume	SBR		PE		Number of Dry days before rain event
	[g]	[m³]	[g]	%	[g]	%	[d]
26/07/2020	15.6	352	1.4	9.1	9.7	62.3	0
03/08/2020	29.1	133	6.4	22	12	41.2	7
24/09/2020	865.8	544	420.4	48.6	343.4	39.7	6
25/10/2020	262.4	284	51.9	19.8	200.3	76.3	2
29/10/2020	554.3	503	4	0.7	535.5	96.6	0
15/11/2020	381.4	821	182	47.7	193.5	50.7	7
24/12/2020	304.5	607	57.8	19	210.7	69.2	0
05/02/2021	878.9	1216	4	0.5	696.5	79.2	0
11.03.2021	1033.8	2159	220.53	21.3	256.23	24.8	6

Based on the sampling campaign, it can be estimated that at least **558 g_{MP}/ha_{EIA}** (n=7) were transported through the separate drainage system with an average concentration of **122 µg/L**. However, the sampled stormwater runoffs from September 2020 till March 2021 represent only 71 % (≈ 35,155 m³) of the yearly total stormwater runoff of ≈ 50,154 m³ measured from September 2020 till September 2021. Using average concentration from the sampling campaign, one can estimate a yearly polymer emission of about **796 g_{MP}/(ha·a)** from this catchment area.

4.1.2.2. Sampling campaign of combined sewer system during wet weather L3 (2021)

The sampling campaign at L3 under wet weather conditions was able in June and July 2021 to representatively sample 16 stormwater runoff events divided into 7 combined samples with a total runoff volume of about 12,741 m³. With a visual validation using the security camera (blink mini, LLC) (Figure 4-9) mentioned earlier in 3.3.2.1, sampling coverage hydrographs for all seven combined samples could be generated (refer to Figure 4-10 and Figure A 19 till Figure A 25 in appendix 8.5.1). The sampling coverage hydrographs were very helpful in validating the representativity of sampling and calculating MP concentrations based on actual sampled runoffs.

Figure 4-9 Snapshot from a video showing the sampling of stormwater runoff at L3 in real time (09.07.2021 14:41:30)

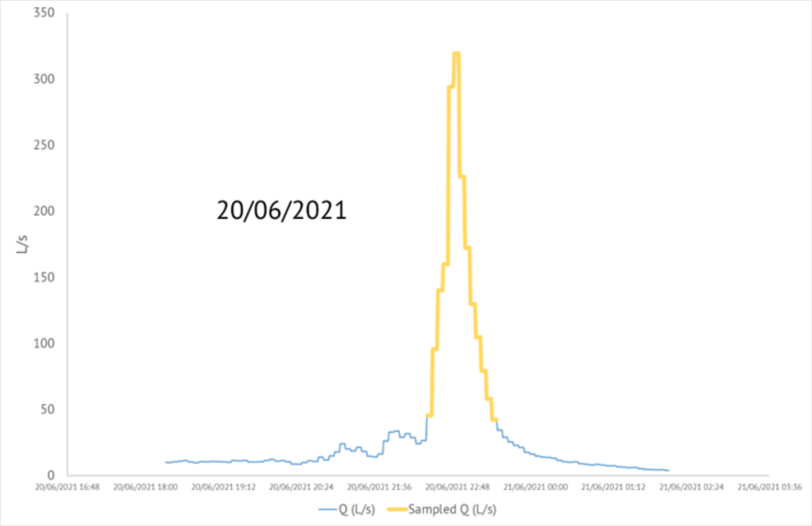

Figure 4-10 Sampling coverage hydrograph of the sample on 20.06.2021 at L3. Runoff hydrograph (blue), sampling hydrograph (yellow)

The results of the sampling campaign in combined system show that mainly PE and SBR occur in the stormwater-borne MP. These two polymers represent about 96 % of all MP identified in all runoff samples (

Table 4-9), which illustrates the high relevance of their urban occurrence. PE occurred in all samples with a minimum average concentration of **46 µg/L** (0.3 - 261 µg/L, n=7) in the size fraction **5-50 µm** and a high average concentration of **378 µg/L** (100 - 807 µg/L, n=7) in the size fraction **100-500 µm** (similar to results from L4)**.** SBR concentrations occurred in all samples with a minimum average concentration of **33.5 µg/L** (0 - 186 µg/L, n=7) in the size fraction **5-50 µm** (similar to PE) and a high average concentration of **384 µg/L** (1 - 1413 µg/L, n=7) in the size fraction **50-100 µm.** In comparison to the results from L4 (small catchment in separate system), SBR most abundant in the size fraction 50-100 µm and not 100-500 µm. Figure 4-11 shows the concentrations of the detected polymers in the size fractions of 5-1000 µm. The minimum, maximum average, and median concentrations of PE and SBR over all fractions and combined flow samples are shown in Table 4-8, the remaining concentrations are shown in appendix (Table A 6). The majority (60 - 85 %) of all MP loads are linked to fractions larger than 50 µm.

A mass balance analysis of MP loads of dry weather portion within combined flow was conducted. Based on average MP concentrations in dry weather flow from (4.1.1.2) and by summing the sampling duration within runoff times, showed that this portion constitutes less than 7 % of total combined flow, and less than 4 % of the total MP load in combined flow under wet weather. Hence, no further analysis was conducted to differentiate between dry and wet weather components at L3[18].

Table 4-8 Summary of PE and SBR concentrations in combined flow under wet weather per size fraction (L3)

	MP concentrations of all size fractions							
	500_1000µm		100_500µm		**50_100µm**		**5_50µm**	
	PE	SBR	PE	SBR	**PE**	**SBR**	**PE**	**SBR**
Average	119.19	117.37	377.59	246.04	151.97	383.97	46.84	33.52
median	61.84	41.58	377.64	91.43	117.60	43.57	1.15	0.92
min	45.52	0.42	99.86	0.37	21.82	0.23	0.26	0.04
max	219.73	515.61	807.73	782.25	471.25	1413.64	261.49	186.61

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[18] A detailed account of this analysis can be provided by the author as an excel file.

Table 4-9 Loads, concentrations, and percentages of SBR and PE polymers within the samples of the wet weather campaign in combined system at L3 (n=7)

Sampling date	Total MP		SBR			PE		
	Load [g]	C [µg/L]	Load [g]	C [µg/L]	%	Load [g]	C [µg/L]	%
20/06/2021	1002	1729	247	426	25	698.4	1204	70
22/06/2021	742	980	22	30	3	677	893	91
24/06/2021	3101	1717	832	461	27	2005	1110	65
29/06/2021	260	401	3.4	5.3	1	244	375	94
06/07/2021	604	633	79	82	13	518	543	86
09/07/2021	8174	3859	6584	3108	81	1569	740	19
14/07/2021	3647	3801	3342	3482	92	286	298	8

Based on the flow measurements at L3 and the data curation method using python code (refer to 3.4.1.2), a total stormwater runoff volume of about 30,252 m^3 was recorded during the sampling campaign in June till July 2021, which represents only 17 % of the total runoff volume recorded in 2021 of about 183,114 m^3. With an average MP concentration of **554.8 µg$_{MP}$/L**, a basic linear interpolation leads to a specific emission load of **3,098 g/(ha.a).**

Furthermore, based on the assumption that SBR emissions are comparable all year long if the number of commuting cars in the area is stable, and according to the seasonal emission factors suggested for other MP (refer to 3.4.2.2) one can estimate an average yearly MP emission of about **2913.5 g/(ha·a)** from the catchment in the combined system. Moreover, specific SBR emissions can be estimated to be **1903.5 g/(ha.a),** while other MP has a specific emission of **1010.1 g/(ha·a)**.

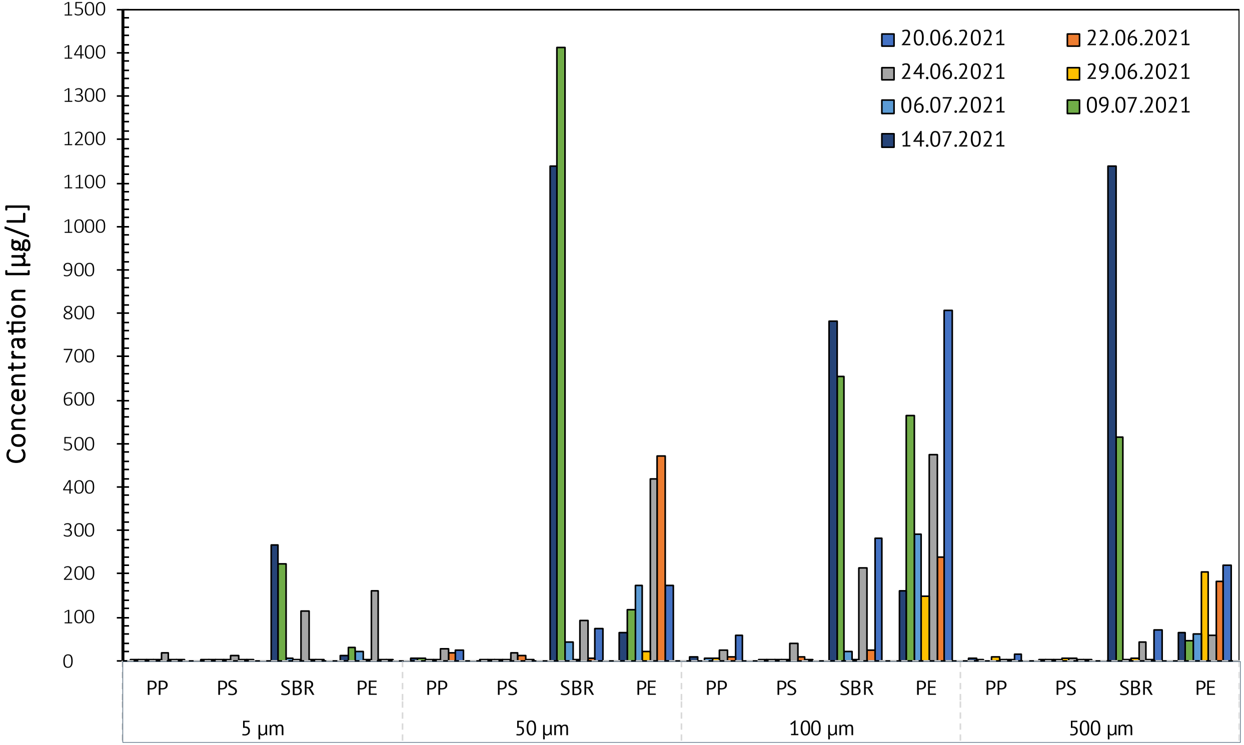

Figure 4-11 Polymer concentrations in combined wet weather flow at SRT in combined system (L3, wet weather, n = 7)

4.1.2.3. Extrapolation of MP emissions to the UDS of Kaiserslautern

Upon further examination of the two primary constituents of stormwater runoff, namely PE and SBR, it becomes evident that the specific annual emission of PE in the larger catchment area with intensified anthropogenic activities (L3) is almost double in magnitude compared to the emission rate from the smaller catchment (L4) with less activities (as shown in Table 4-10). This disparity can likely be attributed to higher population density in the catchment with the combined system and higher potential for litter accumulation. On the other hand, the size of the catchment and its significantly higher and different in type traffic density in the larger catchment (L3) are manifested by the elevated specific load of SBR (almost 8 folds), in contrast to the specific load observed in the smaller catchment with less traffic density.

Table 4-10 Comparison between specific yearly emissions of PE and SBR in the two catchment areas

Polymer	**Combined system**		**Separate system**	
	Large catchment at L3		**Small catchment at L4**	
	Total annual load (2021) [kg/a]	Specific annual load [g/(ha·a)]	Total annual load (2021) [kg/a]	Specific annual load [g/(ha·a)]
PE	30.3	922	3.97	517
SBR	62.4	1,903.5	1.94	253
∑ MP	95.6	2,913.5	6.1	796
Traffic density [vehicle/d]	4200		500 (estimated)	

To conclude, the city of Kaiserslautern has a unique UDS that consists principally of stormwater retention structures with few structures with overflows, which concentrates the pathway for MP to the WWTP Kaiserslautern. However, specific emissions from urban catchment areas are comparable to other catchments with different drainage schemes. Therefore, to understand the significance of wet weather pathway compared to dry weather one, the emission rates from L3 were chosen to be a baseline to apply two extrapolation methodologies for all sub-catchments that build-up the UDS of the city of Kaiserslautern and connected directly to the WWTP Kaiserslautern. The first methodology is a straightforward one in which the specific wet weather emissions from L3 ($B_{MP\text{-}SBR,ha,a}$ = 1010 g/(ha.a) and $B_{SBR,ha,a}$ =1903.5 g/(ha.a)) are multiplied by the effective impervious areas (A_{EIA}) of each sub-catchment without applying any factors (see Table A 7 in appendix 8.4.2). The second methodology is the one described in pages 103-98 and equation 15, with factors F1, F2 and F3 applied to extend the emission rates from the sub-catchments level into the entire catchment of the WWTP. Also, the entire UDS has an effective impervious area of about 2343 ha. Based on the hydrological-hydrodynamic deterministic pollutant load calculation model mentioned earlier in 3.4.2.2, the sub-catchments (n=64) that build-up the entire UDS have an effective impervious area (A_{EIA}) of about 1314.4 ha combined. Table 4-11 presents the results from the two different approaches in relation to the two MP groups: MP (without SBR) and SBR. The results are given in terms of total annual load (in kilograms per year) and specific annual load (in grams per hectare per year) for the year 2021.

Table 4-11 Absolute and specific wet weather MP emissions from the entire catchment of UDS of Kaiserslautern based on two extrapolation methods and specific wet weather emissions at L3

Polymer	**Approach 1 (no factors)**		**Approach 2 (factors 1,2,3)**	
	Total annual load (2021) [kg/a]	**Specific annual load [g/(ha·a)]**	**Total annual load (2021) [kg/a]**	**Specific annual load [g/(ha·a)]**
MP (without SBR)	1,327.6	1,010	1,344	1,023
SBR	2,502	1,903.5	1,250	951
∑ MP	3,829.6	2,913.5	2,594	1,974

Approach 1 represented a baseline scenario without any additional factors under the assumption that all sub-catchments will behave in a similar way. Approach 2 considers population and traffic densities, and the type of anthropogenic activities in the catchment at L3. For instance, the average population density per drained area for all catchments (n=64) is 47 ± 48 p.e./ha, while the density in the catchment at L3 is 119 p.e./ha. Similarly, due to its location neighboring main streets connecting Kaiserslautern with southern regions and connecting the university campus to the downtown of Kaiserslautern, traffic density is also higher than Kaiserslautern's average. In addition, the factors described earlier were derived based on a 1st order analysis assuming a linear MP-release correlation based on the emissions from the catchment at L3. In order to run a sensitivity analysis to validate the factors 1,2 and 3, more catchments with varied population and traffics densities need to be monitored.

4.1.3. Correlations between MP concentrations and wastewater parameters

Discovering correlations between the presence of MP in urban wastewater streams and other wastewater factors such as total solids (TS), chemical oxygen demand (COD), and loss on ignition (LoI) is highly advantageous for MP research. This is particularly important considering the difficulties associated with directly monitoring MP, as previously demonstrated. The three above mentioned parameters were chosen because they reflect the organic and particulate nature of MP.

The initial part of this section presents the results of correlation tests, utilizing the Pearson method (refer to section 3.4.3), between the concentrations of identified MP types (PE, SBR, PP, and PS) within the particle size fractions of 5-50 µm, 50-100 µm, 100-500 µm, and 500-1000 µm, and the above-mentioned wastewater parameters at sampling locations L3 (under both dry and wet weather conditions) and L4. Only results from smaller catchments were examined to enhance the likelihood of detecting a trend, as well as due to the greater abundance of samples at these locations. In total, 135 tests were conducted using an Excel tool. The latter part of this section focuses on correlation tests between the loads of the two predominant MP types, namely PE and SBR, and the parameters of runoff volume and maximum runoff rate at the respective sampling location.

The correlation tests conducted on TS concentrations within different fraction sizes yielded low probabilities of correlations. Figure 4-12 demonstrates the correlation test results between TS concentrations and MP concentrations during wet weather flow at L3. Notably, two significant correlations were observed between PP and TS in the size fractions of 100-500 µm and 500-1000 µm. A similar pattern was seen in the correlation tests of TS and MP during wet weather runoff at L4 (Figure 4-13). In this case, there were correlations between PP concentrations and TS in the fractions larger than 50 µm. However, it should be noted that PP occurred in very low concentrations in this medium, which increases the probability of it being a random phenomenon. The remaining correlation tests (refer to appendix 8.5.2 Figure A 26 till Figure A 28 and Table A 9 till Table A 13) showed unfortunately no remarkable trends between the other wastewater parameters and MP concentrations.

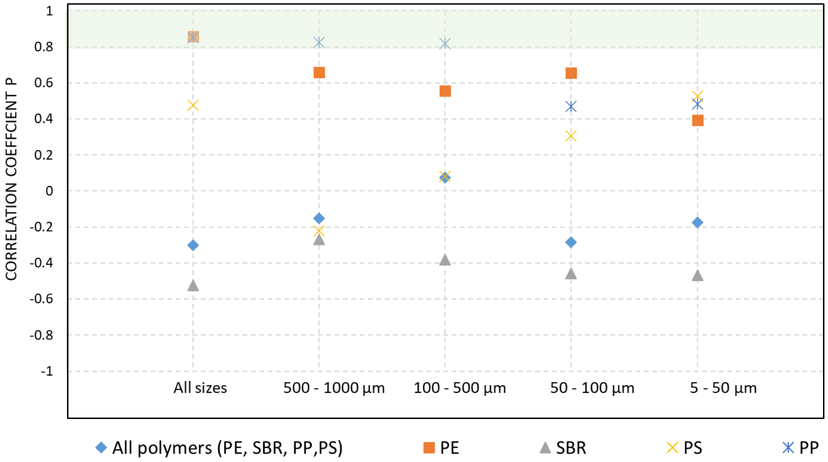

Figure 4-12 Pearson correlation test between total solids and MP in stormwater runoff at L3 in each size fraction

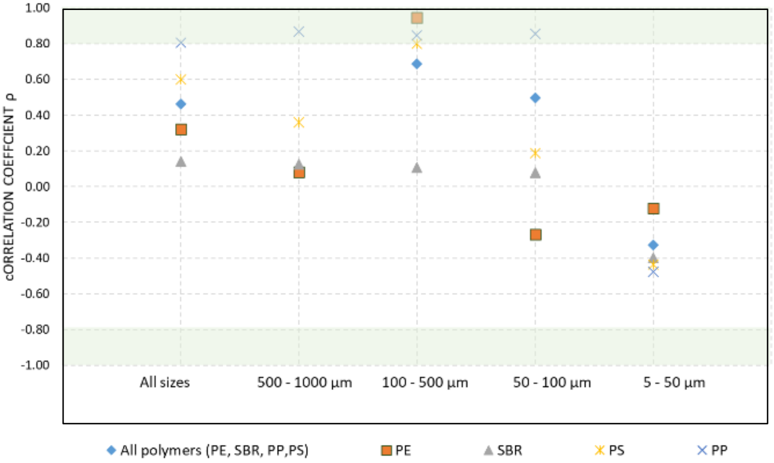

Figure 4-13 Pearson correlation test between total solids and MP in stormwater runoff at L4 in each size fraction

To conclude, a correlation pattern between MP and the parameters that reflect its organic and particulate nature is rather difficult to obtain. The reason behind is probably the very low quantities of the different MP fractions within the solid matrix as whole. Therefore, a sudden and slight random change in MP occurrence in the matrix can affect the correlation test immensely.

4.1.4. Evaluation of monitoring campaigns

The work results confirm the high complexity of the task of detecting MP contamination in dry weather runoff within urban wastewater systems. The findings obtained on MP sampling during dry weather can be summarized as follows:

In the course of a sampling campaign, other locations in a wastewater system in addition to the WWTP must be systematically sampled, especially those that are considered potential emission hotspots. Sampling at the WWTP only allows conclusions to be drawn about the total amount of MP in the drainage system ("end-of-pipe") and the elimination performance prior to discharge into the water body. Information on release patterns and sources of MP can only be obtained at selected individual points in the drainage system. Based on the results from this work which showed the relative high occurrence of certain polymers, such as PE and SBR, in wastewater samples, new emissions **hotspots** can be defined. Possible hotspots or sampling locations can be street runoffs, commercial centers with high littering level, industrial hubs, such as logistic centers, and events centers.

With the investigated sampling points for MP in domestic wastewater or in dry weather runoff of the combined system and influent of WWTP, first important occurrence data on amounts and relevance of different MP species in different fractions could be obtained. These results confirm a high, partially dominant relevance of PE in the wastewater system during dry weather.

From the dry weather runoff analyses, it is evident that sewer networks have a discernible retention and accumulation effect for MP. For example, stormwater-borne SBR from tire abrasion is still latently detected in dry weather runoff after rain events. However, more well-founded, spatially differentiated statements on the transport behavior of MP in the wastewater system are not possible based on the results. This would require monitoring based on a much greater density of sampling points.

The experience gained with sampling shows that after familiarization and establishment of the workflows for the overall process of MP detection (sampling, sample preparation, thermal analysis), at least one week of time should be planned. This is to be regarded as the ideal case, since other boundary conditions (including weather conditions, wastewater-related fluctuations in use) can lead to considerable delays. Against this background, an amount of about 10-12 24 h composite samples per year during dry weather can be considered as a guideline.

Information and data already available on flow conditions and composition of the wastewater matrix accelerate and improve the sampling planning process. Sampling sites with such favorable, known boundary conditions should be included in the sampling implementation. Thus, adjusting sampling parameters and estimating the sample preparation effort becomes much simpler.

The sample volume to be collected should be based on the requirements of sample preparation, considering analytical detection limits, and should be determined accordingly. Thus, for each subsample or size fraction collected, there should be a sufficiently high solid yield to ensure the representativeness of the analysis and to exceed the detection limit by at least 5 orders of magnitude. For example, a minimum of 300 mg of solids per size fraction is required for MP detection with TED-GC/MS.

Various findings were also obtained on the specifics of MP sampling during wet weather:

The effort required to install and operate a sampling point for wet weather sampling of MP is more complex and labor-intensive compared to dry weather sampling. This is true with respect to the identification of a suitable sampling point, the technical equipment of the sampling point, the personnel time and effort required, and the logistical requirements in the course of sample collection and preparation. The discontinuous occurrence of stormwater runoff and the high temporal dynamics of the precipitation event result in complex planning boundary conditions for sampling that require careful design of the sampling strategy. In order to improve the representativity of the sampling, the control unit can be trained to switch between parametrization scenarios according to real-time data, such as, actual rain intensity, length of dry period prior to rain event and filling degree of LVS.

Comparing stormwater samples in combined and separate systems, both sampling and sample preparation are higher in the combined system than in the separate system due to the influence of dry weather flow component(i.e., higher organic contents). Due to the dilution effect of combined flow under wet weather conditions, automated sampling is possible despite the dry weather flow component. However, this requires a careful preliminary analysis of the dry weather runoff conditions (extraneous water accumulation, daily pattern of dry weather runoff).

The results obtained confirm the high relevance or occurrence dominance of the two polymers PE and SBR in stormwater runoff. However, with regard to reliable estimations of emission loads, a much larger sampling scope than the one introduced in this work, extended over longer periods of time, is required in which a sufficiently broad variety of rainfall events and accumulation phases are represented. In particular, this is also seen as a need for further research, e.g., linking automated sampling setups with nowcasting information on the immediately upcoming rainfall event.

The monitoring strategies in this study represent an initial comprehensive sampling initiative aimed at monitoring the release of MP starting from their sources and tracing them to receiving water through retention and treatment facility. The sampling campaigns took into consideration various meteorological conditions and the diverse transportation patterns anticipated through different wastewater drainage routes.

Moreover, the investigation focused on the configuration of the sewage network, distinguishing between separate and combined systems, and adopted distinct methodologies for campaign design, execution, and data analysis for each network configuration. Furthermore, the prevalent use of grab samples without accounting for flow rates or patterns in the studied region significantly restricts the scope of insights that can be derived regarding annual or seasonal emission loads.

Also, previous studies utilized MP counts and spectroscopic detection techniques, which can be converted into emission loads (Gies et al. 2018; Carr et al. 2016 ; Carr and Thompson 2020; Talvitie et al. 2017). However, these methods exhibit lower reliability compared to mass-based detection methods. The TED-GC/MS detection method adopted here provided very low detection limits for the studied polymers (>0.01 µg in detection crucible). Hence, accurate estimations for real MP emissions and possible uncertainties are very straightforward to obtain.

4.1.5. Uncertainty considerations

Uncertainty sources in monitoring campaign of waterborne MP are interconnected, resulting in a complex combined effect. The sources of uncertainty can be categorized into five main groups: flow and volume measurement related, losses of particulate matter during sample preparation, sieving efficiency, sampling representativeness and uncertainty of the thermal

MP analysis. Volume-based uncertainties pertain to the measurement of sample volume and flow stream volumes during sampling and laboratory analysis. This includes measurements flow measurements using ultrasonic sensors and sample volume in sampling tanks. However, it's important to note that the TS concentrations used to assess volume-based uncertainties are also influenced by other sources of uncertainty, such as errors of the sensitive scale measurements.

Uncertainties regarding sampling representativeness arise at every step of the sampling process. The representativeness of a sample is directly related to the dominant particle size of the particulate matter. In other words, the finer the particles, the higher the representativeness. The reason behind is that smaller particles are homogenized easily in an environmental sample. To enhance the separation efficiency of particles during laboratory analysis, one method is to dilute the samples before testing. Utilizing larger volume samples can decrease separation uncertainties. Additionally, the proper sieving and handling of samples plays a crucial role in improving separation efficiency.

Particle separation efficiency refers to the extent to which coarse particles are separated from fine particles within the sieve cascade used to prepare samples for analysis. In most cases, the separation efficiency is very low, but samples with higher concentrations of coarse particles displayed better separation efficiency. However, this source of uncertainty is considered systematic and can be corrected by performing multiple re-sievings of the coarse fraction retained by a certain sieve.

For more accurate results from lab analysis, it is highly recommended to re-sieve the samples. This process helps to eliminate any inconsistencies and ensures more precise measurements. It also helps to prevent the accumulation of filter cakes, which can affect the separation process and introduce additional uncertainties.

A major source of uncertainty lies in the measurement of flow. This uncertainty is estimated to be around 10 % (Abusafia 2017), indicating a relatively substantial potential for error in flow measurement. Proper calibration and monitoring of flow measurement instruments are essential to minimize this uncertainty and obtain reliable data.

4.2. The Fate of MP in Urban Drainage Systems

In the preceding section, the author quantified the absolute MP emissions from various wastewater streams at different distances from receiving waters.

However, the UDS (Urban Drainage System) under study in Kaiserslautern primarily consists of stormwater retention tanks and lacks direct access to its small receiving water creek, Lauter. Consequently, the fate of waterborne MP within the system closely aligns with the fate of MP entering the WWTP. Since each UDS is unique, featuring distinct designs, combined system distributions, and diverse stormwater retention structures in terms of size, shape, and function, the MP's fate in each system requires individual examination. Nevertheless, we can apply the specific emission rates from this study to determine the fate scenarios for the respective UDS under consideration, as estimating the fate is an essential output of any monitoring strategy.

In this section, the author will explore the fate of MP in the studied UDS, comparing emissions during wet and dry weather conditions. Additionally, hypothetical UDS distribution scenarios, such as having a higher number of stormwater retention structures with overflow into receiving waters, will be examined. Moreover, the impact of widespread micropollutant removal systems on the fate of MP entering WWTPs will be discussed, along with the effects of new regulatory frameworks in Germany concerning the removal of fine TS particles smaller than 63 µm. Finally, the influence of ongoing decentralization on the fate of MP in modern urban drainage systems will be addressed as well.

4.2.1. The fate of MP under dry and wet weather conditions

During dry weather conditions, the wastewater generated from the entire catchment easily flows to the WWTP without any obstacles. At the WWTP, the MP emissions are extensively reduced and eliminated from the treated wastewater (refer to 4.1.1.1). A significant portion of these emissions is likely to end up in the sewage sludge, the fate of which depends on the location of the WWTP and the regulatory guidelines governing sludge disposal practices in the region. Figure 4-14 provides an illustration of the fate of different types of MP under dry weather conditions, as they pass through four treatment stages at the WWTP, including a micropollutant treatment unit equipped with ozonation and GAC filtration. This state-of-the-art treatment process demonstrated in the Figure 4-14 is capable of removing approximately 99.83 % of all MP entering the WWTP behind screens. It is commonly assumed that dry weather emissions primarily originate from indoor sources, such as households, commercial establishments, and industries. However, the presence of SBR in the dry weather flow suggests two hypotheses: first, MP in the combined system undergoes longer residence times as expected and accumulates in temporary or permanent sinks; second, primary MP have an opportunity for further disintegration and degradation during this extended residence time. The prolonged exposure to the outdoor environment enhances the potential for fractionation, increasing the surface area and facilitating the transport of other micro pollutants.

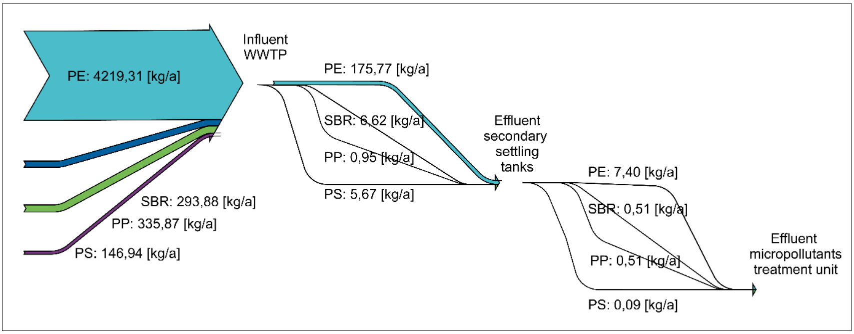

Figure 4-14 The fate of yearly MP emissions from the entire catchment area of the WWTP under **dry weather conditions**

The wet weather emissions shown in Table 4-11 are "absolute" values entering the UDS and will not reach receiving waters through UDS completely. However, the UDS in Kaiserslautern has a unique configuration with mainly retention structures in the city itself. However, this is not the case in other UDSs elsewhere. Therefore, to understand the fate of MP emissions under wet weather and to be able to compare it with dry weather emissions reaching receiving waters through WWTP, the following scenario analysis is applied on the emission values shown earlier in assuming two fictional UDS with the first UDS (case A) consisting of 100 % retention structures with overflows, and the second UDS (case B) consisting of only 50 % retention structures with overflows. The results from the scenario analysis (Table 4-12) show that even under the best case scenario with 50 % retention structures and 50 % removal efficiency, yearly MP emissions of **649 kg/a** would probably reach receiving waters. The detailed calculations of this part are shown in Appendix Table A 8 as well as a separate excel sheet provided by the author. Considering a yearly MP emission rate of 189 kg/a from the WWTP Kaiserslautern (without further treatment steps), stormwater retention and treatment structures are responsible for two to four times more MP emissions reaching receiving waters. The analysis conducted earlier assumes that MP is thoroughly mixed within the wastewater matrix during transport, resulting in a higher density. Consequently, the removal potential of MP is similar to that of other organic components existing in wastewater and stormwater runoff.

Table 4-12 Scenario analysis of removal potential of wet weather MP emissions with case A: 100 % structures with overflows in catchment, and case B: 50 % structures with overflows, 50 % without overflows and removal potentials of 30, 40 and 50 % in the respective structures

Type of retention structures	**MP removal rate** [%]	**Approach 1**[19] **Total annual emission** [kg/a]	**Approach 2**[20] **Total annual emission** [kg/a]
Case A: 100 % structures with overflows	no removal	3830	2594
	30	2681	1816
	40	2298	1557
	50	1915	1297
Case B: 50 % retention structures with overflows, 50 % without overflows	30	1340	908
	40	1149	778
	50	957	649

The following figures display the amounts of hypothetically released MP under wet weather conditions, based on four scenarios presented in Table 4-12. The scale used in the figures is identical to that of the dry weather figure (Figure 4-14), allowing readers to visually compare wet weather emissions to those during dry weather and make estimations accordingly.

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[19] Approach 1: extrapolation MP emissions to entire UDS in Kaiserslautern without catchment-specific factors

[20] Approach 2: extrapolation MP emissions to entire UDS in Kaiserslautern with catchment-specific factors

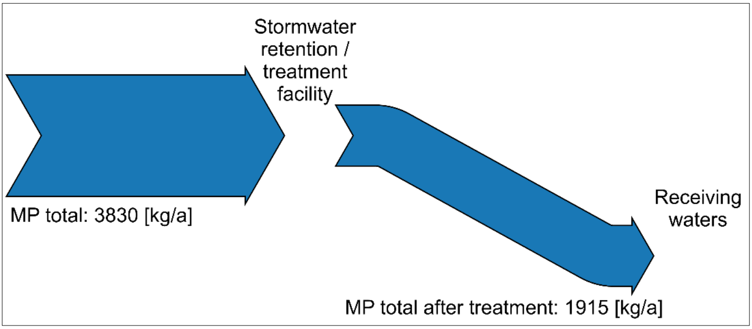


Figure 4-15 Fate of yearly MP emissions under **wet weather** conditions applying extrapolation **approach 1** (no factors) and assuming 100 % stormwater retention structures with overflows in the catchment with 50 % MP removal capacity

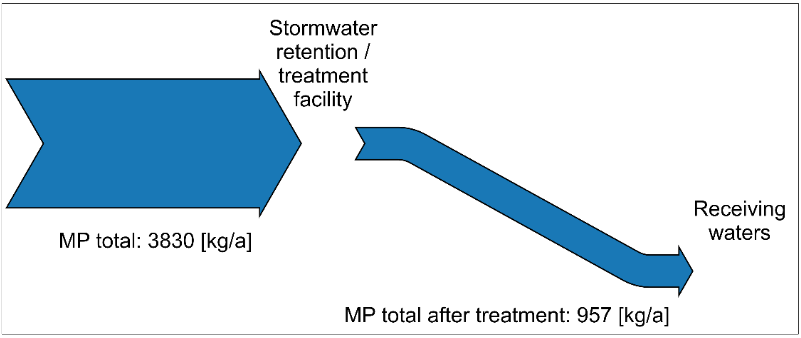


Figure 4-16 The fate of yearly MP emissions under **wet weather** conditions applying extrapolation **approach 1** (no factors) and assuming 50 % stormwater retention structures with overflows in the catchment with 50 % MP removal capacity

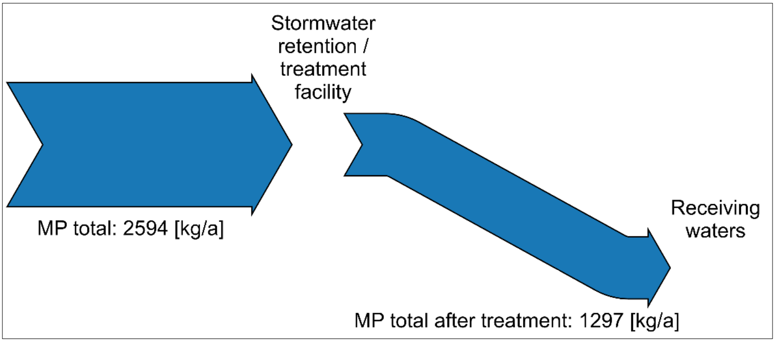


Figure 4-17 The fate of yearly MP emissions under **wet weather** conditions applying extrapolation **approach 2** (factors 1,2 and 3) and assuming 100 % stormwater retention structures with overflows in the catchment with 50 % MP removal capacity

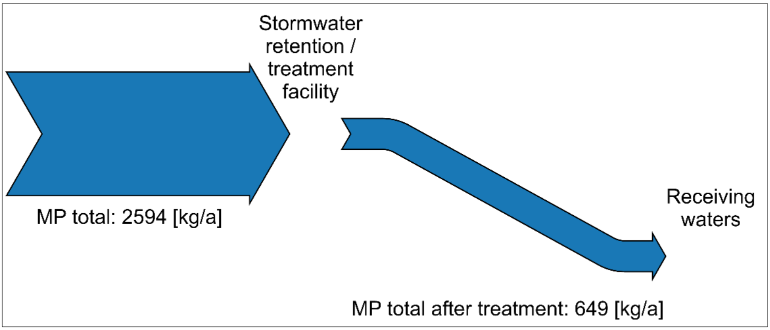


Figure 4-18 The fate of yearly MP emissions under **wet weather** conditions applying extrapolation **approach 2** (factors 1,2 and 3) and assuming 50 % stormwater retention structures with overflows in the catchment with 50 % MP removal capacity

Moreover, in order for wet weather emissions to achieve an equivalent reduction potential as dry weather emissions, stormwater retention and treatment facilities should be capable of eliminating 95% or 86% of all MP emissions during wet weather conditions (represented by Approach 1 cases A and B), as well as 93% or 79% of all MP during wet weather (represented by Approach 2 cases A and B). These percentages highlight the significant role of the wet weather pathway in transporting MP in UDS, and emphasize the substantial challenge faced by stormwater management structures in counteracting MP emissions.

Lastly, the previous analysis assumed that MP particles were fully mixed with other components of the wastewater matrix and exhibited similar removal potentials. However, it is important to note that poorly mixed and extremely lightweight particles (such as Styropor) are likely to bypass sedimentation aggregates, resulting in minimal removal potential. Consequently, alternative treatment methods, such as overflow screens or sieves, should be taken into consideration.

4.2.2. Removal potential in novel drainage and treatment structures

4.2.2.1. Removal of MP as a side effect of micropollutants removal at WWTPs

As a general remark, due to the particulate nature of MP, it is easily captured through filtration processes. This means that additional treatment steps at WWTPs, like ultrafiltration, GAC filtration, or cloth filtration, can significantly reduce MP emissions by a significant factor. The monitoring campaign conducted in this study at the micropollutant treatment plant revealed that it is possible to further remove approximately 97% (equivalent to an additional 180.5 kg per year) of the MP present in the effluent from the secondary treatment tanks. Ultimately, the growing trend of implementing such supplementary treatment units brings positive news in the battle against MP pollution in aquatic environments.

4.2.2.2. Advancements in stormwater treatment and novel regulations

A new regulation was introduced in Germany in 2020 regarding the management of combined and separate stormwater runoff. The regulation, known as "DWA-A 102/BWK-A 3" (2020) establishes guidelines for the planning, construction, and operation of stormwater management systems. The regulation introduces a new parameter called "AFS_{63}" (filterable solid particles smaller than 63µm), which serves as the key parameter for measuring and classifying emission levels from catchment areas. AFS_{63} was chosen because it is the fraction where most pollutants such as PAHs and heavy metals are attached or adsorbed. Moreover, AFS_{63} represents a significant portion (70 to 90%) of all solids found in the influent of wastewater treatment plants (Fuchs et al. 2019).

Based on pollutant emission potentials, urban catchment areas are classified into three categories: Category I corresponds to lightly polluted stormwater runoff, Category II represents moderately polluted stormwater runoff, and Category III signifies heavily polluted stormwater runoff. Table 4-13 provides specifications for these catchment areas. The values for material removal per unit area are determined by reference values based on average conditions in Germany, including the annual precipitation depth (h_{Na} = 800 mm/a) and the runoff-effective annual precipitation from paved areas (Ψ_{aM} = 0.7 and $h_{Na,eff}$ = 560 mm/a = 5600 $m^3/(ha\cdot a)$). Category I does not require any additional treatment. However, for catchment areas classified as Category II or III, a treatment facility must be implemented to reduce the emitted load below the value specified for Category I (i.e., 280 [kg/(ha.a)]).

Table 4-13 Mean concentrations in stormwater runoff and area-specific annual amount of pollutant for AFS_{63} of load categories I, II,III (DWA/BWK 2020)

Category	**Average AFS_{63} concentrations in yearly stormwater runoff in [mg/L]**	**Annual area specific AFS_{63} Load in [kg/(ha.a)]**
Category I	50	280
Category II	95	530
Category III	136	760

The objective of this section is to categorize the two catchment areas at L3 and L4, where stormwater runoffs were investigated for their TS and MP contents, based on DWA A-102/ BWK-A 3 and evaluate the potential release of TS and MP if the regulations are implemented.

TS and MP Loads at L4 (Separate system in Hohenecken) in the shadow of DWA A-102

t_f = 7.56 min, considering longest flow path of 590 m and average v = 1.3 m/s during rain event
A_{EIA} = 7.67 ha
$C_{R,\,AFS63}$ = 74 mg/L → category II
$V_{R,a}$ = 50,154 m^3
$b_{R,a,AFS63} = C_{R,AFS63} \cdot V_{R,a} / A_{e,b,a}$ = 483.9 kg/(ha.a) → Category II
Using the average specific stormwater runoff (5600 $m^3/(ha\cdot a)$) → **414 kg/(ha.a) → Category II**

Equation 17 from DWA A-102 (2020) calculates the resulting AFS_{63} discharge $B_{R,e,AFS63,i}$ after a treatment plant. Based on that, one can estimate the treatment efficiency of the responsible treatment facility to fulfill the requirements imposed by the norm (Eq. 18).

$$B_{R,e,AFS63,i} = A_{EIA} \times (1 - \eta_i) \times b_{\mathrm{R,a,AFS63,i}} \; [kg/a] \qquad (17)$$

$$\eta_i = \frac{B_{R,e,AFS63,i}}{A_{EIA} \times \; b_{\mathrm{R,a,AFS63,i}}} + 1 \; [-] \qquad (18)$$

Thus, to lower the specific AFS_{63} emissions for the catchment area at L4 to be <280 [kg/(ha.a)], η_i of the treatment facility must be > 0.42. Applying this removal efficiency to MP emissions from the catchment, the emission of this catchment into receiving water would be as high as 334 [g_{MP}/(ha.a)].

TS and MP load at L3 (Combined system in Carl-Euler-Str.) in the shadow of DWA A-102

t_f = 17 min, considering longest flow path of 1370 m and average v = 1.3 m/s during rain event
A_{EIA}= 34,83 ha
$C_{R,\ AFS63}$ = 129 mg/L category III
$V_{R,a}$ = 183,114 m^3
$b_{R,a,AFS63} = C_{R,AFS63} \cdot V_{R,a} / A_{e,b,a}$ = **677 kg/(ha.a) → Category III**

In analogy to the analysis in the previous part, to lower the specific AFS_{63} emissions for the catchment area at L3 to be <280 [kg/(ha.a)], η_i of the treatment facility (Eq. 18) must be > 0.58. Applying this removal efficiency to MP emissions from the catchment, the emission of this catchment into receiving water would be as high as 1709 [g_{MP}/(ha.a)].

4.2.2.3. The Effect of Ongoing Decentralization of Urban Drainage Systems

The ongoing decentralization of urban drainage systems can have several effects on the fate of MP. Firstly, decentralization often involves the implementation of green infrastructure practices such as rain gardens, permeable pavements, and vegetated swales. These features can help filter and retain stormwater runoff at the source, reducing the concentration of MP in the runoff. MP has more opportunities to settle or be captured in these decentralized systems.

Decentralized drainage systems incorporate various treatment measures, including sedimentation basins, biofilters, and constructed wetlands. These components are designed to remove pollutants, including MP, from stormwater runoff. For instance, Kuoppamäki et al. (2021) confirmed that no MP is to be expected in the discharge of biofilters. Decentralized systems also provide a distributed network of treatment areas, increasing the potential for MP removal before the water is discharged into receiving water.

In addition, decentralization often promotes source control measures, such as reducing litter and implementing recycling and waste management initiatives. These efforts can help mitigate the entry of MP into UDMs, thereby reducing their fate within these systems. However, new MP sinks in the catchment area are possibly appearing, such as greywater decentralized treatment systems, washing machines filters, street treatment structures, blue green infrastructure.

5 Summary and Conclusions

In this study, a systematic methodology for monitoring and estimating MP emissions in urban wastewater streams was established, expanding monitoring beyond traditional WWTP monitoring. In addition, clear and comprehensive guidelines for sampling and sample preparation have been provided, including practical tips for handling challenging samples and sampling locations in terms of hydrologic and hydraulic variations, and logistic limitations. Additionally, robust data curation methods were outlined.

To address the bias in MP research toward WWTPs, the investigations in this work were extended to upstream locations and the outer edges of the catchment. By extending MP monitoring to upstream urban areas and catchment boundaries, a comprehensive view of MP occurrence and distribution has been demonstrated. The objective was to overcome the lack of standardized tracking methods for waterborne MP in the catchment. In return, an accurate determination of specific emission rates and verification of previous findings at the WWTP level was achieved.

For the first time in MP research, stormwater runoff within an entire UDS was systematically investigated, comparing it with emissions during dry weather conditions. This comprehensive analysis provided insights into the fate of all MP currently emitted and potential changes in fate due to future advancements in urban wastewater management strategies. Additionally, this work aimed to challenge the conventional approach of treating MP as a collective parameter with similar transport and fate scenarios. Instead, it considered the type and size of MP particles at all stages of the analysis.

The experience gained during MP monitoring (sampling, sample preparation, detection) suggests that one week should be planned per intended sampling action. Accordingly, an amount of approx. (10-12) 24h-composite samples distributed over a year are recommended for sampling campaigns under dry weather conditions to cover MP variations and fluctuations in the matrix. This estimation is delineated from the fact that deviations from median daily wastewater yield are rather small within the same short season. In addition, the time and effort required to sample, prepare, and detect MP in its size fractions from urban wastewater streams are extremely high. Hence, 10-12 sampling days per year are considered sufficient.

While for sampling under wet weather conditions all available events during a chosen time frame, i.e., a full year or multiple continuous rain events to cover a release and wash-off cycles, should be aimed at. The sample volume to be obtained must be aligned with the requirements of sample preparation and considering analytical detection limits. Thus, for each sub-sample or size fraction taken, there should be a sufficiently high solid yield to ensure the representativeness of the analysis and to exceed the detection limit by at least 5 orders of magnitude (own recommendation). Therefore, a minimum of 300 mg solids per size fraction is recommended for MP analysis with TED-GC/MS, from which 10 to 50 mg aliquots of the homogeneous sample can be measured directly without further sample preparation. For influent WWTP under dry weather with TS range of 200-400 mg/L, a sample volume of 30 L is recommended, also to minimize preparation effort. Whilst for overflow streams and other wet weather media, a minimum of 200 L (max. 800 L) sample volume is recommended for representative MP and PSD analysis.

Sampling within the sewer system implies dealing with a set of variables and requirements. Flow fluctuations, accessibility at selected sampling points, large objects in wastewater stream, residence time and safety considerations represent many challenges while designing a reliable monitoring program. In particular, monitoring of wet weather flow is more complex and labor intensive since more effort is required for designing, installing, and operating sampling equipment. The intermittent occurrence of rainfall events and the high temporal dynamics of the precipitation quantity create complex planning conditions for sampling, which require adjusted-to-catchment strategies. The mechanism of flushing and accumulation of MP particles from catchment area has a potential effect on the quality of data acquired, as well as the existence of sinks, where MP is possibly released into environment prior reaching the end point of the drainage system. Thus, stormwater-borne SBR from tire abrasion is still latently detected in dry weather influent of the WWTP.

The results of sampling at the WWTP Kaiserslautern show that at least 96 % of MP entering the plant behind screens can be removed at the treatment aggregates. PE is the most abundant MP in the influent and effluent of the WWTP with a share of 86 % and 77 % of the total detected MP load respectively. SBR was also detected in the influent (5.8 %) and effluent (≈1 %) under dry weather conditions. PP represented about 6.6 % of MP load in the influent and 21 % in the effluent of WWTP. The previous results from the WWTP suggest that WWTP is a less-significant entry pathway for MP in urban areas in comparison to direct discharges from stormwater structures into receiving waters. Although absolute annual MP occurrence within dry weather streams is at least double in magnitude compared to emissions within wet weather streams.

Away from the WWTP at the edge of the catchment area, MP emissions in dry weather flow showed different characteristics in terms of quantity and PSD. While average daily MP concentrations in the influent stream of WWTP was 286 µg/L, the average daily MP concentration from a small upstream catchment was with 794 µg/L almost three times higher. The reason behind that can be linked to high extraneous water portion at the WWTP compared to low portion (<10 %) at the small catchment. Also, changes in PSD of MP occur along the journey from source to the WWTP. For instance, the normal-like PSD-curve at the far edge of the UDS under dry weather conditions turns into a flattered one at the entrance of the WWTP.

The new findings from sampling wet weather flow in both separate and combined sewer systems highlight the significant presence of two specific polymers: polyethylene (PE) and styrene-butadiene rubber (SBR). The research also sheds light on how catchment size and traffic density affect the release rates of these polymers. PE is consistently found in high concentrations in catchments with varying characteristics, regardless of weather conditions before rainfall. This suggests a continuous release of this polymer from urban areas and a wide range of sources. In contrast, the concentration of SBR correlates with the number of dry days before rainfall and the amount of traffic. Consequently, emissions of SBR from larger catchments with higher traffic are nearly five times higher than those from smaller catchments.

While dry weather emissions at WWTP are seen as less significant in magnitude to overall MP pollution of urban origin, wet weather emissions play a more significant role due to low treatment possibilities in these urban areas. Extrapolating MP emissions to the entire UDS catchment showed that two to four times more MP is likely reaching receiving waters over wet weather pathways. However, the efficient treatment of MP at WWTP suggests that the ongoing and increasing treatment capacities of wet weather flow will decrease the emissions from this pathway drastically.

In conclusion, although WWTPs proved effective at mitigating MP emissions, it was evident that transport pathways contribute significantly to MP pollution, especially during wet weather conditions. The research emphasized the ongoing need for advancements in MP management and posed a challenge to reevaluate the acceptable levels of MPs in urban waters. The findings serve as a cautionary note that MPs will persist in urban ecosystems for years to come, gradually diminishing in size and potentially serving as vectors for other anthropogenic pollutants. This situation calls for a concerted effort to address the implications of MPs on urban water quality and environmental health, ensuring sustainable management practices in the future.

6 Future work

In order to justify the factors used for extending knowledge of MP emissions from the entire UDS, it is necessary to conduct **additional sampling campaigns**. In addition, the sampling locations can be extended to **commercial and industrial hubs** as well as to effluent of Combined Sewer Overflows (CSOs). Commercial and industrial hubs can enhance our understanding of MP emissions from urban areas, while sampling in the effluent of CSOs can give us insights on the actual “unnoticed” immissions into receiving waters. As this research was carried out in the UDS of Kaiserslautern, with the aim of assessing the overall emissions from this specific system, the low number of CSOs, which discharge overflows into receiving waters, raised significant uncertainty regarding the direct release of MP through this pathway. This effort will help calibrate the factors suggested through sensitivity analysis and transit from a first-order factorization approach to a more accurate mathematical model. A hotspot-analysis based on the findings from this work, i.e., polymer types, concentrations, and PSD, can be useful to densify or exclude potential sampling locations for future studies.

Shifting from the measurement of solid components of MP (polymers) to the **analysis of dissolved trace elements** (additives), such as plasticizers and other additives, is a game changer. These trace elements, include UV absorbers like 2-hydroxybenzophenones (linked to endocrine disruption) and 2-hydroxyphenylbenzotriazoles (known for aquatic toxicity), organic nickel compounds (notably associated with carcinogenicity), and sterically hindered amine light stabilizers (HALS) (known for their environmental persistence) do not require complex sampling and sample preparation steps for monitoring, thus small sample volumes are sufficient. However, identifying these additives requires extensive knowledge of their compounds, including their thermal behavior, as well as a profound understanding of mass spectrometric chemical libraries like the NIST library, which currently contains over 267,350 individual mass spectra (Primpke et al. 2020). By considering the release conditions and degradability in water systems, we can investigate the occurrence of trace elements more rapidly and universally. This approach allows for a comprehensive analysis of MP presence and behavior. Yet, a conventional solid phase analysis of the polymers is still needed at the beginning to allow for correlation of MP total occurrence to the occurrence of selected additives. This process one can compare with identifying tire abrasion amounts by identifying heavy metal contents (e.g., Zink) and corelate it to total tire abrasion amounts.

To enhance the flexibility of the sampling system designed for wet weather flow, it can be designed to **accommodate various sampling scenarios**. For example, the signal from a rain gauge can be utilized to cover the entire duration of a rain event. This ensures that the sampling process captures relevant data accurately.

Furthermore, advancements in technology offer new possibilities for **online measurements**. Creating novel techniques for online measurement of dominant MP types (e.g., PE or SBR) can enhance the real-time monitoring capabilities and boost representativity. These innovative approaches contribute to the continuous improvement of data collection and analysis methods for a representative and meaningful MP monitoring.

7 Publication bibliography

Aatmeeyata; Kaul, D. S.; Sharma, Mukesh (2009): Traffic generated non-exhaust particulate emissions from concrete pavement: A mass and particle size study for two-wheelers and small cars. In Atmospheric Environment 43 (35), pp. 5691–5697. DOI: 10.1016/j.atmosenv.2009.07.032.

AbfKlärV (2017): Verordnung über die Verwertung von Klärschlamm, Klärschlammgemisch und Klärschlammkompost (Klärschlammverordnung - AbfKlärV). AbfKlärV. Source: Online. Available online at https://www.gesetze-im-internet.de/abfkl_rv_2017/AbfKl%C3%A4rV.pdf.

Abusafia, Attaallah (2017): Analysis of the Performance of a Stormwater Treatment Facility in Freiburg-Haid. Uncertainty Analysis. Master Thesis, ISWA, University of Stuttgart.

Abusafia, Attaallah; Scheid, Christian; Meurer, Maren; Altmann, Korinna; Dittmer, Ulrich; Steinmetz, Heidrun (2023): Microplastic sampling strategies in urban drainage systems for quantification of urban emissions based on transport pathways. In *Applied Research*. DOI: 10.1002/appl.202200056.

Albertson, Orris E.; Guidi, Eugene E. (1969): Centrifugation of Waste Sludges. In *Journal (Water Pollution Control Federation)* 41 (4), pp. 607–628. Available online at http://www.jstor.org/stable/25036609.

Altmann, K.; Goedecke, C.; Bannick, C. G.; Abusafia, A.; Scheid, C.; Steinmetz, H.; Braun, U. (2019): Identification and Quantification of Microplastic in Samples of Sewage systems by TED-GC-MS. Conference Paper. Available online at https://cest2019.gnest.org/sites/default/files/presentation_file_list/cest2019_00233_oral_paper.pdf.

Altmann, Korinna; Goedecke, Caroline; Bannick, Claus-Gerhard; Abusafia, Attaallah; Scheid, Christian; Steinmetz, Heidrun et al. (2023): Identification of microplastic pathways within a typical European urban wastewater system. In *Applied Research*. DOI: 10.1002/appl.202200078.

Ambrogi, V.; Carfagna, C.; Cerruti, P.; Marturano, V. (2017): Additives in Polymers. In : Modification of Polymer Properties: Elsevier, pp. 87–108. Available online at https://doi.org/10.1016/B978-0-323-44353-1.00004-X.

Andrady, Anthony L. (2007): Biodegradability of Polymers. In James E. Mark (Ed.): Physical properties of polymer handbook. New York, NY: Springer New York, pp. 951–964.

Andrady, Anthony L. (2011): Microplastics in the marine environment. In *Marine pollution bulletin* 62 (8), pp. 1596–1605. DOI: 10.1016/j.marpolbul.2011.05.030.

Andrady, Anthony L. (2015): Persistence of Plastic Litter in the Oceans. In Melanie Bergmann, Lars Gutow, Michael Klages (Eds.): Marine Anthropogenic Litter. Cham: Springer International Publishing, pp. 57–72.

Andrady, Anthony L. (2022): Weathering and fragmentation of plastic debris in the ocean environment. In *Marine pollution bulletin* 180, p. 113761. DOI: 10.1016/j.marpolbul.2022.113761.

Arthur, Courtney; Baker, Joel; Bamford, Holly (Eds.) (2008): Proceedings of the International Research Workshop. Occurrence, Effects and Fate of Microplastic Marine Debris. University of Washington Tacoma, Tacoma, WA, USA, September 9-11. Available online at https://marinedebris.noaa.gov/proceedings-international-research-workshop-microplastic-marine-debris.

2003-04: ATV-DVWK-A 198:2003-04. Available online at https://www.beuth.de/de/technische-regel/atv-dvwk-a-198/65791053, checked on 10/2/2022.

Baltic Marine (2014): BASE Project: Implementation of the Baltic Sea Action Plan in Russia. Available online at https://www.helcom.fi/wp-content/uploads/2019/08/BASE-Final-Report-implementation-of-BSAP-in-Russia.pdf.

Baresel, Christian; Harding, Mila; Fång, Johan (2019): Ultrafiltration/Granulated Active Carbon-Biofilter: Efficient Removal of a Broad Range of Micropollutants. In *Applied Sciences* 9 (4), p. 710. DOI: 10.3390/app9040710.

Barrows, Abigail P. W.; Neumann, Courtney A.; Berger, Michelle L.; Shaw, Susan D. (2017): Grab vs. neuston tow net: a microplastic sampling performance comparison and possible advances in the field. In *Analytical Methods* 9 (9), pp. 1446–1453. DOI: 10.1039/c6ay02387h.

Bayo, Javier; Olmos, Sonia; López-Castellanos, Joaquín (2021): Assessment of Microplastics in a Municipal Wastewater Treatment Plant with Tertiary Treatment: Removal Efficiencies and Loading per Day into the Environment. In *Water* 13 (10), p. 1339. DOI: 10.3390/w13101339.

Bejgarn, Sofia; MacLeod, Matthew; Bogdal, Christian; Breitholtz, Magnus (2015): Toxicity of leachate from weathering plastics: An exploratory screening study with Nitocra spinipes. In *Chemosphere* 132, pp. 114–119. DOI: 10.1016/j.chemosphere.2015.03.010.

Benstöm, Frank; STEPKES, H.; ROLFS, T.; MONTAG, D.; Pinnekamp, J. (2014): Untersuchung einer bestehenden Filterstufe mit dem Einsatz von Aktivkohle zur Entfernung organischer Restverschmutzung auf der Kläranlage Düren-Merken. Abschlussbericht zum Forschungsvorhaben. Edited by gerichtet an das Ministerium für Klimaschutz, Umwelt, Landwirtschaft, Natur- und Verbraucherschutz des Landes Nordrhein-Westfalen (MKULNV). Available online at https://www.lanuv.nrw.de/fileadmin/forschung/wasser/klaeranlage_abwasser/20140131-Abschlussbericht-WVER-GAK_end.pdf.

Bergmann, Melanie; Wirzberger, Vanessa; Krumpen, Thomas; Lorenz, Claudia; Primpke, Sebastian; Tekman, Mine B.; Gerdts, Gunnar (2017): High Quantities of Microplastic in Arctic Deep-Sea Sediments from the HAUSGARTEN Observatory. In *Environ. Sci. Technol.* 51 (19), pp. 11000–11010. DOI: 10.1021/acs.est.7b03331.

Bertling, J.; Hamann, L.; Bertling, R. (2018): Kunststoffe in der Umwelt. Available online at https://www.umsicht.fraunhofer.de/content/dam/umsicht/de/dokumente/publikationen/2018/kunststoffe-id-umwelt-konsortialstudie-mikroplastik.pdf.

Birks, R.; Hills, S. (2007): Characterisation of indicator organisms and pathogens in domestic greywater for recycling. In *Environmental Monitoring and Assessment* 129 (1-3), pp. 61–69. DOI: 10.1007/s10661-006-9427-y.

Biron, Michel (2018): Outline of the Actual Situation of Plastics Compared to Conventional Materials. In : Thermoplastics and Thermoplastic Composites: Elsevier, pp. 1–30.

Biron, Michel; Marichal, Odile (2018): Thermoplastics and Thermoplastic Composites. 3rd ed. San Diego, Ann Arbor, Michigan: Elsevier Science & Technology Books; ProQuest (Plastics Design Library).

Botterell, Zara L. R.; Beaumont, Nicola; Dorrington, Tarquin; Steinke, Michael; Thompson, Richard C.; Lindeque, Penelope K. (2019): Bioavailability and effects of microplastics on marine zooplankton: A review. In *Environmental pollution (Barking, Essex : 1987)* 245, pp. 98–110. DOI: 10.1016/j.envpol.2018.10.065.

Boucher, J.; Friot, D. (2017): Primary microplastics in the oceans: A global evaluation of sources: IUCN International Union for Conservation of Nature. Available online at https://portals.iucn.org/library/sites/library/files/documents/2017-002-En.pdf.

Braun, Ulrike; Altmann, Korinna (2022): RUSEKU. Repräsentative Untersuchungsstrategien für ein integratives Systemverständnis von spezifischen Einträgen von Kunststoffen in die Umwelt. With assistance of Attaallah Abusafia, Claus Gerhard Bannick, Claudia Crasselt, Stefan Dittmar, Michael Gehde, Christian Hagendorf et al. Edited by Plastik in the environment. Berlin (FKZ: 02WPL1442A). Available online at https://www.bam.de/Content/DE/Projekte/laufend/Ruseku/ruseku.html.

Braun, Ulrike; Altmann, Korinna; Bannick, Claus G.; Becker, Roland; Bitter, Hajo; Bochow, Mathias et al. (2020a): Mikroplastik-Analytik. Probenahme, Probenaufbereitung und Detektionsverfahren. Statuspapier. Edited by Plastik in der Umwelt. Berlin. Available online at https://bmbf-plastik.de/sites/default/files/2020-11/Statuspapier_Mikroplastik%20Analytik_Plastik%20in%20der%20Umwelt_2020.pdf.

Braun, Ulrike; Eisentraut, Paul; Altmann, Korinna; Kittner, Maria; Dümichen, Erik; Thaxton, Kurt et al. (2020b): Accelerated Determination of Microplastics in Environmental Samples Using Thermal Extraction Desorption-Gas Chromatography/Mass Spectrometry (TED-GC/MS). Available online at https://www.researchgate.net/publication/346317512_Accelerated_Determination_of_Microplastics_in_Environmental_Samples_Using_Thermal_Extraction_Desorption-Gas_ChromatographyMass_Spectrometry_TED-GCMS, checked on 11/30/2022.

Braun, Ulrike; Stein, Ulf; Schritt, Hannes; Altmann, Korinna; Bannick, Claus Gerhard; Becker, Roland et al. (2018): Statuspapier im Rahmen des Forschungsschwerpunktes Plastik in der Umwelt. Mikroplastik-Analytik Probenahme, Probenaufbereitung und Detektionsverfahren. Berlin.

Breitbarth, Marco; Urban, Arnd I. (2018): Kunststoffe in kommunalen Kläranlagen. In *Kunststoffe in kommunalen Kläranlagen* 2018 (9), pp. 800–807. DOI: 10.3242/kae2018.09.004.

Bristol Waste (2021): The history of litter. Available online at https://bristolwastecompany.co.uk/history-of-litter/.

Browne, Mark A.; Galloway, Tamara S.; Thompson, Richard C. (2010): Spatial patterns of plastic debris along Estuarine shorelines. In *Environ. Sci. Technol.* 44 (9), pp. 3404–3409. DOI: 10.1021/es903784e.

Bundestag (2009): Gesetz zur Ordnung des Wasserhaushalts (Wasserhaushaltsgesetz). WHG. Available online at https://www.gesetze-im-internet.de/whg_2009/WHG.pdf.

Cabernard, L.; Durisch-Kaiser, E.; Vogel, JC.; Rensch, D.; Niederhauser, P. (2016): MIKROPLASTIK IN ABWASSER U. GEWÄSSERN. AWEL, Zürich (78 | FACHARTIKEL). Available online at http://www.awel.zh.ch/internet/baudirektion/awel/de/wasser/_jcr_content/contentPar/downloadlist/downloaditems/fachartikel_mikropla.spooler.download.1469019564271.pdf/Mikroplastik+in+Abwasser+u+Gew%C3%A4ssern.pdf.

Cabernard, Livia; Roscher, Lisa; Lorenz, Claudia; Gerdts, Gunnar; Primpke, Sebastian (2018): Comparison of Raman and Fourier Transform Infrared Spectroscopy for the Quantification of Microplastics in the Aquatic Environment. In *Environ. Sci. Technol.* 52 (22), pp. 13279–13288. DOI: 10.1021/acs.est.8b03438.

Campanale, Claudia; Massarelli, Carmine; Savino, Ilaria; Locaputo, Vito; Uricchio, Vito Felice (2020): A Detailed Review Study on Potential Effects of Microplastics and Additives of Concern on Human Health. In *International journal of environmental research and public health* 17 (4). DOI: 10.3390/ijerph17041212.

Carr, S. A.; Thompson, J. (2020): Microplastics: Transport and removal at wastewater treatment plants. In Hrissi Karapanagioti, Ioannis K. Kalavrouziotis (Eds.): Microplastics in Water and Wastewater - 2nd Edition. London: IWA Publishing, pp. 45–61.

Carr, Steve A.; Liu, Jin; Tesoro, Arnold G. (2016): Transport and fate of microplastic particles in wastewater treatment plants. In *Water research* 91, pp. 174–182. DOI: 10.1016/j.watres.2016.01.002.

Chalmin, Philippe (2019): The history of plastics: from the Capitol to the Tarpeian Rock. Special Issue 19. In *Field Actions Science Reports [Online]* (Special Issue 19). Available online at URL : http://journals.openedition.org/factsreports/5071, checked on 8/2/2022.

Chamas, Ali; Moon, Hyunjin; Zheng, Jiajia; Qiu, Yang; Tabassum, Tarnuma; Jang, Jun Hee et al. (2020): Degradation Rates of Plastics in the Environment. In *ACS Sustainable Chem. Eng.* 8 (9), pp. 3494–3511. DOI: 10.1021/acssuschemeng.9b06635.

Chandrakanth, Mysore S.; Amy, Gary L. (1996): Effects of Ozone on the Colloidal Stability and Aggregation of Particles Coated with Natural Organic Matter. In *Environ. Sci. Technol.* 30 (2), pp. 431–443. DOI: 10.1021/es9500567.

Chin, David A. (2006): Water-resources engineering. 2nd ed. Upper Saddle River: Pearson Prentice Hall.

DIN EN 60456:2017-05, 2017: Clothes washing machines for household use - Methods for measuring the performance.

Coalition Clean Baltic (Ed.) (2017): Wise stormwater management to minimize inputs of microplastics. Baltic Marine Environment Protection Commission. St. Petersburg, Russia, 27.4.2017. Available online at https://de.scribd.com/document/360203083/Wise-Stormwater-Management-to-Minimize-Inputs-of-Microplastic.

Cole, Matthew; Lindeque, Pennie; Halsband, Claudia; Galloway, Tamara S. (2011): Microplastics as contaminants in the marine environment: a review. In *Marine pollution bulletin* 62 (12), pp. 2588–2597. DOI: 10.1016/j.marpolbul.2011.09.025.

Conley, Kenda; Clum, Allan; Deepe, Jestine; Lane, Haven; Beckingham, Barbara (2019): Wastewater treatment plants as a source of microplastics to an urban estuary: Removal efficiencies and loading per capita over one year. In *Water research X* 3, p. 100030. DOI: 10.1016/j.wroa.2019.100030.

Continental (2020): Nutzfahrzeugreifen (in German). Emissionen · Klimaschutz · Effizienz. Edited by Continental AG. Available online at https://blobs.continental-tires.com/www8/servlet/blob/3582064/7bc7b1f90dc8fa672b04418d5f59ae81/continental-whitepaper-reifen-nfz-data.pdf, checked on 04.11.

Corcoran, Patricia L.; Biesinger, Mark C.; Grifi, Meriem (2009): Plastics and beaches: a degrading relationship. In *Marine pollution bulletin* 58 (1), pp. 80–84. DOI: 10.1016/j.marpolbul.2008.08.022.

Csoka, Levente; Djokovic, Vladimir (2011): Theoretical Description of the Fourier Transform of the Absolute Amplitude Spectra and Its Applications. In Mawardi Bahri, Ryuichi Ashino (Eds.): Two-Dimensional Quaternionic Windowed Fourier Transform: INTECH Open Access Publisher. Available online at DOI: 10.5772/15368.

Cunha-Lopes, I.; Alves, C. A.; Casotti Rienda, I.; Faria, T.; Lucarelli, F.; Querol, X. et al. (2022): Characterisation of non-exhaust emissions from road traffic in Lisbon. In *Atmospheric Environment* 286, p. 119221. DOI: 10.1016/j.atmosenv.2022.119221.

Degaffe, Fanule S.; Turner, Andrew (2011): Leaching of zinc from tire wear particles under simulated estuarine conditions. In *Chemosphere* 85 (5), pp. 738–743. DOI: 10.1016/j.chemosphere.2011.06.047.

Degussa (2007): Laufflächenmischungsrezeptur moderner Pkw-Reifen. In *Neue ReifenZeitung, Profil-Verlag GmbH* 9/2007, 2007, checked on 02/2022.

Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlamm-Untersuchung. Physikalische, chemische, biologische und bakteriologische Verfahren (1993). Weinheim: VCH.

DFB (2022): MICROPLASTIC DISCHARGE FROM EXISTING SYNTHETIC TURF PITCHESTURF PITCHES. DFB RECOMMENDATIONS FOR ACTION FOR FOOTBALL CLUBS & LOCAL AUTHORITIES. With assistance of Matthias Eiles (DFB), Eva Immerheiser (DFB). Edited by German Football Association. Frankfurt, Germany. Available online at https://assets.dfb.de/uploads/000/256/883/original_DFB-Recommendations-Microplastic__2022.pdf?1647624173, checked on 9/1/2022.

D'Hont, Anouk; Gittenberger, Adriaan; Leuven, Rob S. E. W.; Hendriks, A. Jan (2021): Dropping the microbead: Source and sink related microplastic distribution in the Black Sea and Caspian Sea basins. In *Marine pollution bulletin* 173 (Pt A), p. 112982. DOI: 10.1016/j.marpolbul.2021.112982.

DIN 38409-2:1987-03, Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung; Summarische Wirkungs- und Stoffkenngrößen (Gruppe_H); Bestimmung der abfiltrierbaren Stoffe und des Glührückstandes_(H_2).

DIN CEN ISO/TR 21960 (2021-02-00), Plastics - Environmental aspects - State of knowledge and methodologies (ISO/TR 21960:2020); English version CEN ISO/TR 21960:2020.

DIN EN ISO 5667-1:2007-04, Wasserbeschaffenheit_- Probenahme_- Teil_1: Anleitung zur Erstellung von Probenahmeprogrammen und Probenahmetechniken (ISO_5667-1:2006); Deutsche Fassung EN_ISO_5667-1:2006.

DIN EN ISO 5667-14:2016-12, Wasserbeschaffenheit_- Probenahme_- Teil_14: Anleitung zur Qualitätssicherung und Qualitätskontrolle bei der Entnahme und Handhabung von Wasserproben (ISO_5667-14:2014); Deutsche Fassung EN_ISO_5667-14:2016.

Dris, Rachid; Gasperi, Johnny; Mirande, Cécile; Mandin, Corinne; Guerrouache, Mohamed; Langlois, Valérie; Tassin, Bruno (2017): A first overview of textile fibers, including microplastics, in indoor and outdoor environments. In *Environmental pollution (Barking, Essex : 1987)* 221, pp. 453–458. DOI: 10.1016/j.envpol.2016.12.013.

Dris, Rachid; Imhof, Hannes; Sanchez, Wilfried; Gasperi, Johnny; Galgani, Franois; Tassin, Bruno; Laforsch, Christian (2015): Beyond the ocean. Contamination of freshwater ecosystems with (micro-)plastic particles. In *Environ. Chem.* 12 (5), p. 539. DOI: 10.1071/EN14172.

Drobny, Jiri George (2014): Handbook of thermoplastic elastomers. Second edition. Norwich, NY: William Andrew Pub (PDL handbook series).

Duemichen, E.; Eisentraut, P.; Celina, M.; Braun, U. (2019): Automated thermal extraction-desorption gas chromatography mass spectrometry: A multifunctional tool for comprehensive characterization of polymers and their degradation products. In *Journal of chromatography. A* 1592, pp. 133–142. DOI: 10.1016/j.chroma.2019.01.033.

Dümichen, Erik; Barthel, Anne-Kathrin; Braun, Ulrike; Bannick, Claus G.; Brand, Kathrin; Jekel, Martin; Senz, Rainer (2015): Analysis of polyethylene microplastics in environmental samples, using a thermal decomposition method. In *Water research* 85, pp. 451–457. DOI: 10.1016/j.watres.2015.09.002.

DWA (2012): Fremdwasser in Entwässerungssystemen außerhalb von Gebäuden. [Stand:] April 2012. Hennef: DWA, Dt. Vereinigung für Wasserwirtschaft, Abwasser und Abfall (DWA-Regelwerk : Merkblatt, DWA-M, 182).

DWA (Ed.) (2015): Neuartige Sanitärsysteme. Begriffe, Stoffströme, Behandlung von Schwarz-, Braun-, Gelb-, Grau-, und Regenwasser, Stoffliche Nutzung. Weiterbildender Studiengang Wasser und Umwelt; Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall. 2. Auflage. Kromsdorf: Bauhaus-Universitätsverlag als Imprint von VDG Weimar. Available online at https://www.db-thueringen.de/receive/dbt_mods_00032721.

DWA/BWK (2020): Arbeitsblatt DWA-A 102-1/BWK-A 3-1. Dezember 2020, 1. Auflage. Hennef: Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e.V. (DWA) (DWA-Regelwerk, A 102-1/BWK-A 3-1).

DWD (2022): Rain data at the station 2486 in Kaiserslautern. Available online at https://cdc.dwd.de/rest//metadata/station/html/812300048103, checked on 11/2/2022.

Dyachenko, A.; Mitchell, J.; Arsem, N. (2017): Extraction and identification of microplastic particles from secondary wastewater treatment plant (WWTP) effluent. In *Anal. Methods* 9 (9), pp. 1412–1418. DOI: 10.1039/C6AY02397E.

EC (2022): Microplastics. Upcoming initiative on microplastics. With assistance of European Commission, the Directorate-General for Environment. Edited by EC. Available online at https://environment.ec.europa.eu/topics/plastics/microplastics_en, checked on 8/8/2022.

EFG Ltd (2021): Synthetics & Sustainable Synthetics: Global Production. Edited by © Common Objective. Ethical Fashion Group Ltd. London. Available online at https://www.commonobjective.co/article/synthetics-sustainable-synthetics-global-production, checked on 11/2/2022.

Eisentraut, Paul; Dümichen, Erik; Ruhl, Aki Sebastian; Jekel, Martin; Albrecht, Mirko; Gehde, Michael; Braun, Ulrike (2018): Two Birds with One Stone—Fast and Simultaneous Analysis of Microplastics: Microparticles Derived from Thermoplastics and Tire Wear. In *Environ. Sci. Technol. Lett.* 5 (10), pp. 608–613. DOI: 10.1021/acs.estlett.8b00446.

ELPA (2022): The Litter Challenge, Facts and Costs. Edited by Clean Europe Network. The European Litter Prevention Association. Available online at https://cleaneuropenetwork.eu/en/facts-and-costs/aup/, checked on 10/2/2022.

Engineering ToolBox (2001): Polymers - Physical Properties. Densities, tensile strength, elongation, Youngs modulus and Brinell hardness. Available online at https://www.engineeringtoolbox.com, checked on 8/30/2022.

VDI-Norm VDI 3782, 2003: Environmental meteorology - Determination of the emission from motor vehicles, checked on 11.2003.

Enyoh, Christian Ebere; Verla, Andrew Wirnkor; Verla, Evelyn Ngozi; Ibe, Francis Chizoruo; Amaobi, Collins Emeka (2019): Airborne microplastics: a review study on method for analysis, occurrence, movement and risks. In *Environmental Monitoring and Assessment* 191 (11), p. 668. DOI: 10.1007/s10661-019-7842-0.

EPA (2014): Brake and Tire Wear Emissions from On-road Vehicles in MOVES2014: U.S. Environmental Protection Agency, Office of Transportation and Air Quality, Assessment and Standards Division. Available online at https://books.google.de/books?id=6k0tngAACAAJ.

Fältström, Emma; Olesen, Kristina Borg; Anderberg, Stefan (2021): Microplastic Types in the Wastewater System—A Comparison of Material Flow-Based Source Estimates and the Measurement-Based Load to a Wastewater Treatment Plant. In *Sustainability* 13 (10), p. 5404. DOI: 10.3390/su13105404.

Fernández, Lucía (2021): Global synthetic fiber production 1940-2019. Edited by Statista. Available online at https://www.statista.com/aboutus/our-research-commitment, checked on 11/2/2022.

Fischer, Marten; Scholz-Böttcher, Barbara M. (2017): Simultaneous Trace Identification and Quantification of Common Types of Microplastics in Environmental Samples by Pyrolysis-Gas Chromatography-Mass Spectrometry. In *Environ. Sci. Technol.* 51 (9), pp. 5052–5060. DOI: 10.1021/acs.est.6b06362.

Frias, J. P. G. L.; Nash, Roisin (2019): Microplastics: Finding a consensus on the definition. In *Marine pollution bulletin* 138, pp. 145–147. DOI: 10.1016/j.marpolbul.2018.11.022.

Frias, J. P. G. L.; Sobral, P.; Ferreira, A. M. (2010): Organic pollutants in microplastics from two beaches of the Portuguese coast. In *Marine pollution bulletin* 60 (11), pp. 1988–1992. DOI: 10.1016/j.marpolbul.2010.07.030.

Friedler, E.; Hadari, M. (2006): Economic feasibility of on-site greywater reuse in multi-storey buildings. In *Desalination* 190 (1-3), pp. 221–234. DOI: 10.1016/j.desal.2005.10.007.

Fuchs, S; Kemper, M; Nickel, J.P. (Eds.) (2019): Feststoffe in der Regenwasserbehandlung. With assistance of J. Pinnekamp. 52. Essener Tagung für Wasserwirtschaft. Aachen, Germany, 20th – 22nd March.

Fuhrmann, Tim; Urban, Ingo; Scheer, Holger; Lau, Philipp; Reinhold, Luisa; Barjenbruch, Matthias et al. (2021): Mikroplastik-Emissionen aus Kläranlagen. In *Mikroplastik-Emissionen aus Kläranlagen* 2021 (9), pp. 730–741. DOI: 10.3242/kae2021.09.003.

Gaga, Eftade O.; Arı, Akif; Akyol, Nesimi; Üzmez, Özlem Özden; Kara, Melik; Chow, Judith C. et al. (2018): Determination of real-world emission factors of trace metals, EC, OC, BTEX, and semivolatile organic compounds (PAHs, PCBs and PCNs) in a rural tunnel in Bilecik, Turkey. In *The Science of the total environment* 643, pp. 1285–1296. DOI: 10.1016/j.scitotenv.2018.06.227.

Galloway, Tamara S. (2015): Micro- and Nano-plastics and Human Health. In Melanie Bergmann, Lars Gutow, Michael Klages (Eds.): Marine Anthropogenic Litter. Cham: Springer International Publishing, pp. 343–366.

Gaylarde, Christine; Baptista-Neto, Jose Antonio; da Fonseca, Estefan Monteiro (2021): Plastic microfibre pollution: how important is clothes' laundering? In *Heliyon* 7 (5), e07105. DOI: 10.1016/j.heliyon.2021.e07105.

GESAMP (2016): Sources, fate and effects of microplastics in the marine environment: part two of a global assessment. Edited by Kershaw, P.J., and Rochman, C.M. IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/ UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (Rep. Stud. GESAMP, 93).

Geyer, Roland (2020): Production, use, and fate of synthetic polymers. In : Plastic Waste and Recycling: Elsevier, pp. 13–32.

Ghaitidak, Dilip M.; Yadav, Kunwar D. (2013): Characteristics and treatment of greywater--a review. In *Environmental science and pollution research international* 20 (5), pp. 2795–2809. DOI: 10.1007/s11356-013-1533-0.

Gies, Esther A.; LeNoble, Jessica L.; Noël, Marie; Etemadifar, Anahita; Bishay, Farida; Hall, Eric R.; Ross, Peter S. (2018): Retention of microplastics in a major secondary wastewater treatment plant in Vancouver, Canada. In *Marine pollution bulletin* 133, pp. 553–561. DOI: 10.1016/j.marpolbul.2018.06.006.

Goedecke, Caroline; Eisentraut, Paul; Altmann, Korinna; Elert, Anna Maria; Bannick, Claus G.; Ricking, Mathias et al. (2022): Development of a Routine Screening Method for the Microplastic Mass Content in a Wastewater Treatment Plant Effluent. In *Front. Environ. Chem.* 3, Article 844633. DOI: 10.3389/fenvc.2022.844633.

Golwala, Harmita; Zhang, Xueyao; Iskander, Syeed Md; Smith, Adam L. (2021): Solid waste: An overlooked source of microplastics to the environment. In *The Science of the total environment* 769, p. 144581. DOI: 10.1016/j.scitotenv.2020.144581.

Google Earth (2019). Hohenecken Kaiserslautern. 49°25'00.2"N 7°41'44.7"E. Available online at https://earth.google.com/web/@49.41652475,7.69135639,296.15253384a,1211.47031178d,35y,359.99819934h,0t,0r?utm_source=earth7&utm_campaign=vine&hl=en, checked on 6/15/2022.

Griffith, Breda; Nallari, Raj; Yusuf, Shahid (Eds.) (2012): Geography of Growth: Spatial Economics and Competitiveness (Directions in Development): The World Bank Group.

Grupe, Albrecht; Selent, Klaus-Dieter (Eds.) (2018): Die Probenahme von Wasser. Ein Handbuch für die Praxis. 2. Auflage. Essen: DIV, Deutscher Industrieverlag (gwf edition). Available online at https://scifo.de/detail/media/show/Product/?tx_acmmam_acmmam%5bean%5d=9783835673113.

Habibi, Nazima; Uddin, Saif; Fowler, Scott W.; Behbehani, Montaha (2022): Microplastics in the atmosphere: a review. In *JEEA*. DOI: 10.20517/jeea.2021.07.

HACH LANGE GMBH (2019): LCK 514 Chemical Oxygen Demand (COD). Available online at https://de.hach.com/product.detail-downloads.jsa?id=26370260949, checked on 6/15/2022.

Hahladakis, John N.; Velis, Costas A.; Weber, Roland; Iacovidou, Eleni; Purnell, Phil (2018): An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. In *Journal of hazardous materials* 344, pp. 179–199. DOI: 10.1016/j.jhazmat.2017.10.014.

Hann, Simon; Kershaw, Peter; Sherrington, Chris; Bapasola, Ayesha; Jamieson, Olly; Cole, George; Hickman, Molly (2018): Investigating options for reducing releases in the aquatic environment of microplastics emitted by (but not intentionally added in) products. Final Report. Report for DG Environment of the European Commission. Edited by Eunomia Research & Consulting Ltd, ICF. London. Available online at https://ec.europa.eu/environment/marine/good-environmental-status/descriptor-10/pdf/microplastics_final_report_v5_full.pdf, checked on 9/1/2022.

Hartmann, Nanna B.; Hüffer, Thorsten; Thompson, Richard C.; Hassellöv, Martin; Verschoor, Anja; Daugaard, Anders E. et al. (2019): Are We Speaking the Same Language? Recommendations for a Definition and Categorization Framework for Plastic Debris. In *Environmental science & technology* 53 (3), pp. 1039–1047. DOI: 10.1021/acs.est.8b05297.

Hedges & Company (2023): HOW MANY CARS ARE THERE IN THE WORLD IN 2023? AUTOMOTIVE MARKET RESEARCH. Available online at https://hedgescompany.com/blog/2021/06/how-many-cars-are-there-in-the-world/#:~:text=CLICK%20TO%20ENLARGE%3A%20This%20graphic,cars%20by%20region%20or%20continent.

Heeb, Johannes; Ableidinger, Martina; Berger, Till; Hoffelner, Wolfgang (2016): Littering – ein Schweizer Problem? Eine Vergleichsstudie Schweiz - Europa. Edited by Institut für Mensch, Gesellschaft und Umwelt (MGU) der Universität Basel. Basel. Available online at https://gewerbe-basel.ch/content/uploads/2016/12/Littering_Vergleichsstudie_05.pdf, checked on 10/2/2022.

Hernandez, Edgar; Nowack, Bernd; Mitrano, Denise M. (2017): Polyester Textiles as a Source of Microplastics from Households: A Mechanistic Study to Understand

Microfiber Release During Washing. In *Environmental science & technology* 51 (12), pp. 7036–7046. DOI: 10.1021/acs.est.7b01750.

Heß, Maren; Diehl, Peter; Mayer, Jens; Rahm, Harald; Reifenhäuser, Werner; Stark, Jochen; Schwaiger, Julia (2018): Mikroplastik in Binnengewässern Süd- und Westdeutschlands. Bundesländerübergreifende Untersuchungen in Baden-Württemberg, Bayern, Hessen, Nordrhein-Westfalen und Rheinland-Pfalz. Teil 1: Kunststoffpartikel in der oberflächennahen Wasserphase. Edited by Landesanstalt für Umwelt Baden-Württemberg (LUBW), Bayerisches Landesamt für Umwelt (LfU), Hessisches Landesamt für Naturschutz, Umwelt und Geologie (HLNUG), Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen (LANUV), Landesamt für Umwelt Rheinland-Pfalz (LfU RLP). Karlsruhe, Augsburg, Wiesbaden, Recklinghausen, Mainz.

Hidalgo-Ruz, Valeria; Gutow, Lars; Thompson, Richard C.; Thiel, Martin (2012): Microplastics in the marine environment: a review of the methods used for identification and quantification. In *Environ. Sci. Technol.* 46 (6), pp. 3060–3075. DOI: 10.1021/ES2031505.

Hildebrandt, L.; Voigt, N.; Zimmermann, T.; Reese, A.; Proefrock, D. (2019): Evaluation of continuous flow centrifugation as an alternative technique to sample microplastic from water bodies. In *Marine environmental research* 151, p. 104768. DOI: 10.1016/j.marenvres.2019.104768.

ISO/TS 21396 (2017): TS 21396: 2017 Rubber Determination of mass concentration of tire and road wear particles (TRWP) in soil and sediments◎ Pyrolysis-GC.

Järlskog, Ida; Strömvall, Ann-Margret; Magnusson, Kerstin; Galfi, Helén; Björklund, Karin; Polukarova, Maria et al. (2021): Traffic-related microplastic particles, metals, and organic pollutants in an urban area under reconstruction. In *The Science of the total environment* 774, p. 145503. DOI: 10.1016/j.scitotenv.2021.145503.

João P. G. L. Frias; Elena Pagter; Roisin Nash; Ian O'Connor; Olga Carretero; Ana Filgueiras et al. (2018): Standardised protocol for monitoring microplastics in sediments.

Kay, Paul; Hiscoe, Robert; Moberley, Isobel; Bajic, Luke; McKenna, Niamh (2018): Wastewater treatment plants as a source of microplastics in river catchments. In *Environmental science and pollution research international* 25 (20), pp. 20264–20267. DOI: 10.1007/s11356-018-2070-7.

KBA (2022): Fahrzeugbestand in Deutschland zum 01.01.2022. Edited by The Kraftfahrt-Bundesamt. Available online at https://www.kba.de/DE/Statistik/Fahrzeuge/Bestand/bestand_node.html.

Keep America Beautiful (Ed.) (2021): 2020 NATIONAL LITTER STUDY. Summary Report 2021.

Kenyon, Karl W.; Kridler, Eugene (1969): Laysan Albatrosses Swallow Indigestible Matter. In *The Auk* 86 (2), pp. 339–343. DOI: 10.2307/4083505.

Kholodovych, Vladyslav; Welsh, William J. (2007): Densities of Amorphous and Crystalline Polymers. In James E. Mark (Ed.): Physical properties of polymer handbook. New York, NY: Springer New York, pp. 611–617.

Kim, Keug Tae; Park, Sanghwa (2021): Enhancing Microplastics Removal from Wastewater Using Electro-Coagulation and Granule-Activated Carbon with Thermal Regeneration. In *Processes* 9 (4), p. 617. DOI: 10.3390/pr9040617.

KIMO International (2022): The EU knows that microplastic pollution from artificial turf is a problem – how will they respond? Edited by KIMO International Secretariat. KIMO International Secretariat. Shetland, UK. Available online at https://www.kimointernational.org/news/eu-decision-pending-on-microplastics-from-artificial-turf/, checked on 9/1/2022.

Kittner, Maria; Kerndorff, Alexander; Ricking, Mathias; Bednarz, Marius; Obermaier, Nathan; Lukas, Marcus et al. (2022): Microplastics in the Danube River Basin: A First Comprehensive Screening with a Harmonized Analytical Approach. In *ACS EST Water* 2 (7), pp. 1174–1181. DOI: 10.1021/acsestwater.1c00439.

Kocher, Birgit (2010): Stoffeinträge in den Straßenseitenraum. Reifenabrieb. V 188. With assistance of Susanne Brose, Johannes Feix, Claudia Görg, Angela Peters, Klaus Schenker. Bundesanstalt für Straßenwesen. Bergisch Gladbach (Verkehrstechnik, V 188). Available online at https://bast.opus.hbz-nrw.de/opus45-bast/frontdoor/deliver/index/docId/60/file/V188.pdf, checked on 10/2/2022.

Kolisch, G.; Pyro, P.; Steinmetz, H.; Béalu, Z.; Walther, J.; Gretzschel, O. et al. (2022): eloise - Innovative Verfahrenskette aus Elektrolyse und Ozonierung zur Spurenstoffelimination auf kommunalen Kläranlagen. Fördervorhaben des Bundesministerium für Bildung und Forschung. Wupperverbandsgesellschaft für integrale Wasserwirtschaft mbH (WiW). Wuppertal. Available online at https://seafile.rlp.net/f/631483ae9f3c43569588/?dl=1.

Kooi, Merel; Koelmans, Albert A. (2019): Simplifying Microplastic via Continuous Probability Distributions for Size, Shape, and Density. In *Environ. Sci. Technol. Lett.* 6 (9), pp. 551–557. DOI: 10.1021/acs.estlett.9b00379.

Kuoppamäki, Kirsi; Pflugmacher Lima, Stephan; Scopetani, Costanza; Setälä, Heikki (2021): The ability of selected filter materials in removing nutrients, metals, and microplastics from stormwater in biofilter structures. In *Journal of Environmental Quality* 50 (2), pp. 465–475. DOI: 10.1002/jeq2.20201.

Lassen, Carsten; Hansen, Steffen Foss; Magnusson, Kerstin; Norén, Fredrik; Bloch Hartmann, Nanna Isabella; Jensen, Pernille Rehne et al. (2015): Microplastics. Occurrence, effects and sources of releases to the environment in Denmark: Danish Environmental Protection Agency. Available online at https://backend.orbit.dtu.dk/ws/portalfiles/portal/118180844/Lassen_et_al._2015.pdf.

Lehtiniemi, Maiju; Hartikainen, Samuel; Näkki, Pinja; Engström-Öst, Jonna; Koistinen, Arto; Setälä, Outi (2018): Size matters more than shape: Ingestion of primary and secondary microplastics by small predators. In *Food Webs* 17, e00097. DOI: 10.1016/j.fooweb.2018.e00097.

Lenz, Daniel (2020): Analyse und Bewertung verschiedener Steuerungsformen einer Einmündung. Master thesis. TU Kaiserslautern, Kaiserslautern. MOBILITY & TRANSPORT, checked on 5/13/2022.

Lenz, Robin; Enders, Kristina; Stedmon, Colin A.; Mackenzie, David M. A.; Nielsen, Torkel Gissel (2015): A critical assessment of visual identification of marine microplastic using Raman spectroscopy for analysis improvement. In *Marine pollution bulletin* 100 (1), pp. 82–91. DOI: 10.1016/j.marpolbul.2015.09.026.

Leslie, H. A. (2015): Plastic in cosmetics. Are we polluting the environment through our personal care? : plastic ingredients that contribute to marine microplastic litter. Nairobi, Kenya: United Nations Environment Programme. Available online at http://apps.unep.org/publications/index.php?option=com_pub&task=download&file=011718_en.

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. In *Environment international* 101, pp. 133–142. DOI: 10.1016/j.envint.2017.01.018.

Leslie, Heather A.; van J. M. Velzen, Martin; Brandsma, Sicco H.; Vethaak, Dick; Garcia-Vallejo, Juan J.; Lamoree, Marja H. (2022): Discovery and quantification of plastic particle pollution in human blood. In *Environment international*, p. 107199. DOI: 10.1016/j.envint.2022.107199.

Litescu, Simona-Carmen (2012): Chapter Fourier Transform Infrared Spectroscopy - Useful Analytical Tool for Non-Destructive Analysis: InTechOpen.

Liu, Ye; Chen, Haibo; Wu, Sijin; Gao, Jianbing; Li, Ying; An, Zihao et al. (2022): Impact of vehicle type, tyre feature and driving behaviour on tyre wear under real-world driving conditions. In *Science of The Total Environment* 842, p. 156950. DOI: 10.1016/j.scitotenv.2022.156950.

Löder, Martin G. J.; Gerdts, Gunnar (2015): Methodology Used for the Detection and Identification of Microplastics—A Critical Appraisal. In Melanie Bergmann, Lars Gutow, Michael Klages (Eds.): Marine Anthropogenic Litter. Cham: Springer International Publishing, pp. 201–227.

LUBW (2007): Fremdwasser in kommunalen Kläranlagen. Erkennen, bewerten und vermeiden. With assistance of Umweltministerium Baden-Württemberg, LUBW Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg, Universität Stuttgart - Institut für Siedlungswasserbau, Wassergüte, IKT – Institut für Unterirdische Infrastruktur GmbH. Edited by LUBW Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg. Available online at https://pudi.lubw.de/detailseite/-/publication/35669.

Lusher, A. L.; Welden, N. A.; Sobral, P.; Cole, M. (2017): Sampling, isolating and identifying microplastics ingested by fish and invertebrates. In *Analytical Methods* 9 (9), pp. 1346–1360. DOI: 10.1039/C6AY02415G.

Magnusson, Kerstin; Norén, Fredrik (2014): Screening of microplastic particles in and down-stream a wastewater treatment plant. Available online at https://www.diva-portal.org/smash/record.jsf?pid=diva2:773505.

Malamis, S.; Katsou, E.; Inglezakis, V. J.; Kershaw, S.; Venetis, D.; Folini, S. (2016): Urban Environment. In : Environment and development : basic principles, human activities, and environmental implications: Elsevier, pp. 287–362.

Mark, James E. (Ed.) (2007): Physical properties of polymer handbook. With assistance of James E. Mark. 2nd ed. New York: Springer. Available online at https://ebookcentral.proquest.com/lib/kxp/detail.action?docID=324285.

Mason, Sherri A.; Garneau, Danielle; Sutton, Rebecca; Chu, Yvonne; Ehmann, Karyn; Barnes, Jason et al. (2016): Microplastic pollution is widely detected in US municipal wastewater treatment plant effluent. In *Environmental pollution (Barking, Essex : 1987)* 218, pp. 1045–1054. DOI: 10.1016/j.envpol.2016.08.056.

Mattonai, Marco; Nacci, Tommaso; Modugno, Francesca (2022): Analytical strategies for the quali-quantitation of tire and road wear particles – A critical review. In *TrAC Trends in Analytical Chemistry* 154, p. 116650. DOI: 10.1016/j.trac.2022.116650.

McHhee, Terence J. (1991): Water supply and sewerage engineering. 6th ed. New York: McGraw-Hill (McGraw-Hill series in water resources and environmental engineering).

Mintenig, S.; Int-Veen, I.; Löder, M.; Gerdts, G. (2014): Mikroplastik in ausgewählten Kläranlagen des Oldenburgisch- Ostfriesischen Wasserverbandes (OOWV) in Niedersachsen. Probenanalyse mittels Mikro-FTIR Spektroskopie. Oldenburgisch- Ostfriesischer Wasserverband (OOWV). Available online at https://www.muell-im-meer.de/sites/default/files/2020-08/Mintening%20et%20al%20%282014%29_Mikroplastik%20in%20ausgew%C3%A4hlten%20Kl%C3%A4ranlagen%20des%20OOWV%20in%20Niedersachsen.pdf.

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. In *Water research* 108, pp. 365–372. DOI: 10.1016/j.watres.2016.11.015.

MKUEM (2021): LANDESABFALLBILANZ RHEINLAND-PFALZ 2019. With assistance of Sonderabfall-Management-Gesellschaft Rheinland-Pfalz mbH, Landesamt für Umwelt, Witzenhausen-Institut für Abfall, Umwelt und Energie GmbH. Edited by Ministerium für Umwelt, Energie, Ernährung und Forsten Rheinland-Pfalz. Mainz. Available online at https://mkuem.rlp.de/fileadmin/mulewf/Themen/Klima-_und_Ressourcenschutz/Kreislaufwirtschaft/Abfallbilanz/Landesabfallbilanz_Rheinland_Pfalz_2019_Corporate_Design.pdf, checked on 10/2/2022.

Müller, Axel; Goedecke, Caroline; Eisentraut, Paul; Piechotta, Christian; Braun, Ulrike (2020): Microplastic analysis using chemical extraction followed by LC-UV analysis: a straightforward approach to determine PET content in environmental samples. In *Environ Sci Eur* 32 (1), p. 7111. DOI: 10.1186/s12302-020-00358-x.

Murphy, Fionn; Ewins, Ciaran; Carbonnier, Frederic; Quinn, Brian (2016): Wastewater Treatment Works (WwTW) as a Source of Microplastics in the Aquatic

Environment. In *Environmental science & technology* 50 (11), pp. 5800–5808. DOI: 10.1021/acs.est.5b05416.

MWVLW-RLP (2022): Mobility Atlas Rheinland-Pfalz. Ministry of Economy, Transport, Agriculture and Viticulture. Edited by Ministerium für Wirtschaft, Verkehr, Landwirtschaft und Weinbau. Mainz, checked on 5/13/2022.

Nelson, Martin E.; Benedict, Paul C. (1951): Measurement and Analysis of Suspended Sediment Loads in Streams. In *T. Am. Soc. Civ. Eng.* 116 (1), pp. 891–918. DOI: 10.1061/TACEAT.0006548.

Newman, Karen (2007): Cultural Capitals. Early Modern London and Paris. Princeton, NJ: Princeton University Press.

Ng, K. L.; Obbard, J. P. (2006): Prevalence of microplastics in Singapore's coastal marine environment. In *Marine pollution bulletin* 52 (7), pp. 761–767. DOI: 10.1016/j.marpolbul.2005.11.017.

Nickel, Jan Philip; Fuchs, Stephan (2021): Large-Volume Samplers for Efficient Composite Sampling and Particle Characterization in Sewer Systems. In *Water* 13 (20), p. 2831. DOI: 10.3390/w13202831.

NIVUS GmbH (2016): Instruction manual OCM Pro CF. Eppingen, Germany. private communication.

Norén, Fredrik (2007): Small plastic particles in Coastal Swedish waters. In *KIMO Report*, pp. 1–11.

Öborn, Lisa; Österlund, Heléne; Svedin, Jonathan; Nordqvist, Kerstin; Viklander, Maria (2022): Litter in Urban Areas May Contribute to Microplastics Pollution: Laboratory Study of the Photodegradation of Four Commonly Discarded Plastics. In *J. Environ. Eng.* 148 (11), Article 06022004. DOI: 10.1061/%28ASCE%29EE.1943-7870.0002056.

OECD (2022): GLOBAL PLASTICS OUTLOOK POLICY SCENARIOS TO 2060. [S.l.]: ORGANIZATION FOR ECONOMIC. Available online at https://www.oecd.org/publications/global-plastics-outlook-aa1edf33-en.htm#:~:text=The%20Global%20Plastics%20Outlook%3A%20Policy,especially%20leakage%20to%20the%20environment.

Oteng-Peprah, Michael; Acheampong, Mike Agbesi; deVries, Nanne K. (2018): Greywater Characteristics, Treatment Systems, Reuse Strategies and User Perception-a Review. In *Water, air, and soil pollution* 229 (8), p. 255. DOI: 10.1007/s11270-018-3909-8.

Patki, Rahul; Mezghani, Khaled; Phillips, Paul J. (2007): Crystallization Kinetics of Polymers. In James E. Mark (Ed.): Physical properties of polymer handbook. New York, NY: Springer New York, pp. 625–640.

PD ISO/TS 20593:2017 (2017): TS 20593: AmbientAir-determination of the Mass Concentration of Tire and Road Wear Particles (TRWP)-pyrolysis-GC-MS Method.

Periyasamy, Aravin Prince; Tehrani-Bagha, Ali (2022): A review on microplastic emission from textile materials and its reduction techniques. In *Polymer Degradation and Stability* 199, p. 109901. DOI: 10.1016/j.polymdegradstab.2022.109901.

Picó, Yolanda; Soursou, Vasiliki; Alfarhan, Ahmed H.; El-Sheikh, Mohamed A.; Barceló, Damià (2021): First evidence of microplastics occurrence in mixed surface and treated wastewater from two major Saudi Arabian cities and assessment of their ecological risk. In *Journal of hazardous materials* 416, p. 125747. DOI: 10.1016/j.jhazmat.2021.125747.

Piscitello, Amelia; Bianco, Carlo; Casasso, Alessandro; Sethi, Rajandrea (2021): Non-exhaust traffic emissions: Sources, characterization, and mitigation measures. In *Science of The Total Environment* 766, p. 144440. DOI: 10.1016/j.scitotenv.2020.144440.

Pittroff, Marco; Witzig, Cordula; Storck, Florian Rüdiger; (None) (2017): Automatisierte Identifizierung und Charakterisierung von Mikroplastik aus Oberflächengewässern mittels Raman-Mikrospektroskopie. In *Donaueschingen: Ges. Dtsch. Chem.-Fachgr. Wasserchemische Ges., Tagung Wasser* 2017, p. 2017.

Plastics Europe (2021): Plasctics - the Facts 2021. Available online at https://plasticseurope.org/wp-content/uploads/2021/12/Plastics-the-Facts-2021-web-final.pdf, checked on 6/15/2022.

Primpke, Sebastian; Christiansen, Silke H.; Cowger, Win; Frond, Hannah de; Deshpande, Ashok; Fischer, Marten et al. (2020): Critical Assessment of Analytical Methods for the Harmonized and Cost-Efficient Analysis of Microplastics. In *Applied spectroscopy* 74 (9), pp. 1012–1047. DOI: 10.1177/0003702820921465.

Princi, Elisabetta (2019): Rubber. Science and technology. Berlin, Boston: De Gruyter (De Gruyter STEM).

Ramirez Arenas, Lina; Ramseier Gentile, Stéphan; Zimmermann, Stéphane; Stoll, Serge (2021): Nanoplastics adsorption and removal efficiency by granular activated carbon used in drinking water treatment process. In *The Science of the total environment* 791, p. 148175. DOI: 10.1016/j.scitotenv.2021.148175.

Rios Mendoza, L. M.; Balcer, M. (2020): Association of hazardous compounds with microplastics in freshwater ecosystems. In Hrissi Karapanagioti, Ioannis K. Kalavrouziotis (Eds.): Microplastics in Water and Wastewater - 2nd Edition. London: IWA Publishing, pp. 15–25.

Rochman, Chelsea M. (2018): Microplastics research-from sink to source. In *Science* 360 (6384), pp. 28–29. DOI: 10.1126/science.aar7734.

Rødland, Elisabeth S.; Samanipour, Saer; Rauert, Cassandra; Okoffo, Elvis D.; Reid, Malcom J.; Heier, Lene S. et al. (2021): A novel method for the quantification of tire and polymer-modified bitumen particles in environmental samples by pyrolysis gas chromatography mass spectroscopy. In *Journal of hazardous materials* 423 (Pt A), p. 127092. DOI: 10.1016/j.jhazmat.2021.127092.

Roland, Mike; Erman, Burak; Mark, James E. (2013): The science and technology of rubber. Fourth edition. Amsterdam, Boston: Elsevier Academic Press.

Rosal, Roberto (2021): Morphological description of microplastic particles for environmental fate studies. In *Marine pollution bulletin* 171, p. 112716. DOI: 10.1016/j.marpolbul.2021.112716.

Rudin, Alfred; Choi, Phillip (Eds.) (2013): The elements of polymer science and engineering [recurso electrónico]. Third edition. Estados Unidos: Academic.

Ryan, Peter G. (2015): A Brief History of Marine Litter Research. In Melanie Bergmann, Lars Gutow, Michael Klages (Eds.): Marine Anthropogenic Litter. Cham: Springer International Publishing, pp. 1–25.

Šaravanja, Ana; Pušić, Tanja; Dekanić, Tihana (2022): Microplastics in Wastewater by Washing Polyester Fabrics. In *Materials (Basel, Switzerland)* 15 (7). DOI: 10.3390/ma15072683.

Sartorius, Christian (2007): Zukunftsmarkt Dezentrale Wasseraufbereitung und Regenwassermanagement. Edited by UBA. Fraunhofer-Institut für System- und Innovationsforschung (ISI), Karlsruhe. Available online at https://www.umweltbundesamt.de/sites/default/files/medien/publikation/long/3454.pdf.

Scheid, Christian (2022): Data on Catchment area of Kaiserslautern. E-Mail to Attaallah Abusafia, 2022.

Schmitt, Theo (2004): KOSMO. KOntiniuierliche SchmutzfrachtMOdellierung) – Modellbeschreibung, unveröffentlicht. Kaiserslautern.

Scholz, Günter; Gehringer, Manuela (2021): Thermoplastic Elastomers: De Gruyter.

Schwarzer, Michael; Brehm, Julian; Vollmer, Martina; Jasinski, Julia; Xu, Chengzhang; Zainuddin, Shakir et al. (2022): Shape, size, and polymer dependent effects of microplastics on Daphnia magna. In *Journal of hazardous materials* 426, p. 128136. DOI: 10.1016/j.jhazmat.2021.128136.

Shelley, Philip (1977): Sampling of Water and Wastewater. Cincinnati, OHIO: Environmental research information center. Available online at https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=9101QYXK.TXT.

Simon, Márta; van Alst, Nikki; Vollertsen, Jes (2018): Quantification of microplastic mass and removal rates at wastewater treatment plants applying Focal Plane Array (FPA)-based Fourier Transform Infrared (FT-IR) imaging. In *Water research* 142, pp. 1–9. DOI: 10.1016/j.watres.2018.05.019.

Sisanth, K. S.; Thomas, M. G.; Abraham, J.; Thomas, S. (2017): General introduction to rubber compounding. In : Progress in Rubber Nanocomposites: Elsevier, pp. 1–39.

Smith, William F.; Hashemi, Javad (2006): Foundations of materials science and engineering. 4th. ed., International ed. New York: Mcgraw-Hill Pub (McGraw-Hill series in materials science). Available online at http://www.loc.gov/catdir/enhancements/fy0701/2005043865-d.html.

Sørensen, C. G.; Møller, H. B. (2006): OPERATIONAL AND ECONOMIC MODELING AND OPTIMIZATION OF MOBILE SLURRY SEPARATION. In *Applied Engineering in Agriculture* 22 (2), pp. 185–193. DOI: 10.13031/2013.20280.

Stadtentwässerung Kaiserslautern (2021): Kanalnetz - Stadt Kaiserslautern. Available online at https://www.ste-kl.de/index.php?id=196&L=0, updated on 3/11/2021, checked on 3/11/2021.

Statista (2017): Number of passenger cars and commercial vehicles in use worldwide from 2006 to 2015. Edited by Statista GmbH. Available online at https://www.statista.com/statistics/281134/number-of-vehicles-in-use-worldwide/, updated on 10/30/2022.

Sullivan, T. J. (2015): Introduction to Uncertainty Quantification. Cham: Springer International Publishing (63).

Sutton, Rebecca; Mason, Sherri A.; Stanek, Shavonne K.; Willis-Norton, Ellen; Wren, Ian F.; Box, Carolynn (2016): Microplastic contamination in the San Francisco

Bay, California, USA. In *Marine pollution bulletin* 109 (1), pp. 230–235. DOI: 10.1016/j.marpolbul.2016.05.077.

Takada, Hideshige; Karapanagioti, Hrissi K. (Eds.) (2019): Hazardous Chemicals Associated with Plastics in the Marine Environment. 1st ed. 2019. Cham: Springer International Publishing (The Handbook of Environmental Chemistry, 78). Available online at https://ebookcentral.proquest.com/lib/kxp/detail.action?docID=5927101.

Talvitie, Julia; Mikola, Anna; Koistinen, Arto; Setälä, Outi (2017): Solutions to microplastic pollution - Removal of microplastics from wastewater effluent with advanced wastewater treatment technologies. In *Water research* 123, pp. 401–407. DOI: 10.1016/j.watres.2017.07.005.

Tanentzap, Andrew J.; Cottingham, Samuel; Fonvielle, Jérémy; Riley, Isobel; Walker, Lucy M.; Woodman, Samuel G. et al. (2021): Microplastics and anthropogenic fibre concentrations in lakes reflect surrounding land use. In *PLoS biology* 19 (9), e3001389. DOI: 10.1371/journal.pbio.3001389.

Thermo Fisher Scientific, Inc. (2022): Physical Properties Table. Available online at https://tools.thermofisher.com/content/sfs/brochures/D20826.pdf.

Thomas Kroher (2021): Dem Mikroplastik auf der Spur: Weniger Reifenabrieb ist möglich. In *ADAC*, 12/21/2021. Available online at https://www.adac.de/rund-ums-fahrzeug/ausstattung-technik-zubehoer/reifen/reifenkauf/reifenabrieb-mikroplastik/, checked on 5/19/2023.

Thompson, Richard C.; Olsen, Ylva; Mitchell, Richard P.; Davis, Anthony; Rowland, Steven J.; John, Anthony W. G. et al. (2004): Lost at sea: where is all the plastic? In *Science (New York, N.Y.)* 304 (5672), p. 838. DOI: 10.1126/science.1094559.

Treilles, Robin; Gasperi, Johnny; Gallard, Anaïs; Saad, Mohamed; Dris, Rachid; Partibane, Chandirane et al. (2021): Microplastics and microfibers in urban runoff from a suburban catchment of Greater Paris. In *Environmental pollution (Barking, Essex : 1987)* 287, p. 117352. DOI: 10.1016/j.envpol.2021.117352.

Turner, Andrew (2021): Paint particles in the marine environment: An overlooked component of microplastics. In *Water research X* 12, p. 100110. DOI: 10.1016/j.wroa.2021.100110.

Tyree, Corey; Allen, Jonathan (2004): Diffusional Particle Loss Upstream of Isokinetic Sampling Inlets. In *Aerosol Science and Technology* 38 (10), pp. 1019–1026. DOI: 10.1080/027868290519201.

Unice, K. M.; Weeber, M. P.; Abramson, M. M.; Reid, R. C. D.; van Gils, J. A. G.; Markus, A. A. et al. (2019): Characterizing export of land-based microplastics to the estuary - Part I: Application of integrated geospatial microplastic transport models to assess tire and road wear particles in the Seine watershed. In *The Science of the total environment* 646, pp. 1639–1649. DOI: 10.1016/j.scitotenv.2018.07.368.

Uurasjärvi, Emilia; Hartikainen, Samuel; Setälä, Outi; Lehtiniemi, Maiju; Koistinen, Arto (2020): Microplastic concentrations, size distribution, and polymer types in the surface waters of a northern European lake. In *Water Environment Research* 92 (1), pp. 149–156. DOI: 10.1002/wer.1229.

Venghaus, D; Frank Schmerwitz; Reiber J. und Sommer H. (2021): Reifenabrieb in der Umwelt - RAU. Final Report. Edited by Plastik in der Umwelt. Berlin. Available online at https://www.rau.tu-berlin.de/fileadmin/fg118/RAU/20210728_Abschlussbericht_RAU_FINAL_Team.pdf, checked on 5/23/2022.

Walpole, Ronald E.; Myers, Raymond H.; Myers, Sharon L.; Ye, Keying (2007): Probability & statistics for engineers & scientists. Eighth edition, international edition. Upper Saddle River: Pearson Education.

wetterkontor.de (2022): Wetterrückblick Kaiserslautern 2019/2020. Available online at https://www.wetterkontor.de/de/wetter/deutschland/rueckblick.asp?id=K863, checked on 11/3/2022.

Wiggin, Kara J.; Holland, Erika B. (2019): Validation and application of cost and time effective methods for the detection of 3-500 μm sized microplastics in the urban marine and estuarine environments surrounding Long Beach, California. In *Marine pollution bulletin* 143, pp. 152–162. DOI: 10.1016/j.marpolbul.2019.03.060.

Wolff, Sebastian; Weber, Felix; Kerpen, Jutta; Winklhofer, Miriam; Engelhart, Markus; Barkmann, Luisa (2021): Elimination of Microplastics by Downstream Sand Filters in Wastewater Treatment. In *Water* 13 (1), p. 33. DOI: 10.3390/w13010033.

World Bank (2022a): Solid Waste Management. Brief. Available online at https://www.worldbank.org/en/topic/urbandevelopment/brief/solid-waste-management.

World Bank (2022b): Urban population (% of total population) - Germany, World, Belgium, Afghanistan [1960-2021]. World Urbanization Prospects: 2018 Revision. Edited by United Nations Population Division. United Nations. Available online at https://data.worldbank.org/indicator/SP.URB.TOTL.IN.ZS.

Zhang, Kai; Gong, Wen; Lv, Jizhong; Xiong, Xiong; Wu, Chenxi (2015): Accumulation of floating microplastics behind the Three Gorges Dam. In *Environmental pollution (Barking, Essex : 1987)* 204, pp. 117–123. DOI: 10.1016/j.envpol.2015.04.023.

Ziajahromi, Shima; Neale, Peta A.; Rintoul, Llew; Leusch, Frederic D. L. (2017): Wastewater treatment plants as a pathway for microplastics: Development of a new approach to sample wastewater-based microplastics. In *Water research* 112, pp. 93–99. DOI: 10.1016/j.watres.2017.01.042.

Zuccaro, Philip; Thompson, David C.; Boer, Jacob de; Watterson, Andrew; Wang, Qiong; Tang, Song et al. (2022): Artificial turf and crumb rubber infill: An international policy review concerning the current state of regulations. In *Environmental Challenges* 9, p. 100620. DOI: 10.1016/j.envc.2022.100620.

8 Appendices

8.1. Background

Table A 1 First order calculation of MP emissions according to the study from UMSICHT institute (Bertling et al. 2018), own extraction from the text and analysis

Nr.	Source	Emissions (g/(cap a))	%	Relevant for Stormwater Runoff (Min. 35 Quellen)	Relevant for DW flow
		Umsicht			
1.0	**Tire abrasion**	**1228.5**	**42.6**		
1.1	Passenger cars	998	**34.6**	998	
1.2	Trucks	89	**3.1**	89	
1.3	Skateboards, etc.	17.9	**0.6**	17.9	
1.4	Bicycles	15.6	**0.5**	15.6	
1.5	Motorcycles	8	**0.3**	8	
2	**Release during waste disposal**	**302.8**	**10.5**		
2.1	Composting	169	**5.9**		
2.2	Crushing of construction waste	27.6	**1.0**		
2.3	Metal shredding	4.7	**0.2**	4.7	4.7
2.4	Plastic recycling	101	**3.5**	101	101
2.5	Landfills	0.5	**0.0**		
3	**Bitumen abrasion in asphalt**	**228**	**7.9**	228	
4	**Pellet losses**	**182**	**6.3**	182	
5	**Blowing away from sports and playgrounds**	**131.8**	**4.6**		
5.1	Artificial turf soccer fields	96.6	**3.4**	96.6	
5.2	Artificial turf hockey fields	4.9	**0.2**	4.9	
5.3	Riding arenas	1.2	**0.0**	1.2	
5.4	Competition tracks	24.3	**0.8**	24.3	
5.5	Playgrounds	4.8	**0.2**	4.8	
6	**Release at construction sites**	**117.1**	**4.1**		
6.1	asion at the construction site during demolition v	90	**3.1**		
6.2	Processing of plastics at the construction site	25.4	**0.9**		
6.3	Abrasion/cutting losses of insulations	1.7	**0.1**		
7	**Shoe sole abrasion**	**109**	**3.8**	109	11
8	**Abrasion of plastic packaging**	**99.1**	**3.4**		
9	**Road marking abrasion**	**91**	**3.2**	91	
10	**Fiber abrasion in textile washing**	**76.8**	**2.7**		
10.1	Fiber abrasion in household laundry	66	**2.3**	66	66
10.2	Fiber abrasion in laundromats	8.6	**0.3**	8.6	8.6
10.3	Fiber abrasion in commercial laundry	2.2	**0.1**	2.2	2.2

11	**Abrasion of paints and varnishes**	**65**	**2.3**	37		
11.1	Facade abrasion	37	**1.3**	10		
11.2	Abrasion of painted surfaces	inkl.				
11.3	Ship paint abrasion	inkl.				
11.4	Abrasion of wind turbines (WT)	inkl.				
12	**Abrasion of agriculturally used plastics**	**45**	**1.6**			
13	**Flocculants in municipal water management**	**43.5**	**1.5**	43.5	43.5	
14	**Broom and sweeper abrasion**	**38.3**	**1.3**			
14.1	Private sector & municipal cleaning	28.3	**1.0**	28.3	28.3	
14.2	Agricultural sweeper machines	9.6	**0.3**	9.6	9.6	
14.3	Municipal sweeper machines	0.4	**0.0**	0.4	0.4	
15	**Industrial wear protection abrasion, conveyor belts**	**30**	**1.0**			
16	**Wet cleaning of containers**	**23**	**0.8**	23	23	
17	**Microplastics content in cosmetics**	**19**	**0.7**	19	19	
18	**Belt abrasion**	**16.5**	**0.6**			
19	**Pipeline abrasion**	**12**	**0.4**	12	12	
20	**Abrasion of decorative materials, glitter, confetti, etc.**	**5.8**	**0.2**	5.8	5.8	
21	**Ingredients of detergents, care, and cleaning agents in private households**	**4.6**	**0.2**	4.6	4.6	
22	**Abrasion of fishing equipment**	**4.5**	**0.2**			
23	**Abrasion of gears, sliding bearings, slide**	**2.5**	**0.1**			
24	**Abrasion of lawn trimmers/motor scythes**	**1.5**	**0.1**	1.5		
25	**Medication additives**	**1.3**	**0.0**	1.3	1.3	
26	**Dolly rope abrasion**	**1.1**	**0.0**	1.1		
27	**Pyrotechnic fragmentation**	**0.7**	**0.0**	0.7		
28	**Ball abrasion**	**0.4**	**0.0**	0.4		
29	**Abrasion of WT cables due to torsion**	**0.02**	**0.0**			
30	**Buoy and fender abrasion**	**0.01**	**0.0**			
		2880.83		2251.00	341.00	
				87%	**13%**	%

8.2. Sampling

8.2.1. Sampling Locations

8.2.1.1. Stormwater retention tank (SRT) in combined drainage system (L3)

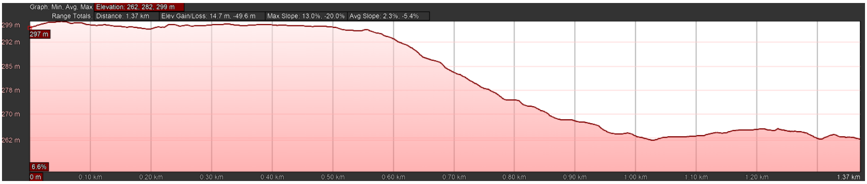


Figure A 1 Elevation profile of the longest flow path in the small sub-catchment area in combined sewer system before L3 (Google Earth 2022)

8.2.1.2. Stormwater retention tank (SRT) in separate drainage system (L4)

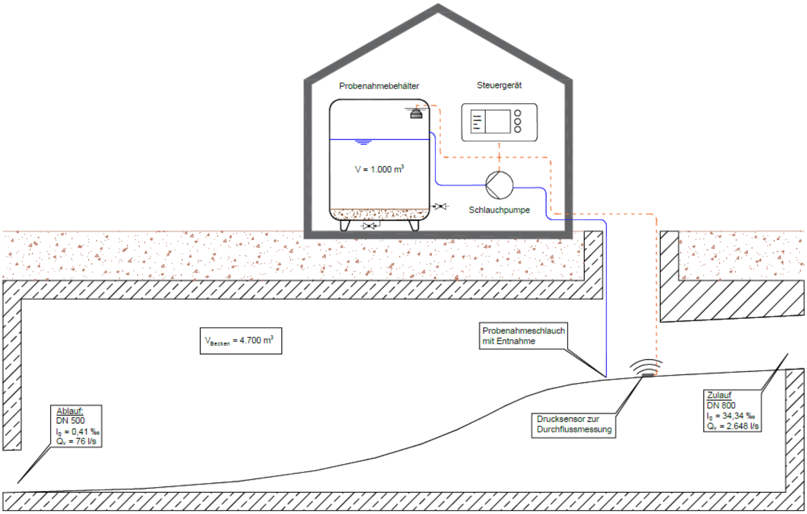


Figure A 2 Schematic representation of the stormwater retention tank (SRT) at L4 with the sampling plant

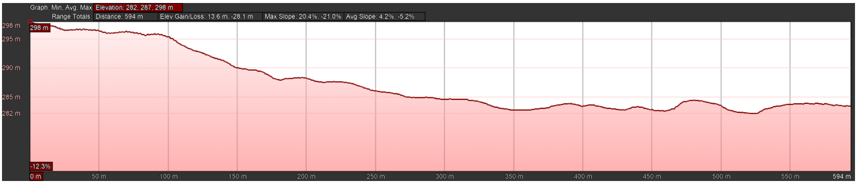
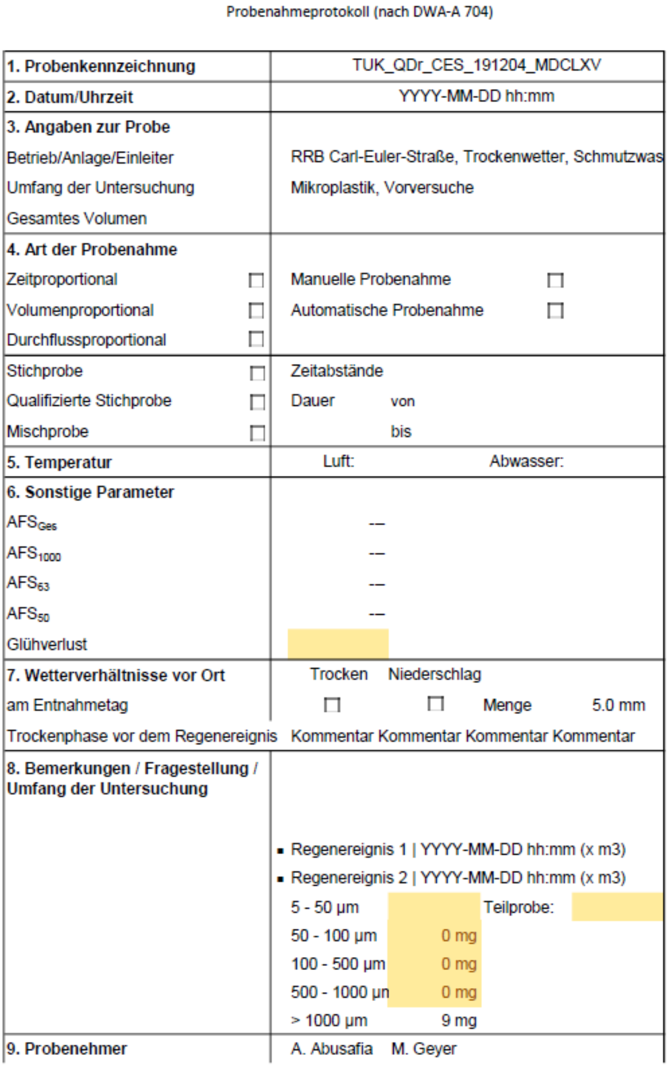

Graph: Min, Avg, Max Elevation: 282, 287, 298 m
Range Totals: Distance: 594 m Elev Gain/Loss: 13.6 m, -28.1 m Max Slope: 20.4%, -21.0% Avg Slope: 4.2%, -5.2%

Figure A 3 Elevation profile of the longest flow path in the small sub-catchment area in separate sewer system before L4 (Google Earth 2022)

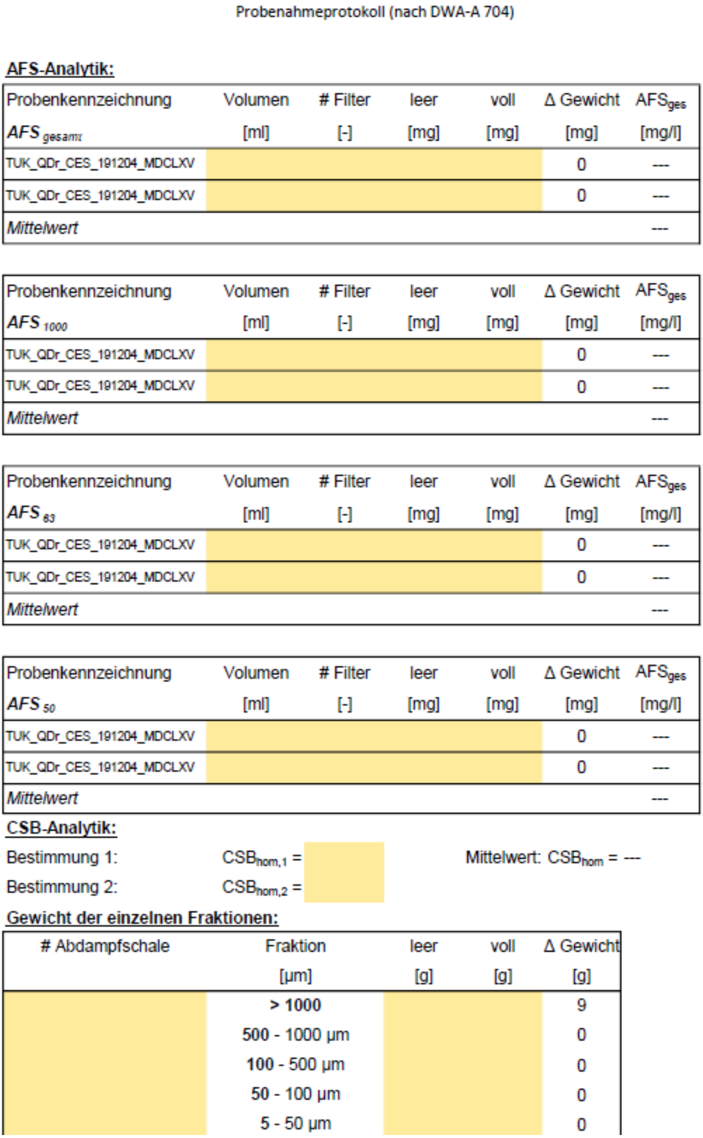
8.2.2. Sampling protocols



Probenahmeprotokoll (nach DWA-A 704)

1. Probenkennzeichnung	TUK_QDr_CES_191204_MDCLXV
2. Datum/Uhrzeit	YYYY-MM-DD hh:mm
3. Angaben zur Probe	
Betrieb/Anlage/Einleiter	RRB Carl-Euler-Straße, Trockenwetter, Schmutzwas
Umfang der Untersuchung	Mikroplastik, Vorversuche
Gesamtes Volumen	
4. Art der Probenahme	
Zeitproportional ☐	Manuelle Probenahme ☐
Volumenproportional ☐	Automatische Probenahme ☐
Durchflussproportional ☐	
Stichprobe ☐	Zeitabstände
Qualifizierte Stichprobe ☐	Dauer von
Mischprobe ☐	bis
5. Temperatur	Luft: Abwasser:
6. Sonstige Parameter	
AFS_{Ges}	---
AFS_{1000}	---
AFS_{63}	---
AFS_{50}	---
Glühverlust	
7. Wetterverhältnisse vor Ort	Trocken Niederschlag
am Entnahmetag	☐ ☐ Menge 5.0 mm
Trockenphase vor dem Regenereignis	Kommentar Kommentar Kommentar Kommentar
8. Bemerkungen / Fragestellung / Umfang der Untersuchung	▪ Regenereignis 1 | YYYY-MM-DD hh:mm (x m3) ▪ Regenereignis 2 | YYYY-MM-DD hh:mm (x m3)
	5 - 50 µm Teilprobe:
	50 - 100 µm 0 mg
	100 - 500 µm 0 mg
	500 - 1000 µn 0 mg
	> 1000 µm 9 mg
9. Probenehmer	A. Abusafia M. Geyer

Figure A 4 Sampling protocol generated by the author in accordance with norm DWA-A 704 (In German) (1)



Probenahmeprotokoll (nach DWA-A 704)

AFS-Analytik:

Probenkennzeichnung	Volumen	# Filter	leer	voll	Δ Gewicht	AFS$_{ges}$
AFS $_{gesamt}$	[ml]	[-]	[mg]	[mg]	[mg]	[mg/l]
TUK_QDr_CES_191204_MDCLXV					0	---
TUK_QDr_CES_191204_MDCLXV					0	---
Mittelwert						---

Probenkennzeichnung	Volumen	# Filter	leer	voll	Δ Gewicht	AFS$_{ges}$
AFS $_{1000}$	[ml]	[-]	[mg]	[mg]	[mg]	[mg/l]
TUK_QDr_CES_191204_MDCLXV					0	---
TUK_QDr_CES_191204_MDCLXV					0	---
Mittelwert						---

Probenkennzeichnung	Volumen	# Filter	leer	voll	Δ Gewicht	AFS$_{ges}$
AFS $_{63}$	[ml]	[-]	[mg]	[mg]	[mg]	[mg/l]
TUK_QDr_CES_191204_MDCLXV					0	---
TUK_QDr_CES_191204_MDCLXV					0	---
Mittelwert						---

Probenkennzeichnung	Volumen	# Filter	leer	voll	Δ Gewicht	AFS$_{ges}$
AFS $_{50}$	[ml]	[-]	[mg]	[mg]	[mg]	[mg/l]
TUK_QDr_CES_191204_MDCLXV					0	---
TUK_QDr_CES_191204_MDCLXV					0	---
Mittelwert						---

CSB-Analytik:

Bestimmung 1: CSB$_{hom,1}$ = Mittelwert: CSB$_{hom}$ = ---

Bestimmung 2: CSB$_{hom,2}$ =

Gewicht der einzelnen Fraktionen:

# Abdampfschale	Fraktion	leer	voll	Δ Gewicht
	[µm]	[g]	[g]	[g]
	> 1000			9
	500 - 1000 µm			0
	100 - 500 µm			0
	50 - 100 µm			0
	5 - 50 µm			0

Figure A 5 Sampling protocol generated by the author in accordance with norm DWA-A 704 (In German) (2)

8.2.3. Electrical wiring diagrams of the stormwater sampling plants.

8.2.3.1. Part 1: communication protocol of all sampling aggregates

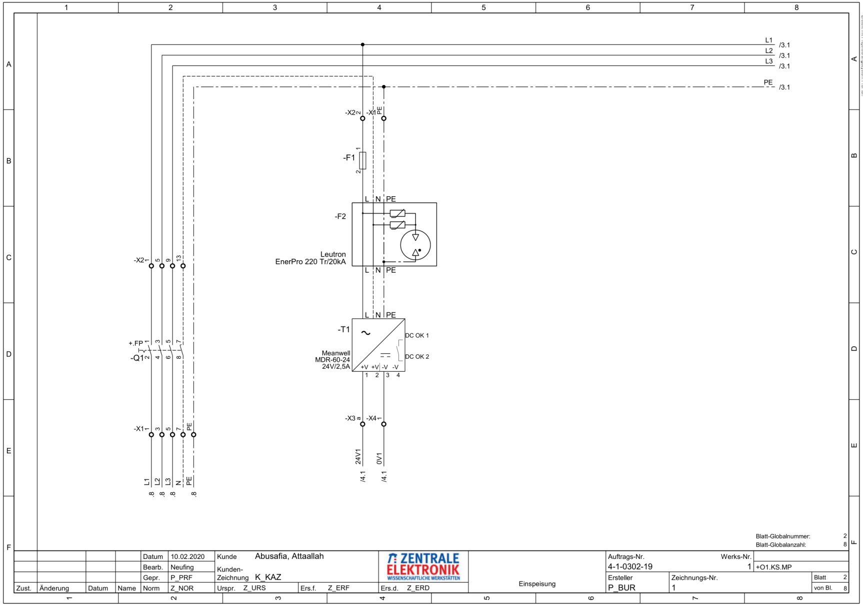


Figure A 6 Communication protocol of all sampling aggregates (1)

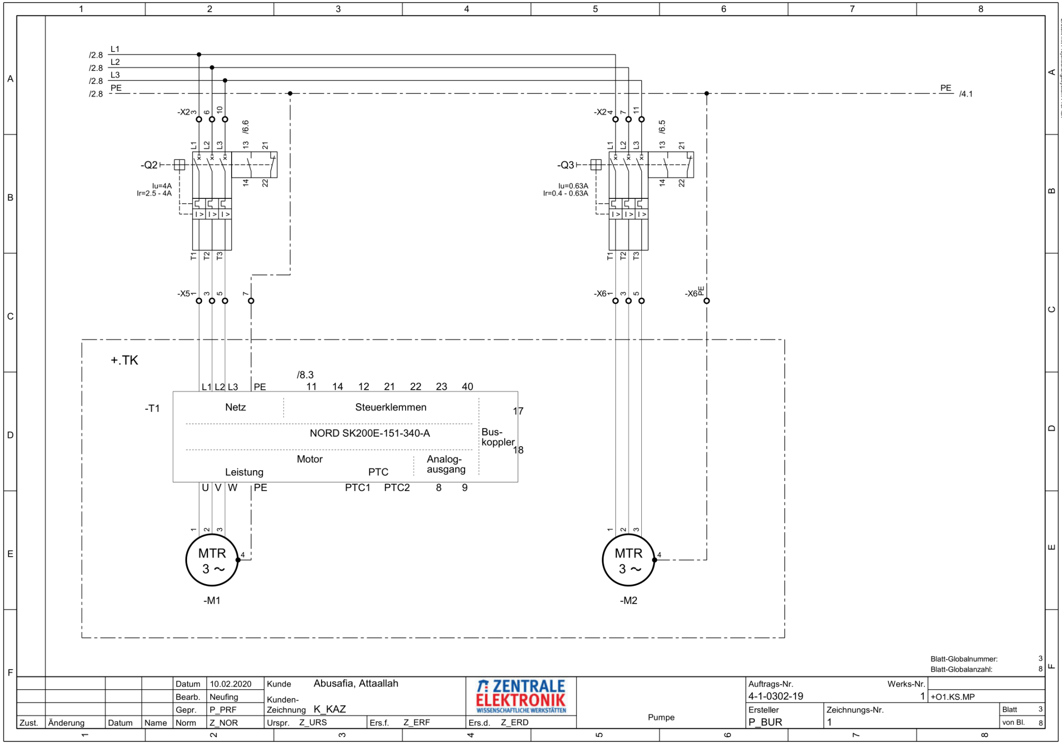


Figure A 7 Communication protocol of all sampling aggregates (2)

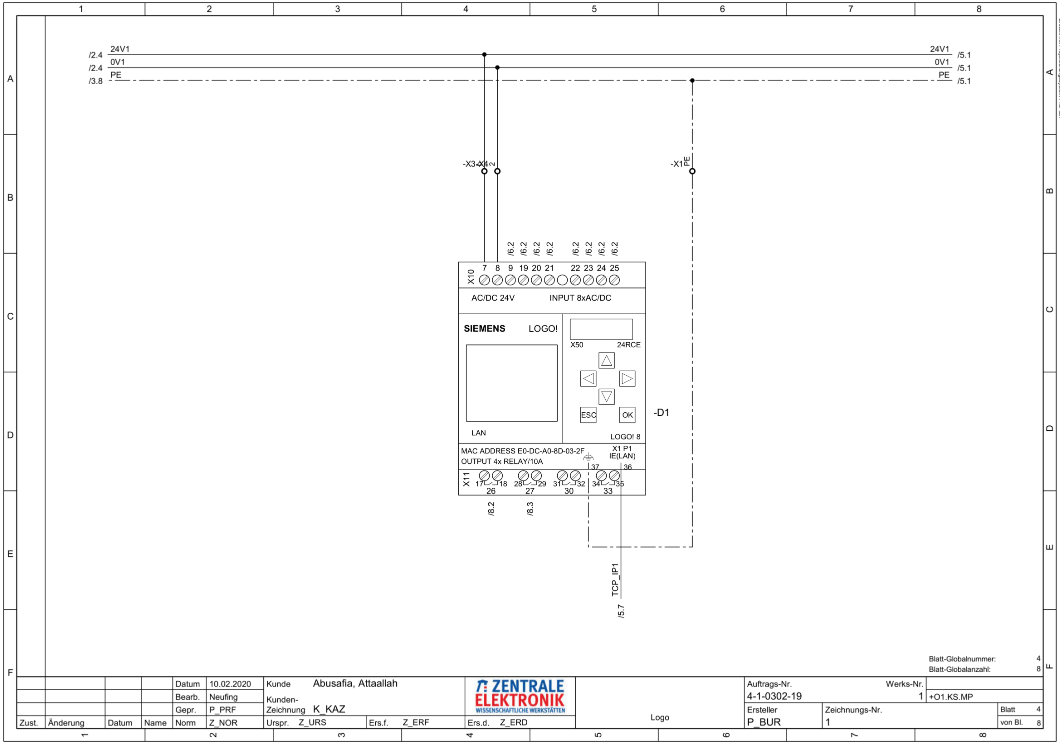


Figure A 8 Communication protocol of all sampling aggregates (3)

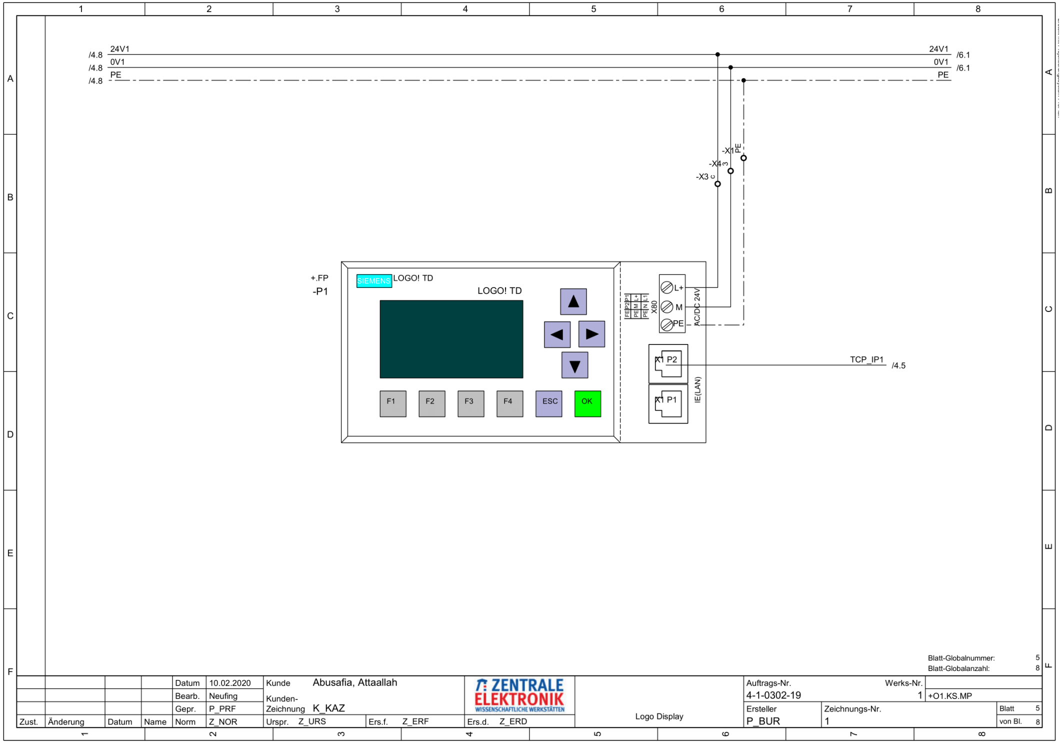


Figure A 9 Communication protocol of all sampling aggregates (4)

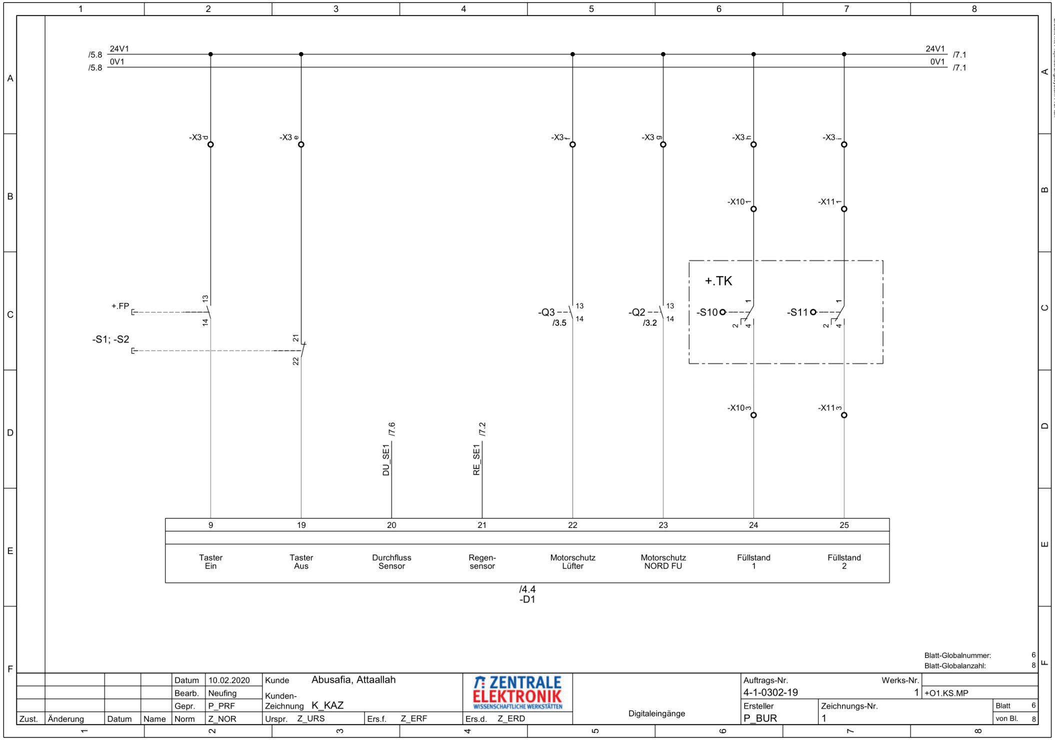


Figure A 10 Communication protocol of all sampling aggregates (5)

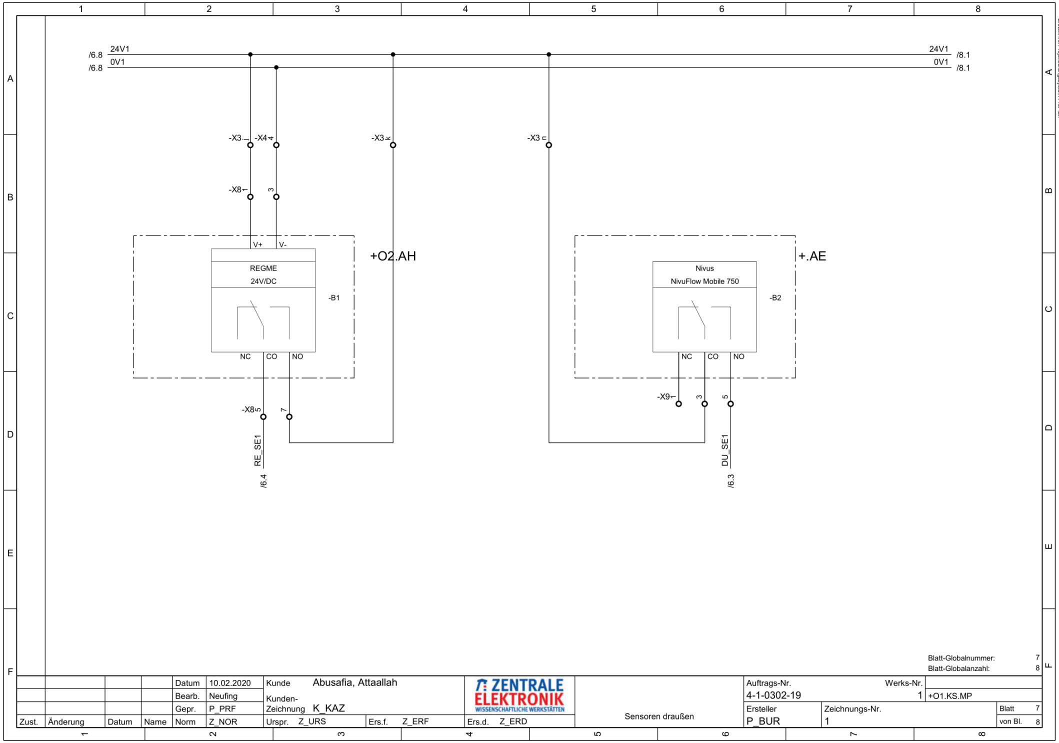


Figure A 11 Communication protocol of all sampling aggregates (6)

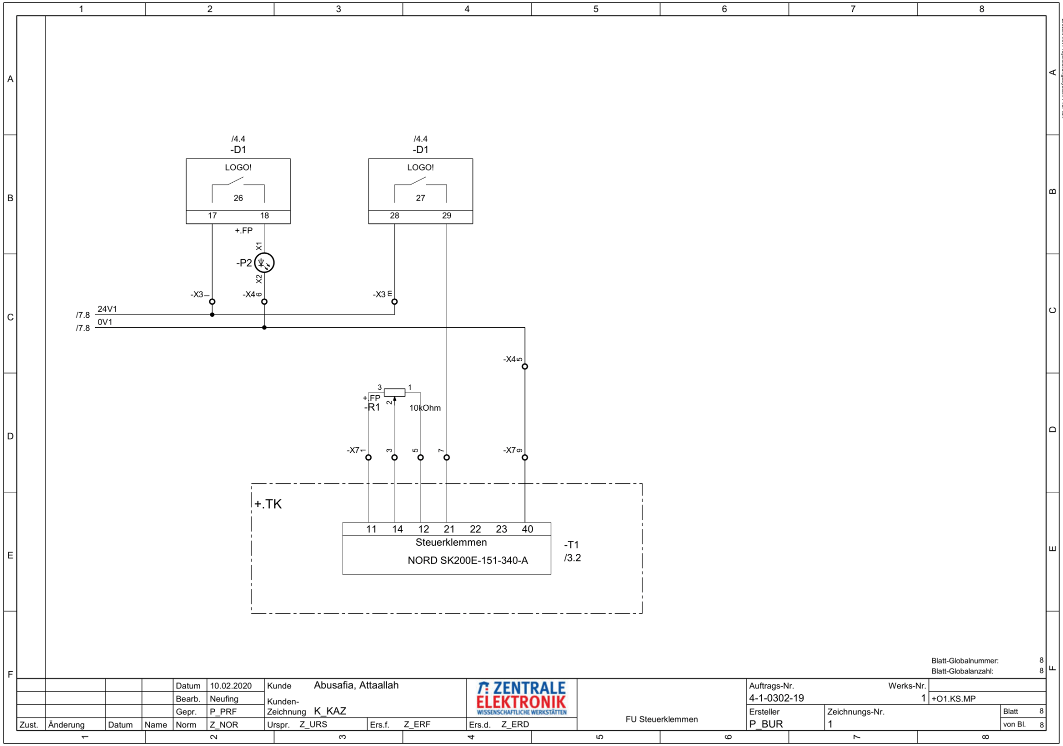


Figure A 12 Communication protocol of all sampling aggregates (7)

8.2.3.2. Part 2 : Programmable logic controller (PLC) communication protocols

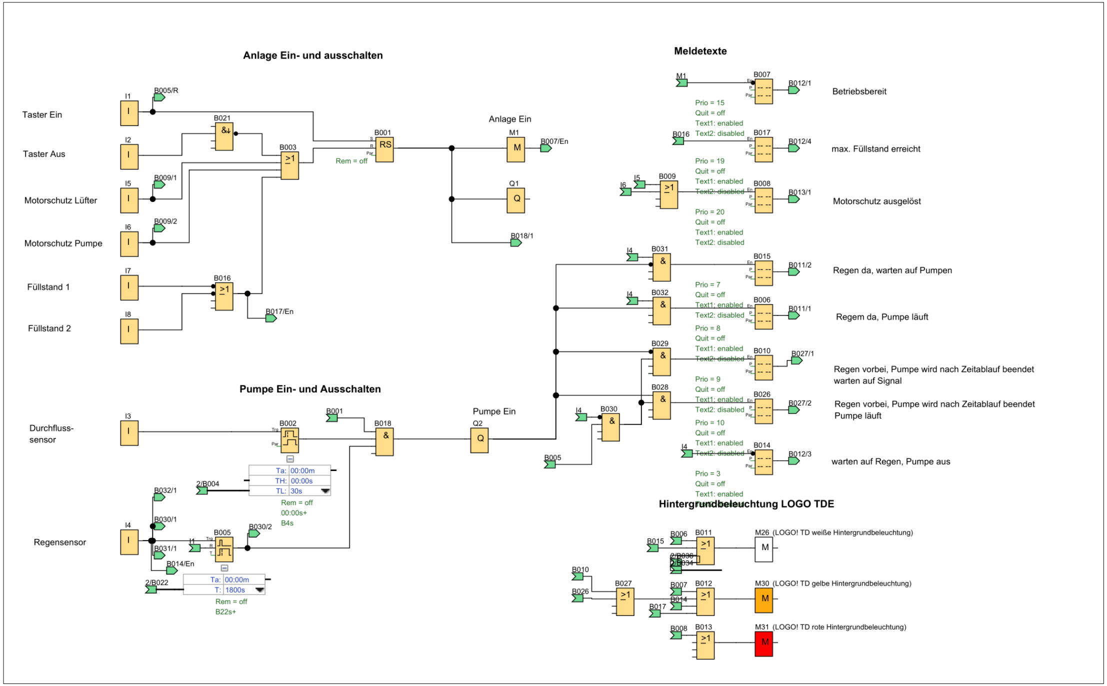


Figure A 13 Programmable logic controller (PLC) communication protocols (1)

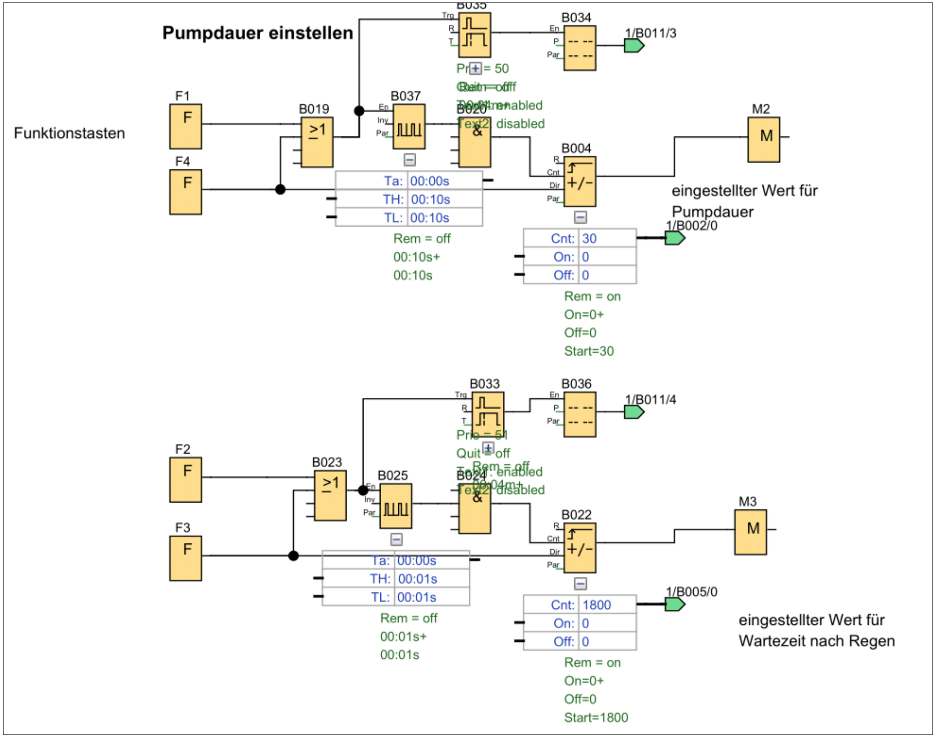
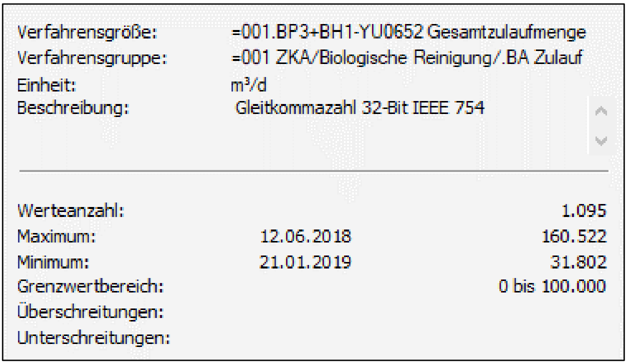


Figure A 14 Programmable logic controller (PLC) communication protocols (2)

8.3. Flow and precipitation data cleaning



Verfahrensgröße: =001.BP3+BH1-YU0652 Gesamtzulaufmenge
Verfahrensgruppe: =001 ZKA/Biologische Reinigung/.BA Zulauf
Einheit: m³/d
Beschreibung: Gleitkommazahl 32-Bit IEEE 754

Werteanzahl: 1.095
Maximum: 12.06.2018 160.522
Minimum: 21.01.2019 31.802
Grenzwertbereich: 0 bis 100.000
Überschreitungen:
Unterschreitungen:

Figure A 15 Summary of wastewater influent data at the WWTP Kaiserslautern L1 from June 2018 till January 2019 (In German)

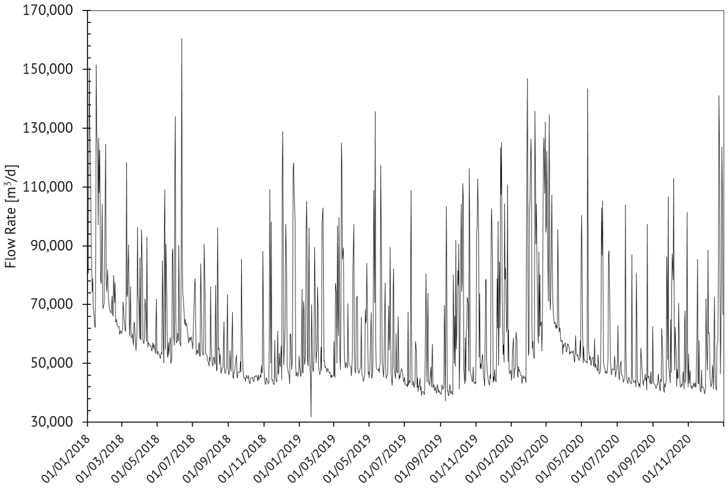


Figure A 16 Daily influent data at the WWTP Kaiserslautern Kaiserslautern (2018-2020) (Stadtentwässerung Kaiserslautern 2021)

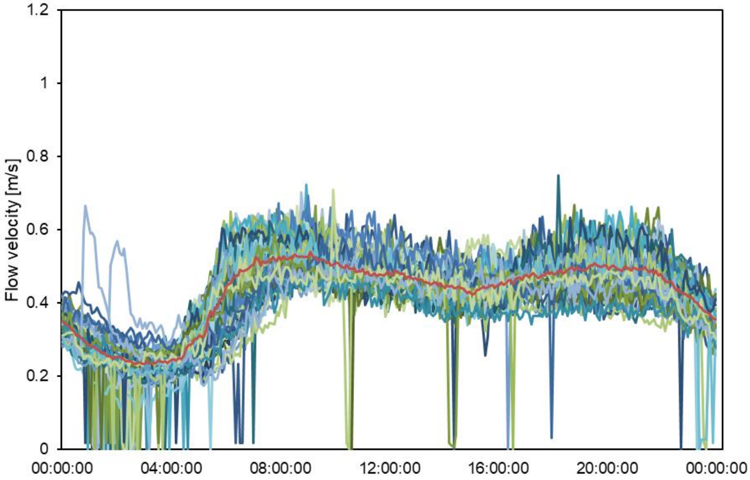
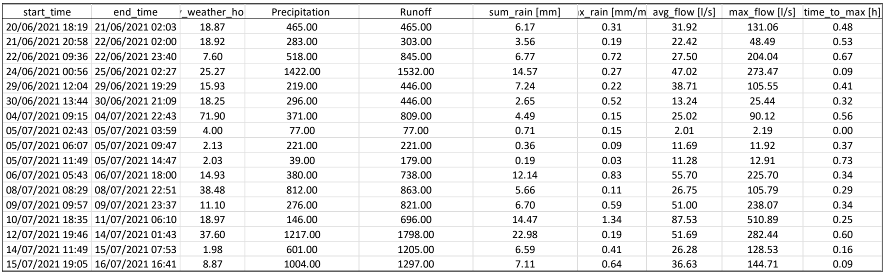


Figure A 17 Diurnal flow velocity pattern at L3 (n=68) from May till December 2019

Table A 2 User-friendly data output generated by a python code to extract and cluster metrics on runoff events at the sampling location L3 (2018-2021 data series) 1 min sequence under wet weather, 5 min sequence under dry weather



start_time	end_time	_weather_ho	Precipitation	Runoff	sum_rain [mm]	x_rain [mm/m	avg_flow [l/s]	max_flow [l/s]	time_to_max [h]
20/06/2021 18:19	21/06/2021 02:03	18.87	465.00	465.00	6.17	0.31	31.92	131.06	0.48
21/06/2021 20:58	22/06/2021 02:00	18.92	283.00	303.00	3.56	0.19	22.42	48.49	0.53
22/06/2021 09:36	22/06/2021 23:40	7.60	518.00	845.00	6.77	0.72	27.50	204.04	0.67
24/06/2021 00:56	25/06/2021 02:27	25.27	1422.00	1532.00	14.57	0.27	47.02	273.47	0.09
29/06/2021 12:04	29/06/2021 19:29	15.93	219.00	446.00	7.24	0.22	38.71	105.55	0.41
30/06/2021 13:44	30/06/2021 21:09	18.25	296.00	446.00	2.65	0.52	13.24	25.44	0.32
04/07/2021 09:15	04/07/2021 22:43	71.90	371.00	809.00	4.49	0.15	25.02	90.12	0.56
05/07/2021 02:43	05/07/2021 03:59	4.00	77.00	77.00	0.71	0.15	2.01	2.19	0.00
05/07/2021 06:07	05/07/2021 09:47	2.13	221.00	221.00	0.36	0.09	11.69	11.92	0.37
05/07/2021 11:49	05/07/2021 14:47	2.03	39.00	179.00	0.19	0.03	11.28	12.91	0.73
06/07/2021 05:43	06/07/2021 18:00	14.93	380.00	738.00	12.14	0.83	55.70	225.70	0.34
08/07/2021 08:29	08/07/2021 22:51	38.48	812.00	863.00	5.66	0.11	26.75	105.79	0.29
09/07/2021 09:57	09/07/2021 23:37	11.10	276.00	821.00	6.70	0.59	51.00	238.07	0.34
10/07/2021 18:35	11/07/2021 06:10	18.97	146.00	696.00	14.47	1.34	87.53	510.89	0.25
12/07/2021 19:46	14/07/2021 01:43	37.60	1217.00	1798.00	22.98	0.19	51.69	282.44	0.60
14/07/2021 11:49	15/07/2021 07:53	1.98	601.00	1205.00	6.59	0.41	26.28	128.53	0.16
15/07/2021 19:05	16/07/2021 16:41	8.87	1004.00	1297.00	7.11	0.64	36.63	144.71	0.09

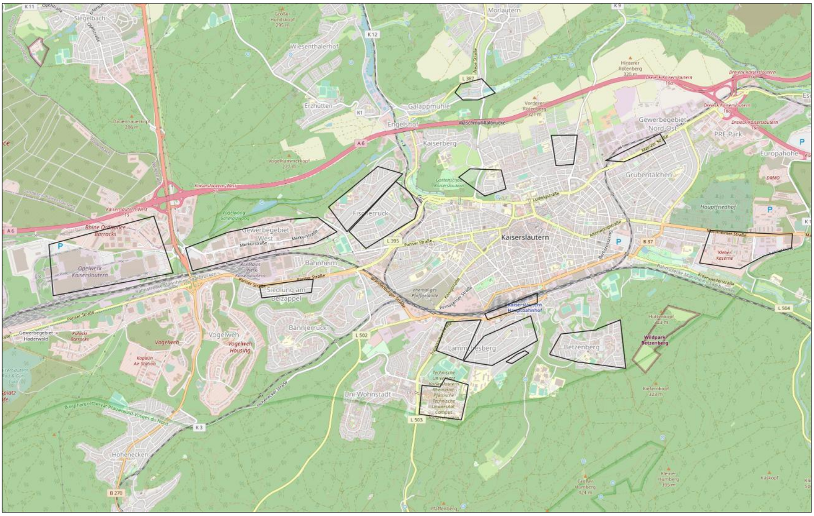


Figure A 18 Sub-catchments within the catchment area of the WWTP Kaiserslautern plotted using QGIS version 3.30.2

8.4. Sampling Results

Table A 3 Summary of samples from all locations (2018-2021)

Code (ATV 198)	Datum PN	Analytik BAM	T (°C)	Fraktionen (µm)	Protokoll	MP	SG	GV	Dotierung
QTSF_KAKL_190225_MDCLXV	25/02/2019	🟩	105	1000,500,100,50,5	Ja	Ja	Ja	Ja	Ja
TSF_KAKL_190218_MDCLXV	18/02/2019	🟩	105	1000,500,100,50,5	Ja	Ja	Ja	Ja	Ja
QTSF_KAKL_190212_MDCLXV	12/02/2019	🟩	105	1000,500,100,50,5	Ja	Ja	Ja	Ja	Ja
QTSF_KAKL_181115_DCL	15/11/2018	🟩	50	500, 100, 50	Ja	Ja	Ja	Ja	_
QTSF_KAKL_181105_DCL	05/11/2018	🟩	50	500, 100, 50	Ja	Ja	Ja	Ja	_
QT_KAKL_180823_MDCLXIIIL	23/08/2018	🟩	105	1000, 500, 100, 63, 50	Ja	_	Ja	Ja	_
QT_KAKL_180821_MDCLXIIIL	21/08/2018	🟩	105	1000, 500, 100, 63, 50	Ja	_	Ja	Ja	_
180618_KAKL_Zu	18/06/2018	🟩	105	500, 100, 50	Ja	_	_	_	_
QABNK_KAKL_210609_MDCLXV_SSF	09/06/2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
QABNK_KAKL_E_210609_MDCLXV_SSF	09/06/2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
QABNK_KAKL_210421_MDCLXV_SSF	21/04/2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
QABNK_KAKL_E_210421_MDCLXV_SSF	21/04/2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
QABNK_KAKL_190304_MDCLXV	04/03/2019	🟩	105	1000,500, 100, 50	Ja	Ja	_	Ja	_
QABNK_KAKL_190218_MDCLXV	18/02/2019	🟩	105	1000,500, 100, 50	Ja	Ja	_	Ja	_
QABNK_KAKL_190212_MDCLXV	12/02/2019	🟩	105	1000,500, 100, 50	Ja	Ja	_	Ja	_
QABNK_KAKL_181127_DCL	27/11/2018	🟩	105	500, 100, 50	Ja	_	_	Ja	_
QABNK_KAKL_190212_MDCLXV_SSF	12/02/2019	🟩	105	500, 100, 50, 5	Ja	_	_	Ja	_
QABNK_KAKL_181123_DCL_SSF	23/11/2018	🟩	105	500, 100, 50	Ja	Ja	Ja	Ja	_
TUK_QDr_CES_210217_MDCLXV	25/02/2021	🟩	105	1000,500,100,50,5	Ja	Ja	_	Ja	_
TUK_QDr_CES_210225_MDCLXV	17/02/2021	🟩	105	1000,500,100,50,5	Ja	Ja	_	Ja	_
TUK_QDr_CES_200205_MDCLXV	05/02/2020	🟩	105	1000,500,100,50,5	Ja	Ja	_	_	_
TUK_QDr_CES_200121_MDCLXV	21/01/2020	🟩	105	1000,500,100,50,5	Ja	Ja	_	_	_
TUK_QDr_CES_191204_MDCLXV	04/12/2019	🟩	105	1000,500,100,50,5	Ja	Ja	_	_	_
QDr_CES_191014_MWTW	14/10/2019	🟩	105	1000,500,100,50,5	Ja	Ja	_	_	_
QDr_CES_190325_MDCLXV	25/03/2019	🟩	105	1000,500,100,50,5	Ja	Ja	_	Ja	_
QDr_CES_190220_MDCLXV	20/02/2020	🟩	105	1000,500,100,50,5	Ja	Ja	_	Ja	_
QDr_CES_180817_MDCLXV	17/08/2018	🟩	105	1000, 500, 100, 63, 50	Ja	Ja	_	Ja	_
180905.KL-CES. Sed	05/09/2018	verloren	_	_	_	Ja	_	_	_
TUK_RW_CES_210816_MDCLXV	16/08/2021	🟨	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_CES_210727_MDCLXV	27/07/2021	🟨	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_CES_210714_MDCLXV	14/07/2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_CES_210709_MDCLXV	08/09.07.2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_CES_2100706_MDCLXV	06/07/2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_CES_210629_MDCLXV	29/06/2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_CES_210624_MDCLXV	24/06/2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_CES_210622_MDCLXV	22/06/2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_CES_210620_MDCLXV	20/06/2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_Hohenecken_210311-14_MDCLXV	14/03/2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_Hohenecken_210205-07_MDCLXV	06/02/2021	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_Hohenecken_201224_MDCLXV	24/12/2020	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_Hohenecken_201115_MDCLXV	15/11/2020	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_Hohenecken_201029_MDCLXV	29/10/2020	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_Hohenecken_201025_MDCLXV	25/10/2020	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_SED_Hohenecken_201007	07/10/2020	🟩	105	_	Ja	Ja	_	Ja	_
TUK_RW_Hohenecken_200924_MDCLXV	24/09/2020	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_RW_Hohenecken_200803_MDCLXV	03/08/2020	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	_	_
TUK_RW_Hohenecken_200726_MDCLXV	26/07/2020	🟩	105	1000, 500, 100, 50, 5	Ja	Ja	_	_	_
TUK_GW_BF210421_MDCLXV	21/04/2021	🟩	105	500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_GW_BF210324_MDCLXV	24/03/2021	🟩	105	500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_GW_BF210217_MDCLXV	17/02/2021	🟩	105	500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_GW_BF201021_MDCLXV	21/10/2020	🟩	105	500, 100, 50, 5	Ja	Ja	_	Ja	_
TUK_GW_BF200615_MDCLXV	15/06/2020	🟩	105	500, 100, 50, 5	Ja	Ja	_	_	_
TUK_GW_BF200206_MDCLXV	06/02/2020	🟩	105	500, 100, 50	Ja	Ja	_	_	_
GW_RE_181011_DCL	11/10/2018	🟩	50	500, 100, 50	Ja	Ja	Ja	Ja	_
GW_RE_180919_DCL	19/09/2018	🟩	50	500, 100, 50	Ja	Ja	Ja	Ja	_
GW_RE_180829_DCL	29/08/2018	🟩	50	500, 100, 50	Ja	_	Ja	Ja	_
TUK_QMW_IAH_200623	23/06/2020	🟩	105	_	Ja	Ja	_	_	_
TUK_QMW_IAH_191205_MDCLXV	05/12/2019	🟩	105	1000, 500, 100, 63, 50, 5	Ja	Ja	_	_	_

8.4.1. Dry weather emissions

Table A 4 Estimating yearly MP loads in the influent of WWTP Kaiserslautern using two methods, 1) average concentration of all sampling days in 2019 (n=4) multiplied by median dry weather influent of the years 2018-2020. 2) MP concentrations of the sampling days

Sample Code (ATV 198)	**Sampling Date**	**Daily influent Volume WWTP**	**Sample Volume**	**MP-concentration**	**MP/p.e.*day**
		[m3]	[L]	[µg/l]	mg/(p.e*d)
180618_KAKL_Zu	18/06/2018	65056	6.4		
QT_KAKL_180821_MDCLXIIIL	21/08/2018	48402	14.5		
QT_KAKL_180823_MDCLXIIIL	23/08/2018	57133	11		
QTSF_KAKL_181105_DCL	05/11/2018	45252	13.885	195.7	42.2
QTSF_KAKL_181115_DCL	15/11/2018	44248	22.8	361.5	77.9
QTSF_KAKL_190212_MDCLXV	12/02/2019	50786	22.6	352.1	75.9
TSF_KAKL_190218_MDCLXV	18/02/2019	48268	22.8		
QTSF_KAKL_190225_MDCLXV	25/02/2019	46121	22.7	235.6	50.8
Total yearly MP load	4996	kg/a	Considering the median value and average concentration		
Total yearly MP load	4728	kg/a	Considering the volume on the measurement days and average concentration		

Table A 5 Daily dry weather flow on sampling days, sample volumes and TS/COD amounts at L3 in combined sewer system

Code (ATV 198)	**Date Sampling**	**Daily Flow**	**Sample Volume**	**TS total**	**COD total**
		m3/d	[L]	[mg/l]	[mg/l]
QDr_CES_180817_MDCLXV	17/08/2018	572	6,5	237	1006
QDr_CES_190220_MDCLXV	20/02/2019	625	17,53	236	845
QDr_CES_190325_MDCLXV	25/03/2019	534	17,97	395	889
QDr_CES_191014_MWTW	14/10/2019	609	25	395	956
TUK_QDr_CES_191204_MDCLXV	04/12/2019	546	25	383	965

TUK_QDr_CES_200121_MDCLXV	21/01/2020	517	25	482,89	1669
TUK_QDr_CES_200205_MDCLXV	05/02/2020	598	25	438	917
TUK_QDr_CES_210217_MDCLXV	17/02/2021	513	27,4	207	854
TUK_QDr_CES_210225_MDCLXV	25/02/2021	494	26,7	568	989

8.4.2. Wet weather emissions

Table A 6 The minimum, maximum average, and median concentrations MP over all fractions and combined flow samples under wet weather (L3)

	Size fractions															
	500_1000µm				100_500µm				50_100µm				5_50µm			
	PE	PP	PS	SBR	PE	PP	PS	SBR	PE	PP	PS	SBR	PE	PP	PS	SBR
Average	119.19	5.19	2.06	117.37	377.59	15.51	11.51	246.04	151.97	8.80	2.01	383.97	46.84	5.68	3.67	33.52
median	61.84	3.55	0.00	41.58	377.64	8.86	0.69	91.43	117.60	4.95	0.02	43.57	1.15	0.17	0.03	0.92
min	45.52	0.00	0.00	0.42	99.86	0.00	0.00	0.37	21.82	0.96	0.00	0.23	0.26	0.01	0.00	0.04
max	219.73	15.01	6.49	515.61	807.73	57.83	65.13	782.25	471.25	24.87	11.20	1413.64	261.49	31.77	20.90	186.61

Table A 7 Stormwater runoff volume per season recorded at L3 in 2021 compared to runoff volume during sampling campaign in June/July 2021

Season	**Volume Stormwater Runoff [m³]**	**MP load [g]**		**Specific MP load [g/(ha.a)]**	
		SBR	Other MP	SBR	Other MP
Winter 2021	61125		9153		
Spring 2021	28974		5578		
Summer 2021	43393		9283		
Fall 2021	47289		9105		
Sum 2021	183114	62414	33112	1010.1	1903.5
Sampling campaign	30252				
C_{MP} [µg/L]	554.8				

8.5. Analysis results

8.5.1. Stormwater sampling coverage in combined sewer system

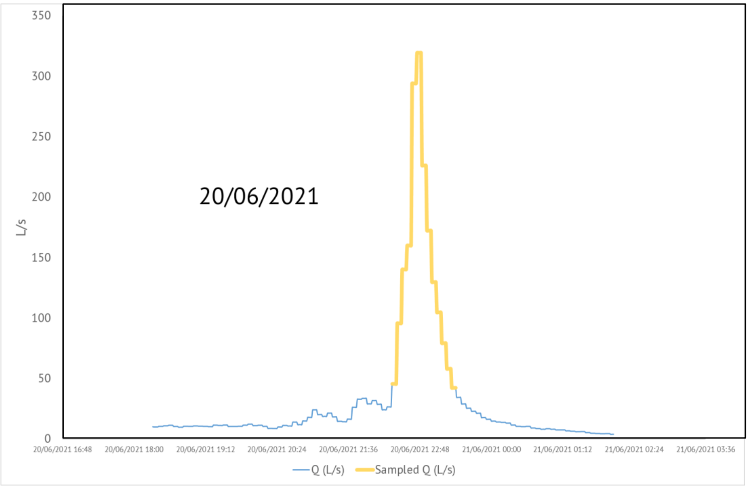


Figure A 19 Sampling coverage of runoff event on 20.06.2021 (yellow=sampling hydrograph, blue= runoff hydrograph)

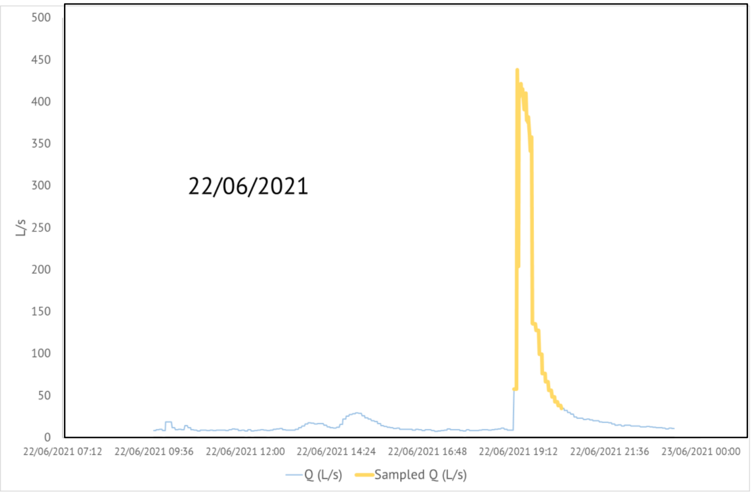


Figure A 20 Sampling coverage of runoff event on 22.06.2021 (yellow=sampling hydrograph, blue= runoff hydrograph)

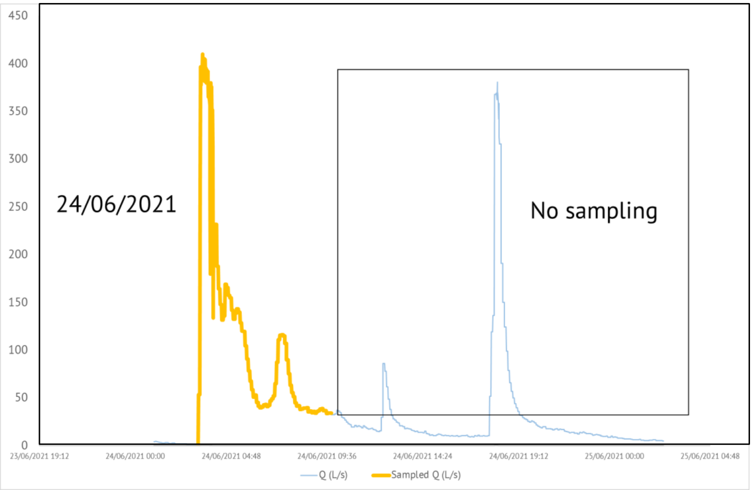


Figure A 21 Sampling coverage of runoff event on 24.06.2021 (yellow=sampling hydrograph, blue= runoff hydrograph)

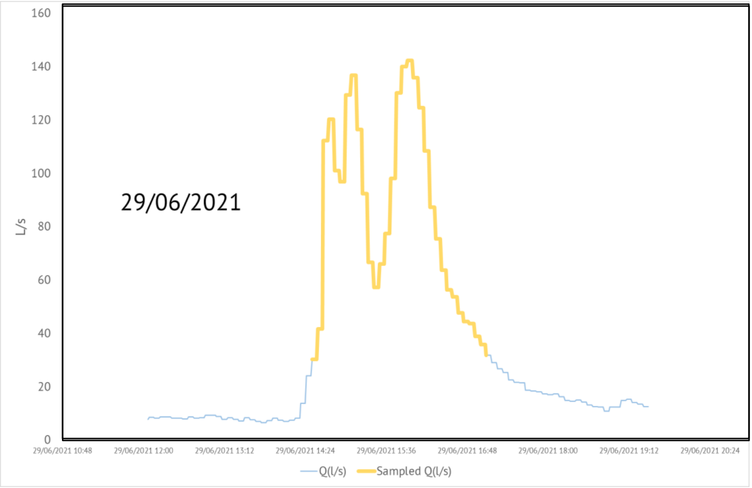


Figure A 22 Sampling coverage of runoff event on 29.06.2021 (yellow=sampling hydrograph, blue= runoff hydrograph)

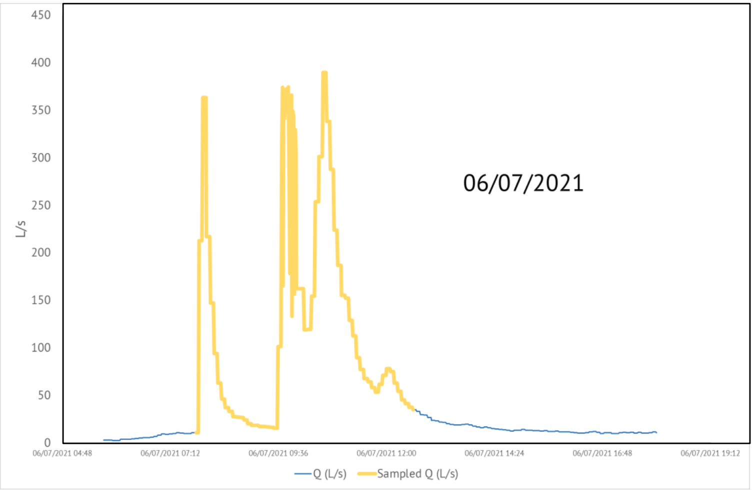


Figure A 23 Sampling coverage of runoff event on 06.07.2021 (yellow=sampling hydrograph, blue= runoff hydrograph)

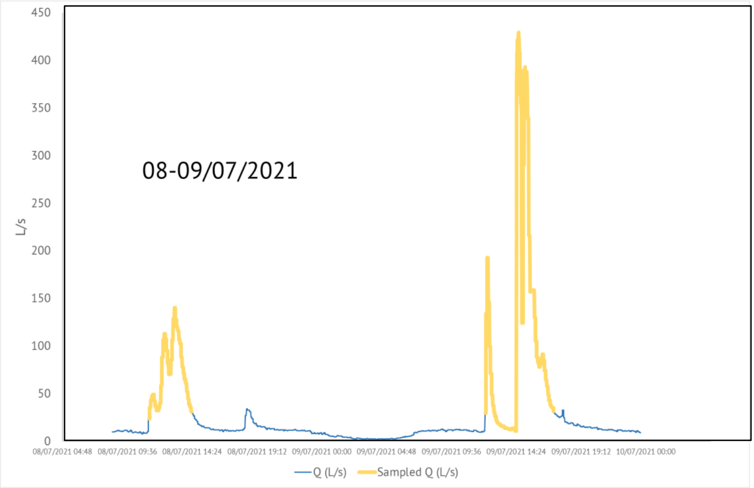


Figure A 24 Sampling coverage of runoff event on 08-09.07.2021 (yellow=sampling hydrograph, blue= runoff hydrograph)

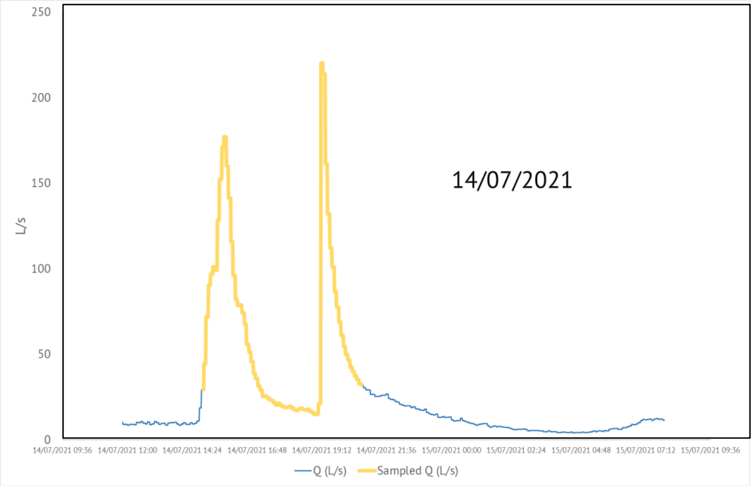


Figure A 25 Sampling coverage of runoff event on 14.07.2021 (yellow=sampling hydrograph, blue= runoff hydrograph)

8.5.1. Extending wet weather emissions to the entire catchment area

Table A 8 extending wet weather MP emissions from the entire UDS catchment based on the emmisions from the small catchment at L3 combined. Approach 1 without factoraization, approach 2 with factorazation accordin to methodology in 3.4.2.2

		Approach 1		Approach 2					
Aek [ha]	Summe Aeb direkt ha	B.SBR [g]	B.MP-SBR [g]	EW.Dichte(EW/ha)	EW (F1)	Entfernung (1, 1.2) (F3)	Verkehr Faktor (F2) (0.8-1.2)	B.SBR [g]	B.MP-SBR [g]
525.8	KASK1_R101_Ent	1000950	531106	84	0.703	1	0.8	562862.6	531158.3
86.2	KASK2_R01_Ent	164125	87085	97	0.813	1	0.9	120068.2	87093.8
85.8	B10 Opelparkplatz	163414	86708	1	0.100	1	1.2	19609.7	86716.4
59.8	90043004	113847	60407	61	0.516	1	1	58775.5	60413.2
51.3	B13 Lothringer Dell	97726	51853	40	0.337	1	1	32980.2	51858.5
34.8	B07 Uni Am Harzhübel **(L3)**	66297	35177	119	1.000	1	1	66296.5	35180.5
34.6	3+B19	65899	34966	70	0.588	1	0.9	34895.7	34969.6
31.3	B11 Merkurstr./Hoch.	59570	31608	2	0.100	1	1	5957.0	31610.9
24.6	TB RÜB Waschmühlbad	46791	24827	61	0.516	1	0.8	19317.7	24829.7
21.5	B02 Bremerstraße neu	41001	21755	70	0.589	1	0.9	21732.4	21757.3
21.2	B05 Tripp./Pfaffenb.	40441	21458	112	0.939	1.1	1.1	41770.2	23606.3
20.2	RÜB 1+ZB1	38358	20353	52	0.440	1	0.9	15179.5	20354.6
19.9	B06 Universität AVZ	37861	20089	2	0.100	1.1	0.8	3028.9	22100.2
19.5	3+B21	37184	19730	51	0.429	1	1	15954.0	19731.8
19.5	B34 Zschockestraße	37123	19697	4	0.100	1	1.2	4454.7	19699.3
18.2	B27 Burggraben / 3+B27	34725	18425	85	0.712	1.1	0.8	19778.5	20269.9
17.1	B22 Gersweilerweg / 3+B22	32527	17259	60	0.506	1.1	0.8	13160.1	18986.5
16.8		32003	16981	52	0.435	1	1	13905.8	16982.6
16.3	S02 Bännjer. Rest	31061	16481	86	0.719	1	1.1	24572.8	16482.8
14.9	B16 Mainzer Str./Nor	28368	15052	39	0.329	1.2	1.2	11195.0	18064.3
13.4	AUS14001 KAD RÜ1	25567	13566	1	1.000	1	1	25567.4	13567.5
12.8	B01 Kantstraße	24432	12964	178	1.496	1		0.0	12965.1
12.3	B03 Schulzentrum Süd	23494	12466	63	0.526	1	0.9	11132.6	12467.2
10.0	B17 Mannheimer Str.	19070	10119	4	0.300	1.2	1.2	6865.3	12143.6
10.0	B29 Kohlenhofstraße	19000	10081	67	0.565	1	0.9	9663.6	10082.4
7.2	RÜB +30/31	13707	7273	55	0.459	1.2	1	6288.8	8728.2
7.0	RUEB_Engel	13375	7097	50	0.418	1	1	5584.7	7097.6
6.8		12873	6830	1	0.100	1	1	1287.3	6831.0
6.6		12654	6714	1	0.100	1	1	1265.4	6714.8
6.2	B09 Keltenw./Lukask.	11851	6288	57	0.475	1	1.2	6759.3	6288.9
6.1	AUS13001	11668	6191	47	0.396	1	1	4624.6	6191.8
5.9	B14 Fischerrück	11187	5936	202	1.696	1.1	0.9	17080.6	6530.0
5.8	QD_S14	10991	5832	21	0.173	1	1	1904.2	5832.7

5.5	B12 Merkurstr./Vogel	10510	5576	4	1.000	1	1.2	12611.6	5577.0
5.1	B80 Hertelsbrunnen I	9743	5170	1	0.100	1	0.9	876.9	5170.4
5.0	AUS13003	9423	5000	1	0.100	1	1	942.3	5000.6
4.2	B104	8013	4252	1	0.100	1	1	801.3	4252.2
3.9		7386	3919	1	0.100	1	1	738.6	3919.4
3.7	B28 Zollamtstr.	7077	3755	4	0.100	1.1	1	707.7	4130.8
3.4	B81 Hertelsbr. IIa+IIb	6511	3455	1	0.100	1	1	651.1	3455.1
3.4		6395	3393	1	0.100	1	1	639.5	3393.7
3.1	RÜB +B33 fiktiv	5822	3089	35	0.291	1	1	1696.2	3089.4
3.0	RÜ Opelsammler	5642	2993	111	0.930	1.1	1.2	6298.4	3293.2
2.2	NÜ W.-Kittel Ost	4247	2253	106	0.893	1.2	1	3792.5	2704.1
2.2	RRB Alex-M.-Str.I	4204	2230	57	0.480	1	1	2016.3	2230.7
2.1	RRB Alex-M.-Str.II	3940	2091	155	1.300	1.1	1	5120.7	2299.9
1.7	NÜ W.-Kittel West	3275	1738	1	0.100	1.2	1	327.5	2085.5
1.7	Dr_S05 Kaisersbergring	3237	1718	22	0.188	1	0.8	486.5	1717.9
1.5	AUS13020	2827	1500	1	0.100	1	1	282.7	1500.2
1.4	Dr_SK Donnersbergerstr.	2671	1417	138	1.162	1	1	3104.4	1417.3
1.3		2467	1309	1	0.008	1	1	20.7	1309.2
1.3		2456	1303	1	0.100	1	1	245.6	1303.5
1.2	B08 Uni Th.-He.-Str.	2367	1256	25	0.210	1.1	1	496.1	1381.5
1.2		2270	1204	5	0.042	1	1	96.0	1204.4
0.9	B04 Im Jungwald	1799	955	6	0.100	1	0.8	143.9	954.7
0.9		1722	914	18	0.149	1	1	256.0	913.7
0.9	RÜ 07	1674	888	56	0.468	1	1	784.1	888.4
0.8	#NV	1617	858	82	0.693	1	1	1120.1	858.0
0.8	RRB_AM_IIIa+b	1597	847	92	0.772	1	1	1232.2	847.3
0.6		1191	632	1	0.008	1	1	10.0	631.8
0.6		1109	589	45	0.375	1	1	416.1	588.6
0.3		638	339	98	0.827	1	1	528.1	338.8
0.3		579	307	1	0.100	1	1	57.9	307.1
0.2	QD_Gers	423	224	72	0.606	1	1	256.0	224.3
Sum 1314.4 ha		2501.97 kg/a	1327.55 kg/a					1250.28 kg/a	1344.30 kg/a
100% CSOs	Removal rate 30%	1751.38 kg/a	929.28 kg/a	2681 kg/a				875.19 kg/a	941.01 kg/a
	Removal Rate 40%	1501.18 kg/a	796.53 kg/a	2298 kg/a				750.17 kg/a	806.58 kg/a
	Removal Rate 50%	1250.99 kg/a	663.77 kg/a	1915 kg/a				625.14 kg/a	672.15 kg/a
	60							500.11 kg/a	537.72 kg/a
	70							375.08 kg/a	403.29 kg/a
	80							250.06 kg/a	268.86 kg/a
	90							125.03 kg/a	134.43 kg/a
	0.951	122.60 kg/a	65.05 kg/a	188 kg/a				61.26 kg/a	65.87 kg/a
	95							62.51 kg/a	67.21 kg/a
50% CSOs and co 50% retention structures	Removal rate 30%	875.69 kg/a	464.64 kg/a	1340 kg/a				437.60 kg/a	470.50 kg/a
	Removal Rate 40%	750.59 kg/a	398.26 kg/a	1149 kg/a				375.08 kg/a	403.29 kg/a
	Removal Rate 50%	625.49 kg/a	331.89 kg/a	957 kg/a				312.57 kg/a	336.07 kg/a
	86.0%	122.60 kg/a	65.05 kg/a	188 kg/a				218.80 kg/a	65.87 kg/a
	70%							187.54 kg/a	
	80%							156.28 kg/a	
		Sum 1904 kg/a	Sum 1010 kg/a					Sum 951 kg/a	Sum 1023 kg/a

8.5.2. Correlation results between MP emissions and wastewater matrix parameters

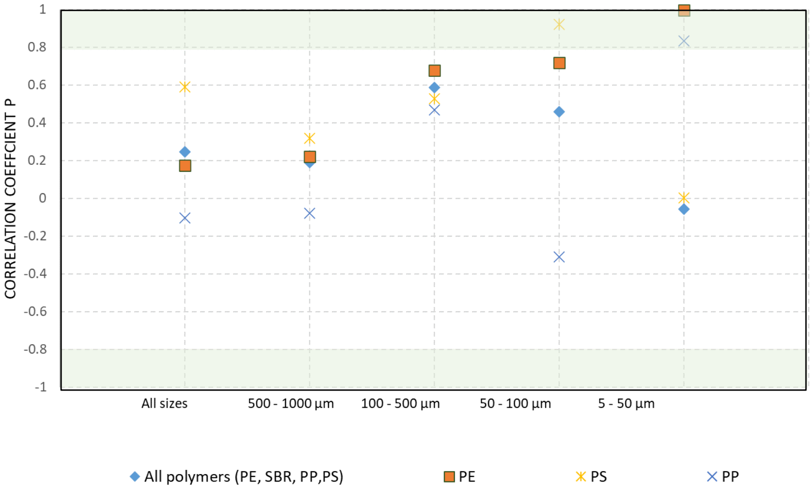


Figure A 26 Pearson correlation test between Total solids (TS) and MP content in dry weather flow samples in combined sewer system (L3)

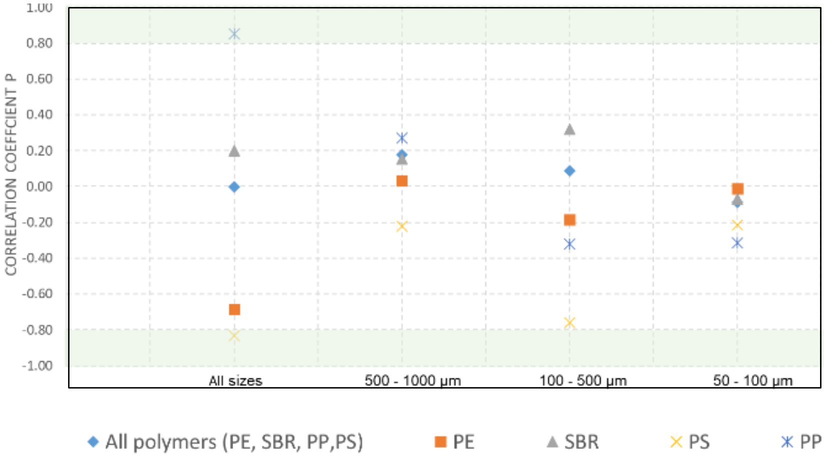


Figure A 27 Pearson correlation test between loss on ignition and MP content in stormwater runoff samples in combined sewer system (L3)

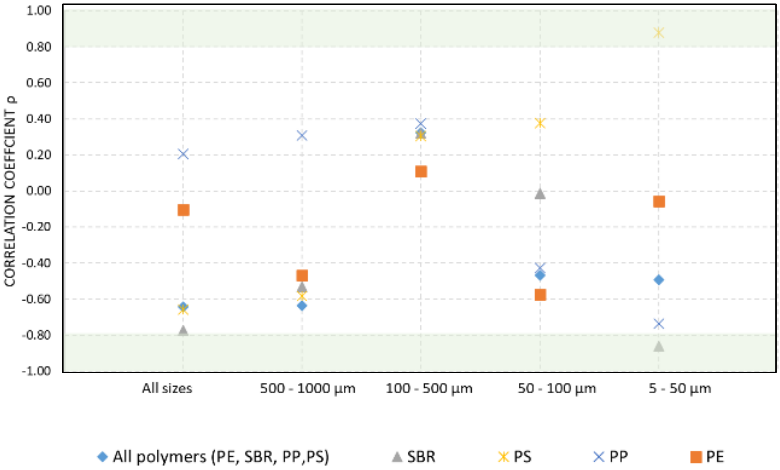


Figure A 28 Pearson correlation test between loss on ignition and MP content in stormwater runoff in separate sewer system (L4)

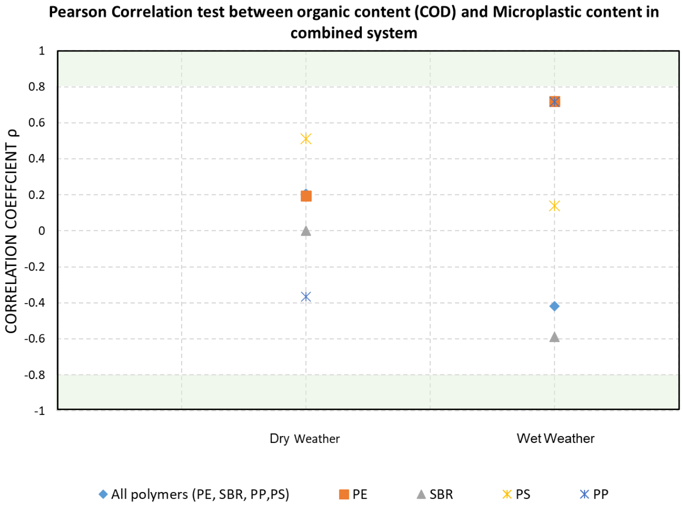


Figure A 29 Pearson correlation test between organic content (COD) and MP content in combined sewer system (L3) and MP

Table A 9 Correlation tests between Solids in all fractions and MP content in stormwater runoff at **(L3)**, raw data

	Total		**500-1000 µm**		**100-500 µm**		**50-100 µm**		**5-50 µm**	
	Solids $_{\text{Total}}$	MP $_{\text{Total}}$	Solids $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	Solids $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	Solids $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	Solids $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
All polymers (PE, SBR, PP,PS)	330.4 mg/L	1729 µg/L	19.2 mg/L	306.0 µg/L	96.0 mg/L	1146.0 µg/L	18.5 mg/L	270.0 µg/L	196.0 mg/L	7.0 µg/L
	294.0 mg/L	980 µg/L	8.2 mg/L	191.0 µg/L	70.0 mg/L	282.0 µg/L	34.2 mg/L	507.0 µg/L	181.0 mg/L	0.5 µg/L
	265.0 mg/L	1718 µg/L	5.4 mg/L	107.4 µg/L	39.3 mg/L	751.9 µg/L	6.8 mg/L	552.1 µg/L	207.0 mg/L	306.2 µg/L
	63.0 mg/L	401 µg/L	3.6 mg/L	222.9 µg/L	19.1 mg/L	154.4 µg/L	5.3 mg/L	23.5 µg/L	58.0 mg/L	0.3 µg/L
	83.0 mg/L	628 µg/L	3.6 mg/L	62.3 µg/L	31.9 mg/L	317.9 µg/L	11.6 mg/L	218.8 µg/L	37.0 mg/L	29.1 µg/L
	40.0 mg/L	3576 µg/L	2.3 mg/L	563.7 µg/L	12.3 mg/L	1219.3 µg/L	5.3 mg/L	1537.0 µg/L	13.0 mg/L	256.2 µg/L
	58.0 mg/L	3649 µg/L	4.4 mg/L	1209.4 µg/L	14.4 mg/L	950.8 µg/L	5.8 mg/L	1209.5 µg/L	27.0 mg/L	279.6 µg/L
Mean	161.9 mg/L	1811.6 µg/L	6.7 mg/L	380.4 µg/L	40.4 mg/L	688.9 µg/L	12.5 mg/L	616.8 µg/L	102.7 mg/L	125.5 µg/L
Standard Deviation S	127.9 mg/L	1328.3 µg/L	5.8 mg/L	400.6 µg/L	31.5 mg/L	438.1 µg/L	10.7 mg/L	554.5 µg/L	87.4 mg/L	146.1 µg/L
Correlation	-0.3007		-0.1508		0.0737		-0.2837		-0.1757	

	Solids $_{\text{Total}}$	MP $_{\text{Total}}$	Solids $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	Solids $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	Solids $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	Solids $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
PE	330.4 mg/L	1204.4 µg/L	19.2 mg/L	219.7 µg/L	96.0 mg/L	807.7 µg/L	18.5 mg/L	173.1 µg/L	196.0 mg/L	3.8 µg/L
	294.0 mg/L	893.4 µg/L	8.2 mg/L	183.1 µg/L	70.0 mg/L	238.8 µg/L	34.2 mg/L	471.3 µg/L	181.0 mg/L	0.3 µg/L
	265.0 mg/L	1110.7 µg/L	5.4 mg/L	59.7 µg/L	39.3 mg/L	474.1 µg/L	6.8 mg/L	417.2 µg/L	207.0 mg/L	159.6 µg/L
	63.0 mg/L	375.4 µg/L	3.6 mg/L	204.1 µg/L	19.1 mg/L	149.2 µg/L	5.3 mg/L	21.8 µg/L	58.0 mg/L	0.3 µg/L
	83.0 mg/L	547.8 µg/L	3.6 mg/L	61.8 µg/L	31.9 mg/L	290.7 µg/L	11.6 mg/L	172.7 µg/L	37.0 mg/L	22.6 µg/L
	40.0 mg/L	759.7 µg/L	2.3 mg/L	45.5 µg/L	12.3 mg/L	565.3 µg/L	5.3 mg/L	117.6 µg/L	13.0 mg/L	31.3 µg/L
	58.0 mg/L	304.0 µg/L	4.4 mg/L	65.9 µg/L	14.4 mg/L	159.7 µg/L	5.8 mg/L	65.9 µg/L	27.0 mg/L	12.5 µg/L
Mean	161.9 µg/L	742.2 µg/L	6.7 µg/L	120.0 µg/L	40.4 µg/L	383.6 µg/L	12.5 µg/L	205.7 µg/L	102.7 µg/L	32.9 µg/L
Standard Deviation S	127.9 µg/L	350.5 µg/L	5.8 µg/L	78.0 µg/L	31.5 µg/L	243.5 µg/L	10.7 µg/L	172.5 µg/L	87.4 µg/L	57.1 µg/L
COVARIANCE	32978.9011		256.5711		3669.1075		1039.7113		1681.9580	
Correlation	0.8584		0.6577		0.5577		0.6564		0.3935	

	Solids $_{\text{Total}}$	MP $_{\text{Total}}$	Solids $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	Solids $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	Solids $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	Solids $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
SBR	330.4 mg/L	426.7 µg/L	19.2 mg/L	71.1 µg/L	96.0 mg/L	280.5 µg/L	18.5 mg/L	72.3 µg/L	196.0 mg/L	2.9 µg/L
	294.0 mg/L	30.2 µg/L	8.2 mg/L	1.1 µg/L	70.0 mg/L	23.5 µg/L	34.2 mg/L	5.5 µg/L	181.0 mg/L	0.1 µg/L
	265.0 mg/L	461.2 µg/L	5.4 mg/L	41.6 µg/L	39.3 mg/L	213.8 µg/L	6.8 mg/L	91.4 µg/L	207.0 mg/L	114.4 µg/L
	63.0 mg/L	5.3 µg/L	3.6 mg/L	4.6 µg/L	19.1 mg/L	0.4 µg/L	5.3 mg/L	0.2 µg/L	58.0 mg/L	0.0 µg/L
	83.0 mg/L	72.4 µg/L	3.6 mg/L	0.4 µg/L	31.9 mg/L	22.6 µg/L	11.6 mg/L	43.6 µg/L	37.0 mg/L	5.8 µg/L
	40.0 mg/L	2807.2 µg/L	2.3 mg/L	515.6 µg/L	12.3 mg/L	654.0 µg/L	5.3 mg/L	1413.6 µg/L	13.0 mg/L	224.0 µg/L
	58.0 mg/L	3324.7 µg/L	4.4 mg/L	1138.6 µg/L	14.4 mg/L	782.3 µg/L	5.8 mg/L	1138.6 µg/L	27.0 mg/L	265.3 µg/L
Mean	161.9 µg/L	1018.2 µg/L	6.7 µg/L	253.3 µg/L	40.4 µg/L	282.4 µg/L	12.5 µg/L	395.0 µg/L	102.7 µg/L	87.5 µg/L
Standard Deviation S	127.9 µg/L	1418.8 µg/L	5.8 µg/L	432.0 µg/L	31.5 µg/L	318.0 µg/L	10.7 µg/L	608.0 µg/L	87.4 µg/L	115.5 µg/L
COVARIANCE	-81502.5188		-576.8925		-3275.1804		-2550.7416		-4051.6315	
Correlation	-0.5241		-0.2669		-0.3813		-0.4569		-0.4683	

	Solids $_{\text{Total}}$	MP $_{\text{Total}}$	Solids $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	Solids $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	Solids $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	Solids $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
PS	330.4 mg/L	0.03 µg/L	19.2 mg/L	0.00 µg/L	96.0 mg/L	0.01 µg/L	18.5 mg/L	0.01 µg/L	196.0 mg/L	0.001 µg/L
	294.0 mg/L	24.65 µg/L	8.2 mg/L	3.18 µg/L	70.0 mg/L	10.22 µg/L	34.2 mg/L	11.20 µg/L	181.0 mg/L	0.041 µg/L
	265.0 mg/L	76.08 µg/L	5.4 mg/L	4.77 µg/L	39.3 mg/L	41.22 µg/L	6.8 mg/L	17.31 µg/L	207.0 mg/L	12.786 µg/L
	63.0 mg/L	7.69 µg/L	3.6 mg/L	6.49 µg/L	19.1 mg/L	0.69 µg/L	5.3 mg/L	0.50 µg/L	58.0 mg/L	0.007 µg/L
	83.0 mg/L	0.01 µg/L	3.6 mg/L	0.00 µg/L	31.9 mg/L	0.00 µg/L	11.6 mg/L	0.00 µg/L	37.0 mg/L	0.000 µg/L
	40.0 mg/L	0.02 µg/L	2.3 mg/L	0.00 µg/L	12.3 mg/L	0.00 µg/L	5.3 mg/L	0.02 µg/L	13.0 mg/L	0.001 µg/L
	58.0 mg/L	0.01 µg/L	4.4 mg/L	0.00 µg/L	14.4 mg/L	0.00 µg/L	5.8 mg/L	0.00 µg/L	27.0 mg/L	0.001 µg/L
Mean	161.9 µg/L	15.5 µg/L	6.7 µg/L	2.1 µg/L	40.4 µg/L	7.5 µg/L	12.5 µg/L	4.2 µg/L	102.7 µg/L	1.8 µg/L
Standard Deviation S	127.9 µg/L	28.2 µg/L	5.8 µg/L	2.7 µg/L	31.5 µg/L	15.4 µg/L	10.7 µg/L	7.1 µg/L	87.4 µg/L	4.8 µg/L
COVARIANCE	1476.9939		-3.0188		34.3994		20.0462		190.8823	
Correlation	0.4777		-0.2200		0.0829		0.3062		0.5277	

	Solids $_{\text{Total}}$	MP $_{\text{Total}}$	Solids $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	Solids $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	Solids $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	Solids $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
PP	330.4 mg/L	98.2 µg/L	19.2 mg/L	15.0 µg/L	96.0 mg/L	57.8 µg/L	18.5 mg/L	24.9 µg/L	196.0 mg/L	0.5 µg/L
	294.0 mg/L	32.1 µg/L	8.2 mg/L	3.6 µg/L	70.0 mg/L	9.3 µg/L	34.2 mg/L	19.2 µg/L	181.0 mg/L	0.0 µg/L
	265.0 mg/L	69.6 µg/L	5.4 mg/L	1.3 µg/L	39.3 mg/L	22.7 µg/L	6.8 mg/L	26.1 µg/L	207.0 mg/L	19.4 µg/L
	63.0 mg/L	12.8 µg/L	3.6 mg/L	7.6 µg/L	19.1 mg/L	4.2 µg/L	5.3 mg/L	1.0 µg/L	58.0 mg/L	0.0 µg/L
	83.0 mg/L	7.9 µg/L	3.6 mg/L	0.0 µg/L	31.9 mg/L	4.6 µg/L	11.6 mg/L	2.5 µg/L	37.0 mg/L	0.7 µg/L
	40.0 mg/L	9.5 µg/L	2.3 mg/L	2.6 µg/L	12.3 mg/L	0.0 µg/L	5.3 mg/L	6.0 µg/L	13.0 mg/L	0.8 µg/L
	58.0 mg/L	20.6 µg/L	4.4 mg/L	5.0 µg/L	14.4 mg/L	8.9 µg/L	5.8 mg/L	5.0 µg/L	27.0 mg/L	1.8 µg/L
Mean	161.9 µg/L	35.8 µg/L	6.7 µg/L	5.0 µg/L	40.4 µg/L	15.4 µg/L	12.5 µg/L	12.1 µg/L	102.7 µg/L	3.3 µg/L
Standard Deviation S	127.9 µg/L	34.8 µg/L	5.8 µg/L	5.1 µg/L	31.5 µg/L	20.1 µg/L	10.7 µg/L	10.9 µg/L	87.4 µg/L	7.1 µg/L
COVARIANCE	3251.6262		20.8473		443.2637		47.1929		257.8025	
Correlation	0.8517		0.8241		0.8183		0.4714		0.4839	

Table A 10 Correlation tests between Solids in all fractions and MP content in dry weather flow at (L3), raw data

	Total		**500-1000µm**		**100-500µm**		**50-100µm**		**5-50µm**	
	Solids $_{\text{Total}}$	MP $_{\text{Total}}$	Solids $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	Solids $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	Solids $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	Solids $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
All polymers (PE, PP,PS)	237.0 mg/L	262 µg/L	31.1 mg/L	38.9 µg/L	58.6 mg/L	200.1 µg/L	8.8 mg/L	22.8 µg/L	0.0 mg/L	96.0 µg/L
	236.0 mg/L	410 µg/L	7.6 mg/L	35.0 µg/L	37.3 mg/L	49.4 µg/L	22.8 mg/L	325.7 µg/L	0.8 mg/L	15.8 µg/L
	395.0 mg/L	388 µg/L	23.2 mg/L	0.0 µg/L	43.7 mg/L	347.3 µg/L	13.6 mg/L	14.5 µg/L	26.8 mg/L	30.5 µg/L
	410.0 mg/L		28.7 mg/L	0.0 µg/L	63.5 mg/L	0.0 µg/L	83.2 mg/L	0.0 µg/L	0.0 mg/L	232.3 µg/L
	383.0 mg/L	1936 µg/L	27.6 mg/L	197.7 µg/L	74.0 mg/L	1084.7 µg/L	17.2 mg/L	403.7 µg/L	249.4 mg/L	13.9 µg/L
	482.9 mg/L	1020 µg/L	52.7 mg/L	6.8 µg/L	102.5 mg/L	721.9 µg/L	26.5 mg/L	263.4 µg/L	28.7 mg/L	55.4 µg/L
	438.0 mg/L	522 µg/L	21.5 mg/L	72.9 µg/L	70.6 mg/L	296.6 µg/L	14.8 mg/L	152.1 µg/L	0.6 mg/L	2.3 µg/L
	234.0 mg/L	962 µg/L	38.8 mg/L	245.7 µg/L	37.9 mg/L	287.9 µg/L	89.5 mg/L	392.7 µg/L	35.2 mg/L	68.0 µg/L
	602.0 mg/L	855 µg/L	36.4 mg/L	170.0 µg/L	11.7 mg/L	136.2 µg/L	146.6 mg/L	477.4 µg/L	71.1 mg/L	408.0 µg/L
Mean	379.8 mg/L	794.3 µg/L	29.7 mg/L	85.2 µg/L	55.5 mg/L	347.1 µg/L	47.0 mg/L	228.0 µg/L	45.8 mg/L	102.5 µg/L
Standard Deviation S	125.9 mg/L	541.8 µg/L	12.6 mg/L	94.3 µg/L	26.3 mg/L	347.5 µg/L	48.1 mg/L	185.9 µg/L	79.9 mg/L	134.3 µg/L
Correlation	0.25		0.19		0.59		0.46		-0.06	

	Solids $_{\text{Total}}$	MP $_{\text{Total}}$	Solids $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	Solids $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	Solids $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	Solids $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
PE	237.0 mg/L	250 µg/L	31.1 mg/L	38.9 µg/L	58.6 mg/L	188.8 µg/L	8.8 mg/L	21.8 µg/L		
	236.0 mg/L	298 µg/L	7.6 mg/L	0.0 µg/L	37.3 mg/L	0.0 µg/L	22.8 mg/L	297.9 µg/L		
	395.0 mg/L	346 µg/L	23.2 mg/L	0.0 µg/L	43.7 mg/L	320.1 µg/L	13.6 mg/L	0.0 µg/L	26.8 mg/L	25.4 µg/L
	410.0 mg/L	0 µg/L	28.7 mg/L		63.5 mg/L		83.2 mg/L			
	383.0 mg/L	1762 µg/L	27.6 mg/L	193.0 µg/L	74.0 mg/L	992.2 µg/L	17.2 mg/L	358.0 µg/L	249.4 mg/L	218.8 µg/L
	482.9 mg/L	890 µg/L	52.7 mg/L	0.0 µg/L	102.5 mg/L	621.7 µg/L	26.5 mg/L	257.0 µg/L	28.7 mg/L	10.8 µg/L
	438.0 mg/L	522 µg/L	21.5 mg/L	72.9 µg/L	70.6 mg/L	296.6 µg/L	14.8 mg/L	152.1 µg/L	0.6 mg/L	0.6 µg/L
	234.0 mg/L	914 µg/L	38.8 mg/L	242.2 µg/L	37.9 mg/L	267.7 µg/L	89.5 mg/L	370.8 µg/L	35.2 mg/L	32.9 µg/L
	602.0 mg/L	762 µg/L	36.4 mg/L	120.6 µg/L	11.7 mg/L	110.5 µg/L	146.6 mg/L	461.9 µg/L	71.1 mg/L	69.4 µg/L
Mean	379.8 µg/L	638.1 µg/L	29.7 µg/L	83.5 µg/L	55.5 µg/L	349.7 µg/L	47.0 µg/L	239.9 µg/L	68.6 µg/L	59.6 µg/L
Standard Deviation S	125.9 µg/L	523.3 µg/L	12.6 µg/L	93.8 µg/L	26.3 µg/L	316.8 µg/L	48.1 µg/L	167.7 µg/L	91.4 µg/L	81.5 µg/L
COVARIANCE	10100.6252		244.5805		5250.9147		5198.5003		6181.5083	
Correlation	0.1724		0.2222		0.6770		0.7175		0.9961	

	Solids $_{\text{Total}}$	MP $_{\text{Total}}$	Solids $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	Solids $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	Solids $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	Solids $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
PS	237.0 mg/L	4 µg/L	31.1 mg/L	0.0 µg/L	58.6 mg/L	3.3 µg/L	8.8 mg/L	0.3 µg/L	0.0 mg/L	0.0 µg/L
	236.0 mg/L	7 µg/L	7.6 mg/L	0.5 µg/L	37.3 mg/L	4.2 µg/L	22.8 mg/L	2.5 µg/L	0.8 mg/L	0.0 µg/L
	395.0 mg/L	5 µg/L	23.2 mg/L	0.0 µg/L	43.7 mg/L	3.5 µg/L	13.6 mg/L	1.5 µg/L	26.8 mg/L	0.3 µg/L
	410.0 mg/L	0 µg/L	28.7 mg/L		63.5 mg/L		83.2 mg/L		0.0 mg/L	
	383.0 mg/L	22 µg/L	27.6 mg/L	4.7 µg/L	74.0 mg/L	16.8 µg/L	17.2 mg/L	0.0 µg/L	249.4 mg/L	0.0 µg/L
	482.9 mg/L	60 µg/L	52.7 mg/L	6.8 µg/L	102.5 mg/L	46.7 µg/L	26.5 mg/L	6.4 µg/L	28.7 mg/L	0.5 µg/L
	438.0 mg/L	0 µg/L	21.5 mg/L	0.0 µg/L	70.6 mg/L	0.0 µg/L	14.8 mg/L	0.0 µg/L	0.6 mg/L	0.0 µg/L
	234.0 mg/L	35 µg/L	38.8 mg/L	3.5 µg/L	37.9 mg/L	15.0 µg/L	89.5 mg/L	16.0 µg/L	35.2 mg/L	0.8 µg/L
	602.0 mg/L	78 µg/L	36.4 mg/L	45.6 µg/L	11.7 mg/L	15.5 µg/L	146.6 mg/L	15.5 µg/L	71.1 mg/L	1.7 µg/L
Mean	379.8 µg/L	23.5 µg/L	29.7 µg/L	7.6 µg/L	55.5 µg/L	13.1 µg/L	47.0 µg/L	5.3 µg/L	45.8 µg/L	0.4 µg/L
Standard Deviation S	125.9 µg/L	28.7 µg/L	12.6 µg/L	15.6 µg/L	26.3 µg/L	15.1 µg/L	48.1 µg/L	6.8 µg/L	79.9 µg/L	0.6 µg/L
COVARIANCE	1899.3646		58.0029		194.5941		270.3252		0.1337	
Correlation	0.5902		0.3176		0.5272		0.9200		0.0030	

	Solids $_{\text{Total}}$	MP $_{\text{Total}}$	Solids $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	Solids $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	Solids $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	Solids $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
PP	237.0 mg/L	9 µg/L	0.0 mg/L	0.0 µg/L	58.6 mg/L	8.0 µg/L	8.8 mg/L	0.8 µg/L	0.0 mg/L	0.0 µg/L
	236.0 mg/L	106 µg/L	34.5 mg/L	0.5 µg/L	37.3 mg/L	45.2 µg/L	22.8 mg/L	25.3 µg/L	0.8 mg/L	0.8 µg/L
	395.0 mg/L	38 µg/L	0.0 mg/L	0.0 µg/L	43.7 mg/L	23.7 µg/L	13.6 mg/L	13.0 µg/L	26.8 mg/L	1.1 µg/L
	383.0 mg/L	152 µg/L	0.0 mg/L	4.7 µg/L	74.0 mg/L	75.7 µg/L	17.2 mg/L	45.7 µg/L	249.4 mg/L	30.6 µg/L
	482.9 mg/L	71 µg/L	0.0 mg/L	6.8 µg/L	102.5 mg/L	53.5 µg/L	26.5 mg/L	0.0 µg/L	28.7 mg/L	17.4 µg/L
	438.0 mg/L	0 µg/L	0.0 mg/L	0.0 µg/L	70.6 mg/L	0.0 µg/L	14.8 mg/L	0.0 µg/L	0.6 mg/L	0.0 µg/L
	234.0 mg/L	13 µg/L	0.0 mg/L	3.5 µg/L	37.9 mg/L	5.2 µg/L	89.5 mg/L	5.9 µg/L	35.2 mg/L	1.5 µg/L
	602.0 mg/L	14 µg/L	3.7 mg/L	45.6 µg/L	11.7 mg/L	10.3 µg/L	146.6 mg/L	0.0 µg/L	71.1 mg/L	0.0 µg/L
Mean	376.0 µg/L	50.2 µg/L	4.8 µg/L	7.6 µg/L	54.5 µg/L	27.7 µg/L	42.5 µg/L	11.3 µg/L	51.6 µg/L	6.4 µg/L
Standard Deviation S	134.1 µg/L	54.8 µg/L	12.1 µg/L	15.6 µg/L	28.0 µg/L	27.4 µg/L	49.4 µg/L	16.5 µg/L	83.5 µg/L	11.4 µg/L
COVARIANCE	-662.2597		-12.9774		313.3731		-221.7924		695.3701	
Correlation	-0.1031		-0.0789		0.4670		-0.3112		0.8338	

Table A 11 Correlation tests between Solids in all fractions and MP content in stormwater runoff at **(L4)**, raw data

	Total		500-1000 µm		100-500 µm		50-100 µm		5-50 µm	
	Solids $_{Total}$	MP $_{Total}$	Solids $_{500-1000}$	MP $_{500-1000µm}$	Solids $_{100-500µm}$	MP $_{100-500µm}$	Solids $_{50-100µm}$	MP $_{50-100µm}$	Solids $_{5-50µm}$	MP $_{5-50µm}$
All polymers (PE, SBR, PP,PS)	23.5 mg/L	44 µg/L	1.2 mg/L	2.3 µg/L	3.5 mg/L	25.3 µg/L	1.5 mg/L	16.7 µg/L	0.4 mg/L	0.0 µg/L
	3.4 mg/L	218 µg/L	0.2 mg/L	1.7 µg/L	1.8 mg/L	120.6 µg/L	0.7 mg/L	53.1 µg/L	0.5 mg/L	43.0 µg/L
	197.4 mg/L	1591 µg/L	13,544,6	270.3 µg/L	51.0 mg/L	999.0 µg/L	16.1 mg/L	51.8 µg/L	116.0 mg/L	270.4 µg/L
	95.0 mg/L	924 µg/L	2.3 mg/L	180.3 µg/L	27.9 mg/L	423.7 µg/L	13.7 mg/L	214.0 µg/L	51,00 mg/L	106.1 µg/L
	55.0 mg/L	1102 µg/L	3.5 mg/L	324.4 µg/L	52.6 mg/L	653.8 µg/L	7.9 mg/L	18.7 µg/L	13,00 mg/L	105.1 µg/L
	38.9 mg/L	465 µg/L	3.1 mg/L	59.5 µg/L	26.8 mg/L	290.9 µg/L	9.0 mg/L	83.8 µg/L	5,00 mg/L	30.4 µg/L
	43.0 mg/L	502 µg/L	2.4 mg/L	59.1 µg/L	26.5 mg/L	201.4 µg/L	9.3 mg/L	76.3 µg/L	8,00 mg/L	164.9 µg/L
	10.0 mg/L	723 µg/L	1.1 mg/L	13.5 µg/L	38.0 mg/L	482.4 µg/L	9.4 mg/L	119.3 µg/L	4,00 mg/L	107.7 µg/L
	245.0 mg/L	479 µg/L	16.0 mg/L	144.5 µg/L	143.2 mg/L	171.0 µg/L	22.3 mg/L	153.5 µg/L	64.0 mg/L	6.9 µg/L
Mean	79.0 mg/L	672.0 µg/L	3.7 mg/L	117.3 µg/L	41.2 mg/L	374.2 µg/L	10.0 mg/L	87.5 µg/L	45.2 mg/L	92.7 µg/L
Standard Deviation S	85.8 mg/L	475.1 µg/L	5.1 mg/L	120.0 µg/L	42.2 mg/L	305.5 µg/L	6.8 mg/L	64.9 µg/L	55.9 mg/L	86.3 µg/L
Correlation	0.4619		0.3237		0.1403		0.6008		0.8063	

	Solids $_{Total}$	MP $_{Total}$	Solids $_{500-1000}$	MP $_{500-1000µm}$	Solids $_{100-500µm}$	MP $_{100-500µm}$	Solids $_{50-100µm}$	MP $_{50-100µm}$	Solids $_{5-50µm}$	MP $_{5-50µm}$
PE	23.5 mg/L	28 µg/L	1.2 mg/L	2 µg/L	3.5 mg/L	13 µg/L	1.5 mg/L	13 µg/L	0.4 mg/L	0 µg/L
	3.4 mg/L	90 µg/L	0.2 mg/L	1 µg/L	1.8 mg/L	70 µg/L	0.7 mg/L	20 µg/L	0.5 mg/L	0 µg/L
	197.4 mg/L	631 µg/L	13,544,6	179 µg/L	51.0 mg/L	363 µg/L	16.1 mg/L	0 µg/L	116.0 mg/L	89 µg/L
	95.0 mg/L	705 µg/L	2.3 mg/L	177 µg/L	27.9 mg/L	340 µg/L	13.7 mg/L	138 µg/L	51,00 mg/L	50 µg/L
	55.0 mg/L	1065 µg/L	3.5 mg/L	322 µg/L	52.6 mg/L	628 µg/L	7.9 mg/L	18 µg/L	13,00 mg/L	96 µg/L
	38.9 mg/L	236 µg/L	3.1 mg/L	27 µg/L	26.8 mg/L	163 µg/L	9.0 mg/L	36 µg/L	5,00 mg/L	11 µg/L
	43.0 mg/L	347 µg/L	2.4 mg/L	24 µg/L	26.5 mg/L	168 µg/L	9.3 mg/L	59 µg/L	8,00 mg/L	96 µg/L
	10.0 mg/L	697 µg/L	1.1 mg/L	13 µg/L	38.0 mg/L	465 µg/L	9.4 mg/L	115 µg/L	4,00 mg/L	104 µg/L
	245.0 mg/L	256 µg/L	16.0 mg/L	60 µg/L	143.2 mg/L	119 µg/L	22.3 mg/L	74 µg/L	64.0 mg/L	4 µg/L
Mean	79.0 µg/L	450.5 µg/L	3.7 µg/L	89.5 µg/L	41.2 µg/L	258.6 µg/L	10.0 µg/L	52.3 µg/L	45.2 µg/L	50.0 µg/L
Standard Deviation S	85.8 µg/L	342.5 µg/L	5.1 µg/L	112.0 µg/L	42.2 µg/L	203.1 µg/L	6.8 µg/L	48.2 µg/L	55.9 µg/L	46.5 µg/L
COVARIANCE	2732.0702		41.9100		957.7718		104.6288		1594.4792	
Correlation	0.1046		0.0825		0.1259		0.3607		0.8681	

	Solids $_{\text{Total}}$	MP $_{\text{Total}}$	Solids $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	Solids $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	Solids $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	Solids $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
SBR	23.5 mg/L	4 µg/L	1.2 mg/L	0 µg/L	3.5 mg/L	4 µg/L	1.5 mg/L	0 µg/L	0.4 mg/L	0 µg/L
	3.4 mg/L	48 µg/L	0.2 mg/L	0 µg/L	1.8 mg/L	32 µg/L	0.7 mg/L	16 µg/L	0.5 mg/L	0 µg/L
	197.4 mg/L	773 µg/L	13,544,6	36 µg/L	51.0 mg/L	525 µg/L	16.1 mg/L	47 µg/L	116.0 mg/L	164 µg/L
	95.0 mg/L	183 µg/L	2.3 mg/L	1 µg/L	27.9 mg/L	67 µg/L	13.7 mg/L	63 µg/L	51,00 mg/L	52 µg/L
	55.0 mg/L	8 µg/L	3.5 mg/L	1 µg/L	52.6 mg/L	0 µg/L	7.9 mg/L	0 µg/L	13,00 mg/L	6 µg/L
	38.9 mg/L	222 µg/L	3.1 mg/L	32 µg/L	26.8 mg/L	125 µg/L	9.0 mg/L	45 µg/L	5,00 mg/L	19 µg/L
	43.0 mg/L	95 µg/L	2.4 mg/L	3 µg/L	26.5 mg/L	21 µg/L	9.3 mg/L	11 µg/L	8,00 mg/L	60 µg/L
	10.0 mg/L	4 µg/L	1.1 mg/L	0 µg/L	38.0 mg/L	3 µg/L	9.4 mg/L	1 µg/L	4,00 mg/L	1 µg/L
	245.0 mg/L	221 µg/L	16.0 mg/L	85 µg/L	143.2 mg/L	52 µg/L	22.3 mg/L	83 µg/L	64.0 mg/L	1 µg/L
Mean	79.0 µg/L	173.0 µg/L	3.7 µg/L	17.5 µg/L	41.2 µg/L	92.0 µg/L	10.0 µg/L	29.7 µg/L	45.2 µg/L	33.7 µg/L
Standard Deviation S	85.8 µg/L	242.5 µg/L	5.1 µg/L	29.1 µg/L	42.2 µg/L	167.1 µg/L	6.8 µg/L	30.8 µg/L	55.9 µg/L	54.2 µg/L
COVARIANCE	12705.9983		126.5779		671.1688		148.4147		2910.5063	
Correlation	0.6871		0.9444		0.1072		0.8012		0.8464	

	Solids $_{\text{Total}}$	MP $_{\text{Total}}$	Solids $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	Solids $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	Solids $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	Solids $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
PS	23.5 mg/L	1 µg/L	1.2 mg/L	0 µg/L	3.5 mg/L	0 µg/L	1.5 mg/L	0 µg/L	0.4 mg/L	0 µg/L
	3.4 mg/L	1 µg/L	0.2 mg/L	1 µg/L	1.8 mg/L	0 µg/L	0.7 mg/L	0 µg/L	0.5 mg/L	0 µg/L
	197.4 mg/L	152 µg/L	13,544,6	32 µg/L	51.0 mg/L	102 µg/L	16.1 mg/L	4 µg/L	116.0 mg/L	14 µg/L
	95.0 mg/L	0 µg/L	2.3 mg/L	0 µg/L	27.9 mg/L	0 µg/L	13.7 mg/L	0 µg/L	51,00 mg/L	0 µg/L
	55.0 mg/L	0 µg/L	3.5 mg/L	0 µg/L	52.6 mg/L	0 µg/L	7.9 mg/L	0 µg/L	13,00 mg/L	0 µg/L
	38.9 mg/L	2 µg/L	3.1 mg/L	0 µg/L	26.8 mg/L	1 µg/L	9.0 mg/L	1 µg/L	5,00 mg/L	0 µg/L
	43.0 mg/L	16 µg/L	2.4 mg/L	1 µg/L	26.5 mg/L	6 µg/L	9.3 mg/L	4 µg/L	8,00 mg/L	6 µg/L
	10.0 mg/L	4 µg/L	1.1 mg/L	0 µg/L	38.0 mg/L	3 µg/L	9.4 mg/L	1 µg/L	4,00 mg/L	1 µg/L
	245.0 mg/L	1 µg/L	16.0 mg/L	0 µg/L	143.2 mg/L	0 µg/L	22.3 mg/L	0 µg/L	64.0 mg/L	0 µg/L
Mean	79.0 µg/L	19.7 µg/L	3.7 µg/L	3.8 µg/L	41.2 µg/L	12.6 µg/L	10.0 µg/L	1.0 µg/L	45.2 µg/L	2.3 µg/L
Standard Deviation S	85.8 µg/L	49.8 µg/L	5.1 µg/L	10.6 µg/L	42.2 µg/L	33.7 µg/L	6.8 µg/L	1.6 µg/L	55.9 µg/L	4.7 µg/L
COVARIANCE	1889.0069		-0.5076		99.3290		1.7638		243.8532	
Correlation	0.4975		-0.2660		0.0785		0.1883		0.8549	

	Solids $_{\text{Total}}$	MP $_{\text{Total}}$	Solids $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	Solids $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	Solids $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	Solids $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
PP	23.5 mg/L	12 µg/L	1.2 mg/L	0 µg/L	3.5 mg/L	9 µg/L	1.5 mg/L	3 µg/L	0.4 mg/L	0 µg/L
	3.4 mg/L	79 µg/L	0.2 mg/L	0 µg/L	1.8 mg/L	19 µg/L	0.7 mg/L	18 µg/L	0.5 mg/L	43 µg/L
	197.4 mg/L	36 µg/L	13,544,6	22 µg/L	51.0 mg/L	9 µg/L	16.1 mg/L	1 µg/L	116.0 mg/L	3 µg/L
	95.0 mg/L	36 µg/L	2.3 mg/L	2 µg/L	27.9 mg/L	17 µg/L	13.7 mg/L	13 µg/L	51,00 mg/L	4 µg/L
	55.0 mg/L	29 µg/L	3.5 mg/L	1 µg/L	52.6 mg/L	25 µg/L	7.9 mg/L	1 µg/L	13,00 mg/L	2 µg/L
	38.9 mg/L	5 µg/L	3.1 mg/L	0 µg/L	26.8 mg/L	2 µg/L	9.0 mg/L	2 µg/L	5,00 mg/L	0 µg/L
	43.0 mg/L	43 µg/L	2.4 mg/L	31 µg/L	26.5 mg/L	6 µg/L	9.3 mg/L	2 µg/L	8,00 mg/L	4 µg/L
	10.0 mg/L	18 µg/L	1.1 mg/L	0 µg/L	38.0 mg/L	12 µg/L	9.4 mg/L	3 µg/L	4,00 mg/L	3 µg/L
	245.0 mg/L	1 µg/L	16.0 mg/L	0 µg/L	143.2 mg/L	0 µg/L	22.3 mg/L	0 µg/L	64.0 mg/L	1 µg/L
Mean	79.0 µg/L	28.9 µg/L	3.7 µg/L	6.4 µg/L	41.2 µg/L	11.0 µg/L	10.0 µg/L	4.7 µg/L	45.2 µg/L	6.7 µg/L
Standard Deviation S	85.8 µg/L	23.9 µg/L	5.1 µg/L	11.7 µg/L	42.2 µg/L	8.1 µg/L	6.8 µg/L	6.2 µg/L	55.9 µg/L	13.6 µg/L
COVARIANCE	-591.5902		-5.7755		-121.1054		-16.1071		-413.1787	
Correlation	-0.3251		-0.1209		-0.3973		-0.4350		-0.4772	

Table A 12 Correlation tests between loss on ignition (LoI) in all fractions and MP content in Stormwater runoff at Carl-Euler-Str. **(L3)**, raw data

	LoI $_{\text{Total}}$	MP $_{\text{Total}}$	LoI $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	LoI $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	LoI $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	LoI $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
All polymers (PE, SBR, PP,PS)	67.0%	1729 µg/L	90.0%	306.0 µg/L	61.0%	1146.0 µg/L	51.0%	270.0 µg/L		7.0 µg/L
	69.0%	980 µg/L	76.0%	191.0 µg/L	35.0%	282.0 µg/L	95.0%	507.0 µg/L		0.5 µg/L
	44.0%	1718 µg/L	78.0%	107.4 µg/L	32.0%	751.9 µg/L	24.0%	552.1 µg/L		306.2 µg/L
	87.0%	401 µg/L	96.0%	222.9 µg/L	90.0%	154.4 µg/L	76.0%	23.5 µg/L		0.3 µg/L
	71.0%	628 µg/L	92.0%	62.3 µg/L	68.0%	317.9 µg/L	52.0%	218.8 µg/L		29.1 µg/L
	78.0%	3576 µg/L	93.0%	563.7 µg/L	81.0%	1219.3 µg/L	60.0%	1537.0 µg/L		256.2 µg/L
	74.0%	3649 µg/L	88.0%	1209.4 µg/L	76.0%	950.8 µg/L	57.0%	1209.5 µg/L		279.6 µg/L
Mean	0.7 mg/L	1811.6 µg/L	0.9 mg/L	380.4 µg/L	0.6 mg/L	688.9 µg/L	0.6 mg/L	616.8 µg/L	_	125.5 µg/L
Standard Deviation S	0.1 mg/L	1328.3 µg/L	0.1 mg/L	400.6 µg/L	0.2 mg/L	438.1 µg/L	0.2 mg/L	554.5 µg/L	_	146.1 µg/L
Correlation	-0.0018		0.1760		0.0884		-0.0882		_	
	LoI $_{\text{Total}}$	MP $_{\text{Total}}$	LoI $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	LoI $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	LoI $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	LoI $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
PE	67.0%	1204.4 µg/L	90.0%	219.7 µg/L	61.0%	807.7 µg/L	51.0%	173.1 µg/L		3.8 µg/L
	69.0%	893.4 µg/L	76.0%	183.1 µg/L	35.0%	238.8 µg/L	95.0%	471.3 µg/L		0.3 µg/L
	44.0%	1110.7 µg/L	78.0%	59.7 µg/L	32.0%	474.1 µg/L	24.0%	417.2 µg/L		159.6 µg/L
	87.0%	375.4 µg/L	96.0%	204.1 µg/L	90.0%	149.2 µg/L	76.0%	21.8 µg/L		0.3 µg/L
	71.0%	547.8 µg/L	92.0%	61.8 µg/L	68.0%	290.7 µg/L	52.0%	172.7 µg/L		22.6 µg/L
	78.0%	759.7 µg/L	93.0%	45.5 µg/L	81.0%	565.3 µg/L	60.0%	117.6 µg/L		31.3 µg/L
	74.0%	304.0 µg/L	88.0%	65.9 µg/L	76.0%	159.7 µg/L	57.0%	65.9 µg/L		12.5 µg/L

Mean	0.7 µg/L	742.2 µg/L	0.9 µg/L	120.0 µg/L	0.6 µg/L	383.6 µg/L	0.6 µg/L	205.7 µg/L	_	32.9 µg/L
Standard Deviation S	0.1 µg/L	350.5 µg/L	0.1 µg/L	78.0 µg/L	0.2 µg/L	243.5 µg/L	0.2 µg/L	172.5 µg/L	_	57.1 µg/L
COVARIANCE	-27.3741		0.1624		-8.6206		-0.4098		_	
Correlation	-0.6869		0.0317		-0.1848		-0.0125		_	
	LoI $_{Total}$	MP $_{Total}$	LoI $_{500-1000}$	MP $_{500-1000µm}$	LoI $_{100-500µm}$	MP $_{100-500µm}$	LoI $_{50-100µm}$	MP $_{50-100µm}$	LoI $_{5-50µm}$	MP $_{5-50µm}$
SBR	67.0%	426.7 µg/L	90.0%	71.1 µg/L	61.0%	280.5 µg/L	51.0%	72.3 µg/L		2.9 µg/L
	69.0%	30.2 µg/L	76.0%	1.1 µg/L	35.0%	23.5 µg/L	95.0%	5.5 µg/L		0.1 µg/L
	44.0%	461.2 µg/L	78.0%	41.6 µg/L	32.0%	213.8 µg/L	24.0%	91.4 µg/L		114.4 µg/L
	87.0%	5.3 µg/L	96.0%	4.6 µg/L	90.0%	0.4 µg/L	76.0%	0.2 µg/L		0.0 µg/L
	71.0%	72.4 µg/L	92.0%	0.4 µg/L	68.0%	22.6 µg/L	52.0%	43.6 µg/L		5.8 µg/L
	78.0%	2807.2 µg/L	93.0%	515.6 µg/L	81.0%	654.0 µg/L	60.0%	1413.6 µg/L		224.0 µg/L
	74.0%	3324.7 µg/L	88.0%	1138.6 µg/L	76.0%	782.3 µg/L	57.0%	1138.6 µg/L		265.3 µg/L
Mean	0.7 µg/L	1018.2 µg/L	0.9 µg/L	253.3 µg/L	0.6 µg/L	282.4 µg/L	0.6 µg/L	395.0 µg/L	_	87.5 µg/L
Standard Deviation S	0.1 µg/L	1418.8 µg/L	0.1 µg/L	432.0 µg/L	0.2 µg/L	318.0 µg/L	0.2 µg/L	608.0 µg/L	_	115.5 µg/L
COVARIANCE	32.3101		4.4136		19.5019		-7.9078		_	
Correlation	0.2003		0.1557		0.3202		-0.0687		_	
	LoI $_{Total}$	MP $_{Total}$	LoI $_{500-1000}$	MP $_{500-1000µm}$	LoI $_{100-500µm}$	MP $_{100-500µm}$	LoI $_{50-100µm}$	MP $_{50-100µm}$	LoI $_{5-50µm}$	MP $_{5-50µm}$
PS	67.0%	0.03 µg/L	90.0%	0.00 µg/L	61.0%	0.01 µg/L	51.0%	0.01 µg/L		0.001 µg/L
	69.0%	24.65 µg/L	76.0%	3.18 µg/L	35.0%	10.22 µg/L	95.0%	11.20 µg/L		0.041 µg/L
	44.0%	76.08 µg/L	78.0%	4.77 µg/L	32.0%	41.22 µg/L	24.0%	17.31 µg/L		12.786 µg/L
	87.0%	7.69 µg/L	96.0%	6.49 µg/L	90.0%	0.69 µg/L	76.0%	0.50 µg/L		0.007 µg/L
	71.0%	0.01 µg/L	92.0%	0.00 µg/L	68.0%	0.00 µg/L	52.0%	0.00 µg/L		0.000 µg/L
	78.0%	0.02 µg/L	93.0%	0.00 µg/L	81.0%	0.00 µg/L	60.0%	0.02 µg/L		0.001 µg/L
	74.0%	0.01 µg/L	88.0%	0.00 µg/L	76.0%	0.00 µg/L	57.0%	0.00 µg/L		0.001 µg/L
Mean	0.7 µg/L	15.5 µg/L	0.9 µg/L	2.1 µg/L	0.6 µg/L	7.5 µg/L	0.6 µg/L	4.2 µg/L	_	1.8 µg/L
Standard Deviation S	0.1 µg/L	28.2 µg/L	0.1 µg/L	2.7 µg/L	0.2 µg/L	15.4 µg/L	0.2 µg/L	7.1 µg/L	_	4.8 µg/L
COVARIANCE	-2.6742		-0.0395		-2.2288		-0.2893		_	
Correlation	-0.8337		-0.2194		-0.7577		-0.2144		_	
	LoI $_{Total}$	MP $_{Total}$	LoI $_{500-1000}$	MP $_{500-1000µm}$	LoI $_{100-500µm}$	MP $_{100-500µm}$	LoI $_{50-100µm}$	MP $_{50-100µm}$	LoI $_{5-50µm}$	MP $_{5-50µm}$
PP	67.0%	98.2 µg/L	90.0%	15.0 µg/L	61.0%	57.8 µg/L	51.0%	24.9 µg/L		0.5 µg/L
	69.0%	32.1 µg/L	76.0%	3.6 µg/L	35.0%	9.3 µg/L	95.0%	19.2 µg/L		0.0 µg/L
	44.0%	69.6 µg/L	78.0%	1.3 µg/L	32.0%	22.7 µg/L	24.0%	26.1 µg/L		19.4 µg/L
	87.0%	12.8 µg/L	96.0%	7.6 µg/L	90.0%	4.2 µg/L	76.0%	1.0 µg/L		0.0 µg/L
	71.0%	7.9 µg/L	92.0%	0.0 µg/L	68.0%	4.6 µg/L	52.0%	2.5 µg/L		0.7 µg/L
	78.0%	9.5 µg/L	93.0%	2.6 µg/L	81.0%	0.0 µg/L	60.0%	6.0 µg/L		0.8 µg/L
	74.0%	20.6 µg/L	88.0%	5.0 µg/L	76.0%	8.9 µg/L	57.0%	5.0 µg/L		1.8 µg/L
Mean	0.7 µg/L	35.8 µg/L	0.9 µg/L	5.0 µg/L	0.6 µg/L	15.4 µg/L	0.6 µg/L	12.1 µg/L	_	3.3 µg/L
Standard Deviation S	0.1 µg/L	34.8 µg/L	0.1 µg/L	5.1 µg/L	0.2 µg/L	20.1 µg/L	0.2 µg/L	10.9 µg/L	_	7.1 µg/L
COVARIANCE	-2.5023		0.0901		-1.2279		-0.6449		_	
Correlation	-0.6318		0.2715		-0.3197		-0.3124		_	

Table A 13 Correlation tests between loss on ignition (LoI) in all fractions and MP content in Stormwater runoff at **(L4)**, raw data

	Total		**500-1000 µm**		**100-500 µm**		**50-100 µm**		**5-50 µm**	
	LoI $_{\text{Total}}$	MP $_{\text{Total}}$	LoI $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	LoI $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	LoI $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	LoI $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
All polymers (PE, SBR, PP,PS)	34.0%	1591 µg/L	40.0%	270.3 µg/L	36.0%	999.0 µg/L	25.0%	51.8 µg/L	_	
	47.0%	924 µg/L	76.0%	180.3 µg/L	41.0%	423.7 µg/L	21.0%	214.0 µg/L	51.0%	106.1 µg/L
	46.0%	1102 µg/L	56.0%	324.4 µg/L	31.0%	653.8 µg/L	30.0%	18.7 µg/L	69.0%	105.1 µg/L
	41.0%	465 µg/L	66.0%	59.5 µg/L	27.0%	290.9 µg/L	30.0%	83.8 µg/L		
	58.0%	502 µg/L	100.0%	59.1 µg/L	37.0%	201.4 µg/L	36.0%	76.3 µg/L		
	50.0%	723 µg/L	73.0%	13.5 µg/L	11.0%	482.4 µg/L	15.0%	119.3 µg/L	100.0%	107.7 µg/L
	47.0%	479 µg/L	54.0%	144.5 µg/L	10.0%	171.0 µg/L	28.0%	153.5 µg/L	97.0%	6.9 µg/L
Mean	0.5 mg/L	826.5 µg/L	0.7 mg/L	150.2 µg/L	0.3 mg/L	460.3 µg/L	0.3 mg/L	102.5 µg/L	0.8 mg/L	81.5 µg/L
Standard Deviation S	0.1 mg/L	416.1 µg/L	0.2 mg/L	116.1 µg/L	0.1 mg/L	291.2 µg/L	0.1 mg/L	65.7 µg/L	0.2 mg/L	49.7 µg/L
Correlation	-0.6437		-0.6374		0.3246		-0.4669		-0.4918	

	LoI $_{\text{Total}}$	MP $_{\text{Total}}$	LoI $_{\text{500-1000}}$	MP $_{\text{500-1000µm}}$	LoI $_{\text{100-500µm}}$	MP $_{\text{100-500µm}}$	LoI $_{\text{50-100µm}}$	MP $_{\text{50-100µm}}$	LoI $_{\text{5-50µm}}$	MP $_{\text{5-50µm}}$
PE	34.0%	631 µg/L	40.0%	179 µg/L	36.0%	363 µg/L	25.0%	0 µg/L	_	
	47.0%	705 µg/L	76.0%	177 µg/L	41.0%	340 µg/L	21.0%	138 µg/L	51.0%	50 µg/L
	46.0%	1065 µg/L	56.0%	322 µg/L	31.0%	628 µg/L	30.0%	18 µg/L	69.0%	96 µg/L
	41.0%	236 µg/L	66.0%	27 µg/L	27.0%	163 µg/L	30.0%	36 µg/L		
	58.0%	347 µg/L	100.0%	24 µg/L	37.0%	168 µg/L	36.0%	59 µg/L		
	50.0%	697 µg/L	73.0%	13 µg/L	11.0%	465 µg/L	15.0%	115 µg/L	100.0%	104 µg/L
	47.0%	256 µg/L	54.0%	60 µg/L	10.0%	119 µg/L	28.0%	74 µg/L	97.0%	4 µg/L
Mean	0.5 µg/L	562.4 µg/L	0.7 µg/L	114.6 µg/L	0.3 µg/L	320.7 µg/L	0.3 µg/L	62.7 µg/L	0.8 µg/L	63.7 µg/L
Standard Deviation S	0.1 µg/L	300.6 µg/L	0.2 µg/L	115.8 µg/L	0.1 µg/L	185.6 µg/L	0.1 µg/L	50.3 µg/L	0.2 µg/L	46.1 µg/L
COVARIANCE	-2.0045		-8.9489		2.1198		-1.6995		-0.4583	
Correlation	-0.1048		-0.4683		0.1067		-0.5752		-0.0565	

	LoI$_{\text{Total}}$	MP$_{\text{Total}}$	LoI$_{\text{500-1000}}$	MP$_{\text{500-1000µm}}$	LoI$_{\text{100-500µm}}$	MP$_{\text{100-500µm}}$	LoI$_{\text{50-100µm}}$	MP$_{\text{50-100µm}}$	LoI$_{\text{5-50µm}}$	MP$_{\text{5-50µm}}$
SBR	34.0%	773 µg/L	40.0%	36 µg/L	36.0%	525 µg/L	25.0%	47 µg/L	_	
	47.0%	183 µg/L	76.0%	1 µg/L	41.0%	67 µg/L	21.0%	63 µg/L	51.0%	52 µg/L
	46.0%	8 µg/L	56.0%	1 µg/L	31.0%	0 µg/L	30.0%	0 µg/L	69.0%	6 µg/L
	41.0%	222 µg/L	66.0%	32 µg/L	27.0%	125 µg/L	30.0%	45 µg/L		
	58.0%	95 µg/L	100.0%	3 µg/L	37.0%	21 µg/L	36.0%	11 µg/L		
	50.0%	4 µg/L	73.0%	0 µg/L	11.0%	3 µg/L	15.0%	1 µg/L	100.0%	1 µg/L
	47.0%	221 µg/L	54.0%	85 µg/L	10.0%	52 µg/L	28.0%	83 µg/L	97.0%	1 µg/L
Mean	0.5 µg/L	215.0 µg/L	0.7 µg/L	22.5 µg/L	0.3 µg/L	113.2 µg/L	0.3 µg/L	35.9 µg/L	0.8 µg/L	14.9 µg/L
Standard Deviation S	0.1 µg/L	262.7 µg/L	0.2 µg/L	31.5 µg/L	0.1 µg/L	186.5 µg/L	0.1 µg/L	32.3 µg/L	0.2 µg/L	24.8 µg/L
COVARIANCE	-12.9055		-2.7617		6.4025		-0.0232		-3.7585	
Correlation	-0.7719		-0.5308		0.3207		-0.0122		-0.8611	

	LoI$_{\text{Total}}$	MP$_{\text{Total}}$	LoI$_{\text{500-1000}}$	MP$_{\text{500-1000µm}}$	LoI$_{\text{100-500µm}}$	MP$_{\text{100-500µm}}$	LoI$_{\text{50-100µm}}$	MP$_{\text{50-100µm}}$	LoI$_{\text{5-50µm}}$	MP$_{\text{5-50µm}}$
PS	34.0%	152 µg/L	40.0%	32 µg/L	36.0%	102 µg/L	25.0%	4 µg/L	_	
	47.0%	0 µg/L	76.0%	0 µg/L	41.0%	0 µg/L	21.0%	0 µg/L	51.0%	0 µg/L
	46.0%	0 µg/L	56.0%	0 µg/L	31.0%	0 µg/L	30.0%	0 µg/L	69.0%	0 µg/L
	41.0%	2 µg/L	66.0%	0 µg/L	27.0%	1 µg/L	30.0%	1 µg/L		
	58.0%	16 µg/L	100.0%	1 µg/L	37.0%	6 µg/L	36.0%	4 µg/L		
	50.0%	4 µg/L	73.0%	0 µg/L	11.0%	3 µg/L	15.0%	1 µg/L	100.0%	1 µg/L
	47.0%	1 µg/L	54.0%	0 µg/L	10.0%	0 µg/L	28.0%	0 µg/L	97.0%	0 µg/L
Mean	0.5 µg/L	25.0 µg/L	0.7 µg/L	4.8 µg/L	0.3 µg/L	16.1 µg/L	0.3 µg/L	1.2 µg/L	0.8 µg/L	0.2 µg/L
Standard Deviation S	0.1 µg/L	56.2 µg/L	0.2 µg/L	12.0 µg/L	0.1 µg/L	38.1 µg/L	0.1 µg/L	1.7 µg/L	0.2 µg/L	0.3 µg/L
COVARIANCE	-2.3490		-1.1583		1.2475		0.0378		0.0423	
Correlation	-0.6571		-0.5837		0.3058		0.3762		0.8794	

	LoI$_{\text{Total}}$	MP$_{\text{Total}}$	LoI$_{\text{500-1000}}$	MP$_{\text{500-1000µm}}$	LoI$_{\text{100-500µm}}$	MP$_{\text{100-500µm}}$	LoI$_{\text{50-100µm}}$	MP$_{\text{50-100µm}}$	LoI$_{\text{5-50µm}}$	MP$_{\text{5-50µm}}$
PP	34.0%	36 µg/L	40.0%	22 µg/L	36.0%	9 µg/L	25.0%	1 µg/L	_	
	47.0%	36 µg/L	76.0%	2 µg/L	41.0%	17 µg/L	21.0%	13 µg/L	51.0%	4 µg/L
	46.0%	29 µg/L	56.0%	1 µg/L	31.0%	25 µg/L	30.0%	1 µg/L	69.0%	2 µg/L
	41.0%	5 µg/L	66.0%	0 µg/L	27.0%	2 µg/L	30.0%	2 µg/L		
	58.0%	43 µg/L	100.0%	31 µg/L	37.0%	6 µg/L	36.0%	2 µg/L		
	50.0%	18 µg/L	73.0%	0 µg/L	11.0%	12 µg/L	15.0%	3 µg/L	100.0%	3 µg/L
	47.0%	1 µg/L	54.0%	0 µg/L	10.0%	0 µg/L	28.0%	0 µg/L	97.0%	1 µg/L
Mean	0.5 µg/L	24.1 µg/L	0.7 µg/L	8.2 µg/L	0.3 µg/L	10.2 µg/L	0.3 µg/L	3.1 µg/L	0.8 µg/L	2.6 µg/L
Standard Deviation S	0.1 µg/L	16.2 µg/L	0.2 µg/L	12.8 µg/L	0.1 µg/L	8.7 µg/L	0.1 µg/L	4.4 µg/L	0.2 µg/L	1.0 µg/L
COVARIANCE	0.2107		0.6527		0.3497		-0.1110		-0.1236	
Correlation	0.2047		0.3084		0.3746		-0.4263		-0.7349	

Table A 14 Correlation tests between chemical oxygen demand (COD) and total MP content in stormwater runoff at L3, raw data

All polymers (PE, SBR, PP,PS)	COD Total	MP Total	**SBR**	COD Total	MP Total	**PP**	COD Total	MP Total
	330.4 mg/L	1729 µg/L		330.4 mg/L	426.7 µg/L		330.4 mg/L	98.2 µg/L
	283.0 mg/L	980 µg/L		283.0 mg/L	30.2 µg/L		283.0 mg/L	32.1 µg/L
	216.0 mg/L	1718 µg/L		216.0 mg/L	461.2 µg/L		216.0 mg/L	69.6 µg/L
	228.0 mg/L	401 µg/L		228.0 mg/L	5.3 µg/L		228.0 mg/L	12.8 µg/L
	153.0 mg/L	628 µg/L		153.0 mg/L	72.4 µg/L		153.0 mg/L	7.9 µg/L
	176.0 mg/L	3576 µg/L		176.0 mg/L	2807.2 µg/L		176.0 mg/L	9.5 µg/L
	128.0 mg/L	3649 µg/L		128.0 mg/L	3324.7 µg/L		128.0 mg/L	20.6 µg/L
Mean	216.3 mg/L	1811.6 µg/L	**Mean**	216.3 µg/L	1018.2 µg/L	**Mean**	216.3 µg/L	35.8 µg/L
Standard Deviation S	71.9 mg/L	1328.3 µg/L	**Standard Deviation S**	71.9 µg/L	1418.8 µg/L	**Standard Deviation S**	71.9 µg/L	34.8 µg/L
Correlation	-0.4184		**COVARIANCE**	-51564.7293		**COVARIANCE**	1536.7670	
Correlation	-0.4184		**Correlation**	-0.5896		**Correlation**	0.7158	
PE	COD Total	MP Total	**PS**	COD Total	MP Total			
	330.4 mg/L	1204.4 µg/L		330.4 mg/L	0.03 µg/L			
	283.0 mg/L	893.4 µg/L		283.0 mg/L	24.65 µg/L			
	216.0 mg/L	1110.7 µg/L		216.0 mg/L	76.08 µg/L			
	228.0 mg/L	375.4 µg/L		228.0 mg/L	7.69 µg/L			
	153.0 mg/L	547.8 µg/L		153.0 mg/L	0.01 µg/L			
	176.0 mg/L	759.7 µg/L		176.0 mg/L	0.02 µg/L			
	128.0 mg/L	304.0 µg/L		128.0 mg/L	0.01 µg/L			
Mean	216.3 µg/L	742.2 µg/L	**Mean**	216.3 µg/L	15.5 µg/L			
Standard Deviation S	71.9 µg/L	350.5 µg/L	**Standard Deviation S**	71.9 µg/L	28.2 µg/L			
COVARIANCE	15529.5321		**COVARIANCE**	243.9975				
Correlation	0.7188		**Correlation**	0.1403				

Table A 15 Correlation tests between chemical oxygen demand (COD) and total MP content in dry weather flow at L3, raw data.

All polymers (PE, PP,PS)	CSB $_{\text{Gesamt}}$	MP $_{\text{Gesamt}}$
	1006.0 mg/L	262 µg/L
	845.0 mg/L	410 µg/L
	889.0 mg/L	388 µg/L
	965.0 mg/L	1936 µg/L
	1669.0 mg/L	1020 µg/L
	917.0 mg/L	522 µg/L
	854.0 mg/L	962 µg/L
	989.0 mg/L	855 µg/L
Mean	1016.8 mg/L	794.3 µg/L
Standard Deviation S	270.3 mg/L	541.8 µg/L
COVARIANCE	30302.5055	
Correlation	0.21	

PE	CSB $_{\text{Gesamt}}$	MP $_{\text{Gesamt}}$
	1006.0 mg/L	250 µg/L
	845.0 mg/L	298 µg/L
	889.0 mg/L	346 µg/L
	956.0 mg/L	0 µg/L
	965.0 mg/L	1762 µg/L
	1669.0 mg/L	890 µg/L
	917.0 mg/L	522 µg/L
	854.0 mg/L	914 µg/L
	989.0 mg/L	762 µg/L
Mean	1010.0 µg/L	638.1 µg/L
Standard Deviation S	253.6 µg/L	523.3 µg/L
COVARIANCE	23094.2706	
Correlation	0.1958	

PS	CSB $_{\text{Gesamt}}$	MP $_{\text{Gesamt}}$
	1006.0 mg/L	4 µg/L
	845.0 mg/L	7 µg/L
	889.0 mg/L	5 µg/L
	956.0 mg/L	0 µg/L
	965.0 mg/L	22 µg/L
	1669.0 mg/L	60 µg/L
	917.0 mg/L	0 µg/L
	854.0 mg/L	35 µg/L
	989.0 mg/L	78 µg/L
Mean	1010.0 µg/L	23.5 µg/L
Standard Deviation S	253.6 µg/L	28.7 µg/L
COVARIANCE	3314.9906	
Correlation	0.5115	

PP	CSB $_{\text{Gesamt}}$	MP $_{\text{Gesamt}}$
	1006.0 mg/L	9 µg/L
	845.0 mg/L	106 µg/L
	889.0 mg/L	38 µg/L
	956.0 mg/L	152 µg/L
	965.0 mg/L	71 µg/L
	1669.0 mg/L	0 µg/L
	917.0 mg/L	13 µg/L
	854.0 mg/L	14 µg/L
	989.0 mg/L	
Mean	1010.0 µg/L	50.2 µg/L
Standard Deviation S	253.6 µg/L	54.8 µg/L
COVARIANCE	-4734.8249	
Correlation	-0.3646	

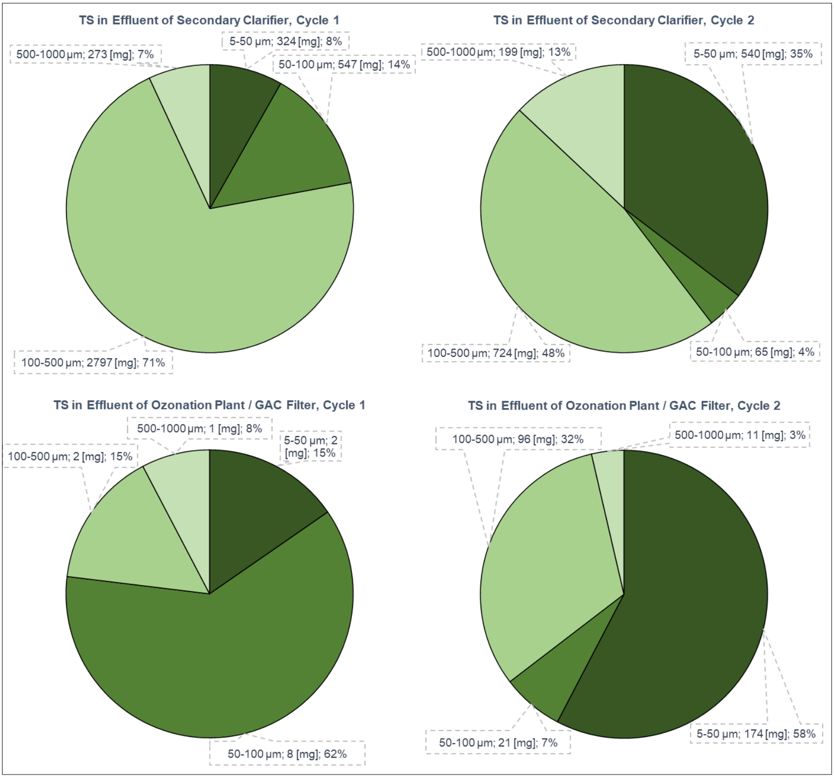


Figure A 30 Removal of TS by the pilot plant for the removal of organic micropollutants in cycle 1 and 2

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