LICENTIATE THESIS

Organic micropollutants in highway stormwater and the role of a gross pollutant trap-biofilter stormwater treatment train

Ali Beryani

Urban Water Engineering

LULEÅ UNIVERSITY OF TECHNOLOGY

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Preface

This research was carried out in the urban water engineering group at the Department of Civil, Environmental, and Natural Resources Engineering, Luleå University of Technology. The research funding for the consisted studies of this thesis was provided by The Swedish Research Council Formas (grant number 2016-20074) and the Swedish Water & Wastewater Association (Svenskt Vatten; grant number 16-116). It was conducted as part of the research center DRIZZLE (Vinnova: Swedish Governmental Agency for Innovation Systems, grant number 2016-05176). The support of MittSverige Vatten & Avfall (MSVA), which is a member of the joint research cluster Stormwater & Sewers (Dag&Nät) and operates the evaluated treatment train, is gratefully acknowledged.

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Lastly, I wish to share my elation with my loving family and Elnaz Karamati for their unwavering support and positive energy. I would also like to acknowledge the late Sir Ken Robinson and his inspiring words that have given me the strength and motivation to overcome the obstacles encountered during my research.

Ali Beryani

Luleå, April 2023

Abstract

The studies which this thesis is based on assessed the stormwater quality in a highway catchment located in Sundsvall, Sweden, and examined the performance of a gross pollutant trap (GPT)-biofilter stormwater treatment train (TT) downstream of the catchment, in terms of removal efficiency, intra-event variability, and environmental risk reduction of organic micropollutants (OMPs) for the receiving water body. Assessing the occurrence and event mean concentrations (EMCs) of all OMPs in the catchment revealed that bisphenol A (BPA), octylphenol (OP), nonylphenol (NP), five carcinogenic and four non-carcinogenic polycyclic aromatic hydrocarbons (PAHs), and C_{16}-C_{40} fractions of petroleum hydrocarbons (PHCs) all potentially pose an environmental risk to freshwater (EMCs >PNEC: *predicted non-effect concentration*), while alkylphenol ethoxylates, six low- molecular weight PAHs, and lighter fractions of PHCs (C_{10}-C_{16}) do not occur at problematic levels.

In order to assess the impact of the downstream TT in mitigating the risks of the studied OMPs, the performance of the TT compartments (a GPT followed by three filter cells) was analyzed and then compared with each other to identify the importance of each design feature (i.e. pre-treatment GPT, sand-based filter media, vegetation, and chalk amendment). Overall, the TT removed most OMPs from highway runoff effectively. The GTP did not contribute to this treatment, thus, the filter sections were responsible for most of the OMP removal. The results showed that, although the non-vegetated sand filter (SF) could moderately (<50% removal for phenolic substances) to substantially (50–80% removal for PAHs and PHCs) treat the OMPs, the vegetated biofilters (BF and BFC) considerably improved the removal performance, especially for BPA, OP, and suspended solids (TSS). This observation was explained by additional filtration processes provided by the vegetation topsoil layer, which not only enhanced the particulate/particle-bound OMP physical retention but also physiochemical adsorption of colloidal and soluble substances/fractions (such as BPA and OP).

Further analysis of intra-event concentration (IEC) variations of OMPs and TSS showed that the IECs in the highway stormwater and GPT outflow varied considerably without any particular patterns over the course of the events, but first flush rarely occurred. The IEC variations were attenuated by the SF and BFC cells so that more even pollutant load discharge with no first flush was observed during the filter cells' outflow events. Yet, the IECs for the SF cell revealed that the IECs often peak at the beginning of the effluent events (within the first 100 m^3 out of maximum record of ~600 m^3) and then decrease and become stabilized towards the end of the event. The early-phase concentration peaks exceeded the PNECs for TSS, five PAHs, BPA, and OP, a fact that was not shown by the EMC-based analysis, thus highlighted the advantage of the IEC analysis.

Sammanfattning

Syftet med denna avhandling var att utvärdera kvalitén av dagvattnet från motorvägen E4 i Sundsvall, Sverige, samt att undersöka prestandan hos en dagvattenanläggning avseende dess förmåga att rena detta vatten från organiska mikroföroreningar (*OMPs*). Anläggningen kombinerar ett försedimenteringssteg (*gross pollutant trap,* GPT) med tre olika biofilter. Förutom reningskapaciteten har också variationer av dagvattenkvalitet inom regn- och avrinningstillfällena och en riskbedömning gjorts. Bedömning av förekomst och medelkoncentrationer (*event mean concentration,* EMCs) av de organiska föroreningarna visade att bisfenol A (BPA), oktylfenol (OP), nonylfenol (NP), fem cancerframkallande och fyra icke-cancerframkallande polyaromatiska kolväten (PAHs) och C_{16}-C_{40} fraktionerna av petroleumkolväten (PHCs) förväntas utgöra en miljörisk i sötvattenrecipienter (EMCs> PNEC: *predicted non-effect concentration*, dvs. koncentrationen som förväntas inte påverka vattenekosystemet), medan alkylfenol etoxylater, sex lågmolekylära PAHer och lättare fraktioner av PHC (C_{10}-C_{16}) inte förekommer i problematiska koncentrationer.

För att bedöma effekten av reningsstegen på de organiska ämnena analyserades och jämfördes prestandan hos de olika reningsstegen: ett gemensamt försedimenteringssteg, ett sandfilter utan växtlighet och två växtbevuxna biofilter, ett med ett sandbaserat filtermaterial och ett med samma filtermaterial dock med tillsats av kalk. Sammantaget renade anläggningen de flesta organiska ämnena från motorvägsavrinningen. Försedimeneringen bidrog dock inte till denna rening. Även om resultaten visade att det icke-växtbevuxna sandfiltret kunde rena <50% för fenoliska ämnen och 50–80% av PAHer och PHCs, var reningen bättre i de två växtbevuxna filtren, särskilt för BPA, OP och suspenderat sediment (TSS). Detta förklarades med ytterligare filtreringsprocesser som tillhandahölls av ett lager växtsubstrat, vilket förbättrade den fysiska filtreringen av partikulärt bundna föroreningar samt fysikalisk-kemisk adsorption av kolloidala och lösta ämnen/fraktioner (som BPA och OP).

Ytterligare analys av variationer av OMP och TSS under regn-/avrinningshändelserna visade att koncentrationen i dagvattnet och utflödet från försedimenteringen varierade signifikant, dock utan att några specifika mönster såsom *first flush* detekterades regelbundet. Variationerna i utflödet från filtren var mindre, dvs. en jämnare föroreningsbelastning (utan *first flush*) observerades. Ändå visade datat att koncentrationen i detta utflöde ofta är relativt hög i början av avrinningshändelserna (inom de första 100 m^3 av totalt 600 m^3) för att sedan sjunka och stabiliseras mot slutet av händelsen. Dessa tidiga koncentrationstoppar överskred regelbundet PNEC för TSS, fem PAHer, BPA och OP. Detta upptäcktes inte när endast medelkoncentrationen betraktas varför mer detaljerade analyser rekommenderas framöver.

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List of papers:

Paper I Beryani A.; Flanagan K.; Viklander M.; Blecken G.T.; *"Occurrence and concentrations of organic micropollutants (OMPs) in highway stormwater: A comparative field study in Sweden"*. Re-submitted to Environmental Science and Pollution Research after revision.

Paper II Beryani A.; Flanagan K.; Viklander M.; Blecken G.T.; *"Performance of a gross pollutant trap-biofilter and sand filter treatment train for the removal of organic micro-pollutants from highway stormwater (Field study)"*. Submitted to Science of The Total Environment (under review).

Paper III Beryani A.; Viklander M.; Blecken G.T. (2021); *"The intra-event dynamics of the removal of organic micro-pollutants (OMP) in stormwater treatment trains: gross pollutant trap and biofilter"*. Presented at the 15th International Conference on Urban Drainage.

Contribution to the papers:

Paper No.	Idea development	Research study design	Data collection	Data processing and analysis	Data interpretation	Publication process	
						Manuscript preparation	Responding to reviewers
I	Shared responsibility	Shared responsibility	Responsible	Responsible	Shared responsibility	Responsible	Shared responsibility
II	Shared responsibility	Shared responsibility	Responsible	Responsible	Shared responsibility	Responsible	Shared responsibility
III	Shared responsibility	Shared responsibility	Responsible	Responsible	Shared responsibility	Responsible	NA

(R) Responsible – developed, consulted (where needed), and implemented a plan for the completion of the task.

(SR) Shared responsibility – made essential contributions towards the task completion in collaboration with other members of the research team

(C) Contributed – worked on some aspects of the task completion

(NC) No contribution – for a valid reason, has not contributed to completing the task (e.g., joining the research project after the task completion)

(NA) – Not applicable

1. Introduction

Anthropogenic activities impact the quality of stormwater in urban areas. Road runoff usually contains large quantities of particulate matter, along with high concentrations of trace metals and organic components, all of which can adversely affect organisms in the receiving water bodies, and public health (Barbosa et al., 2012). Traffic-related activities are known to be one of the major sources of organic micropollutants (OMPs; organic pollutants found in water at trace levels) in road stormwater runoff, discharging to water bodies. A large number of organic pollutants released from traffic-related activities have environmental persistence and a tendency to bioaccumulation, and may have detrimental long-term effects on aquatic life (Markiewicz et al., 2017). Hazardous OMPs such as phthalates, alkylphenols, and polycyclic aromatic hydrocarbons (PAHs) have been frequently detected with such high concentrations in road runoff as to fail environmental quality standards (EQS) for water bodies (Gasperi et al., 2022; Mutzner et al., 2022; Wicke et al., 2021). Thus, to enable mitigation strategies for protecting water resources, as targeted in the UN's sustainable development goals (SDGs), namely, SDG 6 (clean water and sanitation), SDG 11 (sustainable cities and communities), and SDG 14 (life below water), there is a need for a better understanding of the actual concentrations and occurrences of OMPs in road runoff to identify, monitor, and mitigate their environmental impacts/risks.

For this mitigation, biofilter (bioretention) systems, as one of the stormwater control measures (SCMs), have been developed and implemented over recent decades for *in situ* treatment of stormwater (Payne et al., 2015). The overall biofilter's functionality under natural conditions in the urban environment depends upon various factors: suitable design, maintenance level, frequent monitoring of the treatment efficiency, and resiliency in the face of ambient variations/shocks (Blecken et al., 2017; Kratky et al., 2021). All these factors should be addressed over the long term for successful and simplified bioretention design, maintenance, stormwater quality management, and eventual pollution risk management. Among the factors previously mentioned, the general aim of the work for this thesis was related to evaluating and monitoring design suitability and treatment efficiency of stormwater biofilters in regard to OMPs (especially, rarely monitored substances such as phenols).

Earlier investigations have also suggested that common sand-based biofilters can be combined with other treatment steps (e.g. sedimentation pretreatment, submerged zone) or combined with certain materials (e.g. vegetation, biochar, chalk grains) to enhance their removal performance for specific target pollutants (Andersson et al., 2018; Chu et al., 2021; DWA-M 187, 2005). While some research has been carried out on such design development in the laboratory or as pilot studies, less research has been carried out into the monitoring and evaluation of biofilter design features in existing full-scale biofilter facilities under field conditions (Blecken et al., 2017). Furthermore, OMP removal and

intra-event variations in such facilities have not been studied as much as, for example, metals and nutrients. This thesis directly addresses these knowledge gaps.

1.1. Research objectives

The research of this thesis assessed the stormwater quality in a highway catchment and examined the water quality treatment performance of a gross pollutant trap (GPT)-biofilter treatment train (TT) in terms of removal efficiency, intra-event variability, and environmental risk for the receiving water body. All the studied subtopics covered selected OMPs (i.e. phenolic substances, PAHs, and petroleum hydrocarbons) in highway runoff. The main research questions of the study and the papers addressing them are as follows:

1) What are the occurrences, concentrations, and environmental risk levels of OMPs in highway stormwater? (Papers I and II)
2) How efficient are the TT units with different design features (i.e. pretreatment, sand filtration, vegetation, and chalk amendment) in terms of both OMPs removal and OMPs risk reduction? (Paper II)
3) How does OMP water concentration vary during wet weather (intra-event) periods, and what are the influential factors in the variations? (Paper III)
4) What are the transport processes involved in OMP treatment and intra-event concentration variations? (Papers II and III)

1.2. Thesis structure

This licentiate thesis is based on a field study carried out over a three-year period. All the studied subtopics (papers) are based on one extensive dataset gathered during a field sampling campaign from a GPT-biofilter/sand filter treatment train receiving stormwater mostly from the catchment area of a highway and major roads in Sundsvall, Sweden. The research resulted in the three appended papers, referred to as Paper I, Paper II, and Paper III.

For Paper I, a comprehensive evaluation of the concentrations, occurrence, and possible sources of studied OMPs in the untreated stormwater received from the catchment was carried out, as well as a comparison of the results with other major road runoff studies mainly carried out in Europe. For Paper II, the overall performance of the TT in the removal and risk reduction of OMPs was evaluated using EMC analysis and a risk assessment for several rain events over a one-year sampling period. Here, the functionality of the TT compartments including GPT, and various filter cells with different design features, were investigated in relation to OMPs only. Finally, Paper III described the new discoveries of intra-event variations of OMPs in the untreated and treated stormwater at the outlet of different treatment stages for each rain event. The obtained pollutographs here give a novel perspective on how the biofilter cells respond to the variations of environmental factors such as influent concentration, rainfall pattern, and first flush effect.

The pollutographs can deepen our understanding of the dynamics of the processes involved in OMP removal by the TT sections.

A synthesis of the mentioned subtopics (papers) is illustrated in Figure 1. The combination of the papers, in the form of a comprehensive field study, gives a broader perspective of stormwater quality from the source to the point of discharge to water bodies, and highlights the role of GPT-biofilter systems for OMP treatment in stormwater.

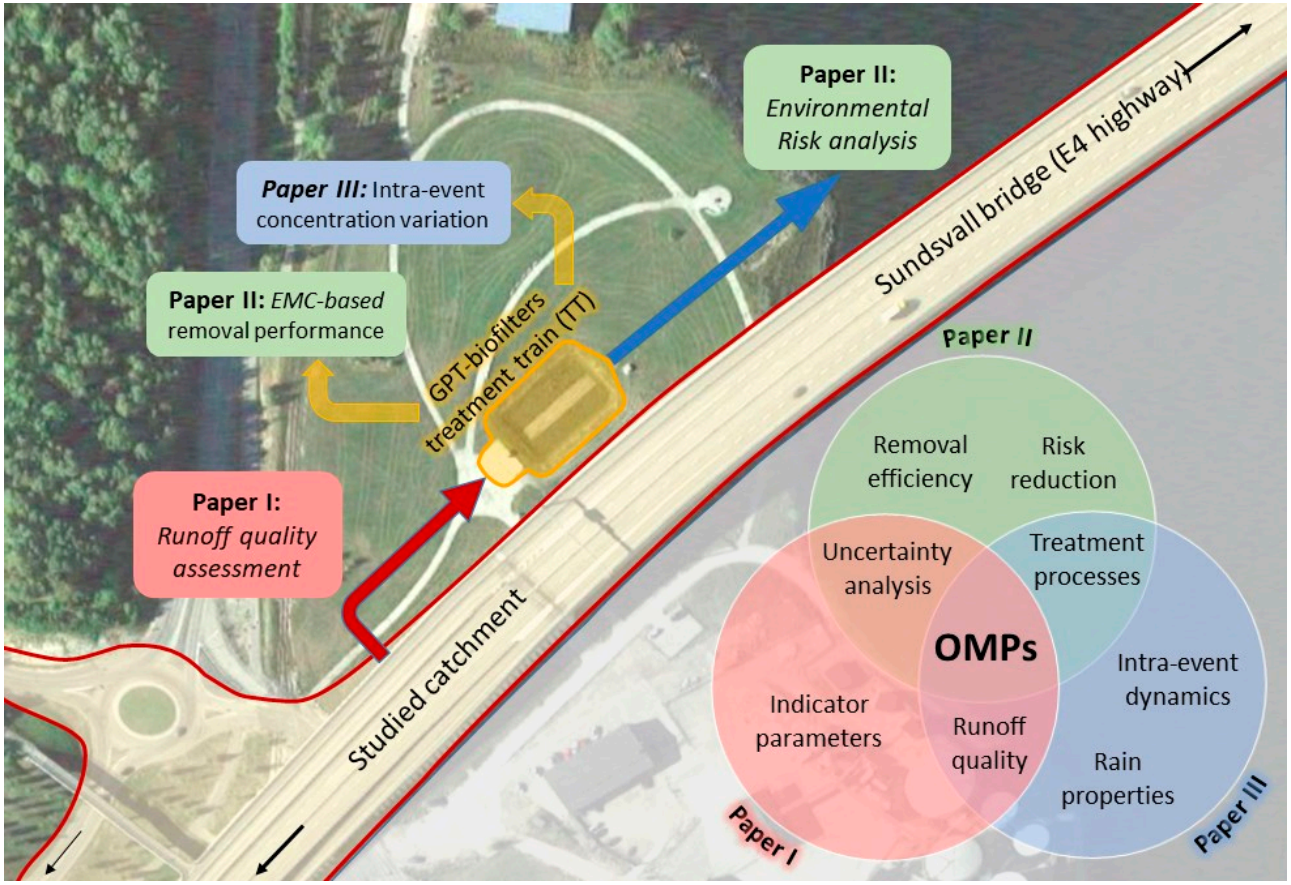


Figure 1. Synthesis of the three studies described in this thesis

2. Background

2.1. Organic micropollutants (OMPs)

Micropollutants (also defined as chemicals of emerging concern, priority substances, xenobiotics etc.) are a wide range of organic and mineral compounds which can have detrimental biological effects on living organisms, even though they occur at very low levels in the environment (usually μg/L to ng/L) (Rousseau et al., 2022). Compounds used in pharmaceuticals and personal care products (PPCPs) (e.g. diclofenac, hormones, caffeine, ibuprofen), perfluoroalkyl and polyfluoroalkyl substances (PFAS), pesticides and herbicides (e.g. diuron, carbendazim, imidacloprid, chlorpyrifos, pentachlorophenol, dichloro-diphenyl-trichloroethane (DDT), methiocarb, oxadiazon, thiacloprid, acetamiprid), along with plastics additives and petroleum-based products (e.g. phthalates, oil and grease, petroleum hydrocarbons (PHCs), poly aromatic hydrocarbons (PAHs), polychlorinated biphenyls, bisphenol A (BPA), alkylphenols (APs)) are among organic micropollutants (OMPs) regularly detected in aquatic environments (Arslan et al., 2017). Once in these aquatic environments, depending on their characteristics, OMPs may persist for a long time, be absorbed into organic matter, degrade through physicochemical processes, bioaccumulate in a food chain, or be metabolized by organisms themselves (Meyer et al., 2019). During their transport through water bodies, many of the OMPs can cause chronic adverse effects and, to a lesser extent, acute toxicity (Farré et al., 2008; Markiewicz et al., 2017).

Due to the ecotoxicologically adverse effects of OMPs, determining their environmental risks and developing legislation for water resources have both recently received much attention. However, many of the current studies have focused on wastewater treatment plant outflows (mostly concerned with PPCPs) and combined sewer overflows (CSOs) (Figuière et al., 2022; Mutzner et al., 2020; Sörengård et al., 2019). In fact, further notable sources of OMPs which has been comparatively less well studied are stormwater sewer systems that often directly discharge untreated stormwater into water bodies during wet weather conditions. Qualitative monitoring of stormwater as a source of the emerging contaminants is a crucial step in the OMP risk assessment process, as well as development and evaluation of control measures (e.g. source control, usage legislation, and stormwater treatment facilities).

2.2. OMPs in stormwater

Although some OMPs can originate in nature, anthropogenic activities and synthetic products in urban areas, which include many impermeable surfaces, are known to be the major sources of OMPs in stormwater. Studies have shown that OMPs can be released into stormwater runoff and eventually water bodies from many different sources: building surface materials used in roofs and facades, vehicular transportation (exhaust emissions, tire wear, road abrasion, anti-icing practices etc.), industrial and construction activities,

waste disposal, urban infrastructure materials (e.g. power lines, drainage pipes and SCMs), car/road/building washing, as well as atmospheric depositions during dry or wet weather conditions (Müller et al., 2020). The sources, types, and concentrations of OMPs in runoff vary a great deal across urban areas with different land uses. Moreover, the fate and transport of OMPs in aquatic environments are complex, and dependent on many factors such as production and consumption amounts of the materials containing OMPs, material durability and disposal methods, environmental degradability of OMPs and their removal or transformation by natural/engineered processes (Golovko et al., 2021). All these complexities essentially mean there is a requirement for proper monitoring measures and programs for OMPs in stormwater with the purposes of: 1) identification of the relevance of different types of OMPs, their sources and releasing processes, 2) identification of their fate and transport pathways, 3) quantification of OMP concentrations/loads discharged from the catchments, 4) assessment of their threat to aquatic environments, 5) performance assessment of pollution control strategies such as OMP removal using SCMs, and 6) enacting legislation such as discharge level permits issued by local authorities (Gasperi et al., 2022; Lundy et al., 2012; Masoner et al., 2019; Müller et al., 2020; Mutzner et al., 2022; Zhang et al., 2014).

There is still a lack of long-term, consistent data for road runoff quality in regard to OMPs in many regions, which makes it difficult to assess the impact of road runoff on the environment and human health accurately. There is still less information about the occurrence and concentration levels of OMPs when compared to trace metals, nutrients, COD, and TSS (Gasperi et al., 2022; Mutzner et al., 2022). According to road stormwater quality literature about OMPs, PAHs have received more attention in previous studies into road catchments since they can be directly emitted from vehicles (due to incomplete combustion of fossil fuels and oils, tire wear) and old pavement surfaces that use tar asphalt (Müller et al., 2020), while other groups of OMPs, such as phenolic substances, have been studied less. In fact, according to a data-driven metastudy by Mutzner et al. (2022), 92 other OMP substances have been detected in road runoff outlets, of which four industrial organic substances including di-(2-ethylhexyl) phthalate (DEHP), para-nonylphenol, 4-tert-octylphenol, and BPA were of the most dangerous or most commonly occurring OMPs. Therefore, more in-depth knowledge as well as regular monitoring of OMPs in stormwater (particularly newly emerged substances) can help identify their potential sources and actual environmental risk to receiving water bodies, and eventually guide quality management efforts to mitigate their impact in the form of both source control and treatment.

2.3. Stormwater biofilters

To reduce the impact of stormwater pollutants, various *in situ* treatment strategies can be employed before discharge of stormwater to water bodies, which include implementing SCMs (also referred to as best management practices (BMPs), sustainable urban drainage systems (SUDS), or water sensitive urban design (WSUD)) such as infiltration trenches,

swales, constructed wetlands, and stormwater biofilters (Fletcher et al., 2015). Such a biofilter (also called bioretention or raingarden) is a low-impact, vertical flow filtration system which receives and treats the urban runoff through physiochemical processes such as filtration and adsorption, as well as microbial degradation and biological uptake (Prince George's County, 2007). As shown in Figure 2, a typical biofilter consists of a layer of engineered soil or filter material (often sand-based) which is placed over a drainage layer and collection pipes. The filter medium layer can be planted with vegetation that is suitable for the local climate and site conditions for both treatment (as discussed below) and aesthetic purposes (Payne et al., 2015).

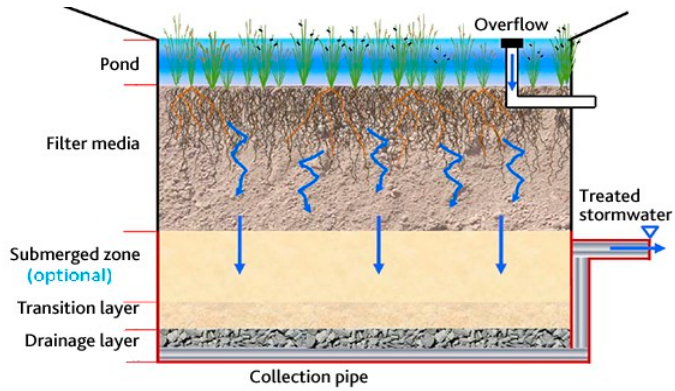


Figure 2. Schematic section view of a typical biofilter cell (Payne et al., 2015)

Biofilters can be used for various catchment sizes and land-use settings for the treatment of a wide range of stormwater pollutants (e.g. sediments, nutrients, heavy metals, organic pollutants). Some field observations (Diblasi et al., 2009; Flanagan, Branchu, Boudahmane, Caupos, Demare, Deshayes, Dubois, Meffray, et al., 2019b; Zhang et al., 2014) and laboratory studies (Hong et al., 2006; Lefevre et al., 2012) have indicated that biofilters show promising results for the removal of OMPs such as PAHs, petroleum hydrocarbons (PHCs), phthalates, trihalomethanes (THMs), oil and grease, and phenols from urban stormwater. However, compared to metals and nutrients, bioretention research is very limited in relation to monitoring and treatment of OMPs using biofilters. Research into OMP treatment using biofilters has increased in recent years, although PAHs have been of more interest, and emerging OMPs such as phenolic substances have been largely ignored, despite their potential environmental risks. According to Scopus, the number of all stormwater biofilter studies that have included PAHs, PHCs, or any kind of phenolic substances is only 12, 7, and 5, respectively. Moreover, the quality performance of full-scale biofilter facilities has not been sufficiently evaluated or validated under actual environmental conditions, especially in Sweden.

2.4. Stormwater treatment train systems

One way to improve the effectiveness of stormwater treatment is to combine SCM technologies with complementary treatment processes (Marsalek et al., 2006). Depending

on the effluent water quality required, many different typical stormwater treatment techniques (e.g. swales and buffer strips, sedimentation ponds, wetlands, biofilter etc.) and processes (sedimentation of different target sediment sizes, sorption and filtration processes, flocculation, membrane filtration etc.) can be combined. Figure 3 shows one example of a stormwater treatment train equipped with a typical gross pollutant trap (GPT) consisting of a pre-sedimentation/oil trap chamber as a pre-treatment stage, a biofilter cell as the middle treatment stage, and an ultrafiltration stage as the post-treatment unit if water reuse is required.

It has been suggested that the installation of a forebay or GPT as a pre-treatment section before biofilters and sand filters will facilitate sedimentation of coarse particles and their associated pollutants (Andersson et al., 2018). Adding a GPT is expected to reduce particle accumulation in the biofilter which will (among other things) reduce clogging and, thus, the need for maintenance, thus improving infiltration capacity, lifespan, and cost-efficiency of the treatment system. Additionally, if the GPT's outlet is submerged, it can effectively trap oils and volatile organic pollutants on the water's surface. Several successful examples of pre-sedimentation tanks (GPTs) used along with infiltration basins and sand filtrations to treat highway runoff have been reported in the USA, Germany, and Austria (Andersson et al., 2018; Hunt et al., 2015; Purvis et al., 2019). However, some field observations (Greenway et al., 2012; Lange et al., 2021) have revealed that GPTs may not meet quality treatment goals for pollutants, such as suspended solids (TSS), nutrients, and microplastics removal, if not appropriately designed according to catchment type and the pollutants of concern. According to the current state of the art, there is limited information on GPT effectiveness for OMP removal.

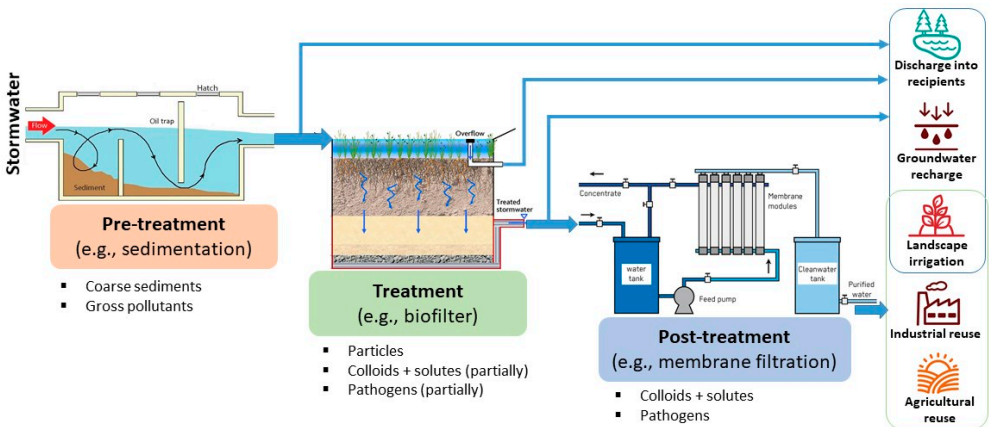


Figure 3. Schematic of a treatment train with a typical gross pollutant trap and tertiary treatment

2.5. Biofilter technology amendments

2.5.1. Filter material composition

Conventional stormwater biofilter soil media are usually based on sand, sandy-loam, or loamy-sand engineered soils, which have low organic matter content to avoid nutrient leaching (DWA-M 187, 2005). Such conventional soil media have often limited treatment efficiencies for dissolved/colloidal heavy metals and nutrients in stormwater (Tirpak et al., 2021). Compared with particulate fractions, dissolved/colloidal fractions are more ecologically relevant to water bodies since they can possess a higher mobility in the aqueous phase, and therefore higher bioavailability and toxicity for organisms (Beesley et al., 2010; Beryani et al., 2022; Mohanty et al., 2016). Moreover, sand-based biofilters may leach pollutants into stormwater (Mohanty et al., 2018) which will lower the removal performance during a sequence of dry/wet periods. Therefore, several supplementary amendments using cheap, long-lasting, natural materials, both inorganic and organic, have been tested on filter media to improve biofilter removal effectiveness, including limestone or chalk, biochar, zeolite, fly ash, and iron-based material.

With regards to chalk amendment, calcium carbonate ($CaCO_3$) can compensate for low organic matter content and increases the buffer capacity of the filter media (DWA-M 187, 2005; Søberg et al., 2019; Tirpak et al., 2021). This buffer capacity, which reduces pH, means that chalk enhances solute adsorption in the solid phase, particularly for metals in highway runoff (i.e. reducing the risk of metals leaching from the filter media) (Grotehusmann et al., 2016). Furthermore, limestone can contribute to the formation of calcium carbonate precipitates, which can enhance removal of phosphorus from stormwater runoff (Shahrokh Hamedani et al., 2021). Nonetheless, the effect of chalk-amended biofilters on OMP treatment performance has been rarely studied. One hypothesis is that organic pollutants are absorbed on the surface organic content of limestone particles (Graber & Borisover, 2003; Wefer-Roehl et al., 2001). Another hypothesis is that there is an increase of mechanical deposition of particle-bound OMPs due to the effects of chalk on the water chemistry (pH and ionic strength) (Behbahani et al., 2021; Diblasi et al., 2009; Randelovic et al., 2016).

2.5.2. Vegetation

Another way of improving biofilters is through the use of vegetation, which can offer several improvements in quality over non-vegetated sand filters. Vegetation cover can filter larger particulate pollutants mechanically and remove total suspended solids (Chu et al., 2021; Le Coustumer et al., 2012). Larger particles are mainly trapped directly in the surface soil or by vegetation, while smaller particles are further transported and removed in the underlying filter media (Chu et al., 2021). This is important because the removal of particulate pollutants (metals or OMPs) can be correlated with TSS removal (Hatt et al., 2008). Also, vegetation can remove stormwater pollutants by directly absorbing them and indirectly through enhancing microbial activities during dry weather

periods (Muerdter et al., 2016). The presence of well-stablished vegetation may positively alter the hydraulic performance of bioretention cells, resulting in higher infiltration rates (by creating macropores in the soil) and reduced peak flow rates, although this may also reduce the removal efficiency (Dagenais et al., 2018). Even though it has not yet been completely investigated, it is likely that vegetation may reduce clogging because of its roots and stems. Due to movement and growth, apertures are formed that generate preferential flow paths for the water. Hence, vegetation plants with thick roots are preferred to those with narrow roots (Le Coustumer et al., 2012).

Although most of the previous studies have primarily focused on the effectiveness of vegetation species in removing TSS, nutrients and, to a lesser extent, metals (Feng et al., 2012; Lange et al., 2020; Leroy et al., 2016; H. Li & Davis, 2008; Read et al., 2008), a vegetation layer in biofilters may improve OMP absorption through the root zone and organic matter content, as well as deposition of particle-bound OMPs on the vegetated top soil. The function of vegetation in OMP removal has not been thoroughly researched, creating a knowledge gap in the field that needs to be addressed in order to obtain reliable evidence for the effect of vegetation on the performance of biofilter systems.

2.6. Intra-event variations

Intra-event concentration (IEC) variations in stormwater runoff refer to changes in pollutant concentrations within a single storm event (Kayhanian et al., 2003). These short-term variations can occur due to several factors, such as changes in rain intensity and depth, antecedent dry periods, and varying traffic intensity conditions (pollutant availability) in the catchment, which all lead to changes in runoff volume and pollutant concentration pattern during an event. The IECs of a specific pollutant is normally plotted as a "pollutograph", with respect to accumulative flow or time (Kayhanian et al., 2003). While measuring event mean concentrations (EMC) is the most common way to investigate the stormwater quality or treatment removal efficiency, pollutographs provide a more complete picture of stormwater quality patterns in a catchment, which can help water managers to monitor, identify, and address water quality issues better. There is very limited information on intra-event variations of the pollutant concentration over time (for instance due to high experimental costs and practical complexities). More specifically regarding OMP concentrations in runoff, to date, a few studies have investigated IEC variations of PAHs (Aryal et al., 2013; Leroy et al., 2015a; Mitsova et al., 2011), oil and grease (Kayhanian et al., 2003), and TPHs (Avellaneda et al., 2010). A recent study by Peter et al. (2020) of an urban catchment in US also evaluated the concentration dynamics of a variety of OMPs (including pharmaceuticals, phenols, and petroleum-based hydrocarbons) in receiving water bodies during storm events.

Understanding intra-event variations in pollutant concentration and their impact on the effectiveness of stormwater management strategies is of vital importance. For example,

some studies of stormwater runoff from urban roadways and parking lots have shown that concentrations of PAHs, metals, and TSS in runoff varied considerably during the event depending on both the rainfall intensity (e.g. peak flows) and the stage of the storm (e.g. first flush event: high fraction of pollutant load at early stages of runoff) (Christian et al., 2020; Lange et al., 2022; Mitsova et al., 2011; Schiff et al., 2016). This suggests that SCMs, like biofilters which are often designed to treat every-day and design rainfall (return period <20 years), may not be effective in capturing all the pollution load during intensive runoff flows, especially at first flush events. Pollutographs are helpful for understanding the relationships between measured OMP concentrations and runoff flow rate as a function of time, as well as helping to identify first flush events.

In terms of possible impact of pollutants on receiving water bodies, IEC variations may also be useful for identifying the potentially risky stages of the storm in relation to the runoff and/or treatment facility effluents during the event. Such information could highlight the need for management strategies that capture runoff from the entire storm event (rather than only some stages) and might help the understanding of concentration variations. Moreover, more regular intra-event data collection for stormwater quantity and quality in the biofilter systems is essential for understanding the actual treatment processes and, in further work, enable reliable modeling of water quality and treatment. An accurate simulation, as a result, would allow us to predict the long-term influences on the reduction of stormwater contaminants levels and loads, which is important for effective stormwater management and/or adequate sizing of biofilter systems for stormwater harvesting (Randelovic et al., 2016).

2.7. Environmental risk analysis

As mentioned before, the presence of many OMPs in the environment, even at low concentrations, may pose a potential ecotoxicological threat to aquatic living organisms. However, in most cases, acute toxicity is less likely to occur at the low concentrations of OMPs usually observed in the aquatic environment. However, their chronic effects are mostly known about and are being investigated (Arslan et al., 2017; Farré et al., 2008). Alongside studying the removal efficiency of a treatment system, analyzing the effluent concentrations in terms of potential environmental risk may provide complementary information for water body protection. In this case, a risk-based approach can be used as a management tool that assists with decision-making, setting pollutant priorities on a comparative basis, and controlling pollution sources through measures such as expenditure allocation (Skivington, 1997).

Environmental risk analysis of a pollutant is a process that assesses the potential environmental hazards (health effects of OMPs) and risks associated with the release of a pollutant into the environment. Environmental risk calculation involves evaluating the probability and consequences of the potential environmental hazards. As recommended in environmental risk assessment (ERA) guidelines (ECHA, 2008; EMEA, 2006),

measured environmental concentrations along with predicted no-effect concentrations (PNEC) or environmental quality standards (EQSs) are commonly used to assess the risk from chemicals to aquatic ecosystems. Several studies have used the ERA method, or a modified version of it, to screen hazardous OMPs for their potential risk to water bodies (Figuière et al., 2022; Schwarz et al., 2021; Villain et al., 2016; Załęska-Radziwiłł et al., 2011). In this work, the same idea of ERA method was used to estimate and compare the risks from OMPs in untreated and treated stormwater in order to identify the most hazardous compounds, using their measured concentrations in treatment train inflow and outflows, and their PNEC values. In this way, the impact of the treatment train in reducing OMP risk to a safe level (before dilution in water bodies) could be assessed. Although PNEC or EQS values concern the concentrations in the receiving water body, using this method for a TT performance evaluation may give overestimations of risks because the outflow concentrations at the discharge point will be diluted by the receiving water body.

3. Methods

A field study of the quality of runoff collected from a road catchment and a treatment train (GPT and three different subsequent bioretention cells) receiving this runoff was carried out in Sundsvall, Sweden, between September 2020 and September 2021. The following sections explain the site characteristics, monitoring and sampling procedures, analytical methods, and how the gathered dataset was analyzed for this thesis.

3.1. Field study

3.1.1. Field site description

3.1.1.1. Catchment area

The catchment area was located in Sundsvall, Sweden, which experiences a Continental Subarctic Climate (Dfc) and cool summers. The total catchment area was 8.2 ha, covering the southern half of a highway bridge over Sundsvall bay and the *Skönsmon* traffic area, which comprises 4.7 ha of impermeable surfaces. The impermeable catchment area included the 1.9 ha E4 highway bridge, carrying an average traffic load of 13,000 vehicles per day, a highway exit way, a highway entrance acceleration ramp, main roads associated with two roundabouts, and sidewalk paths (Figure 4). The remaining 3.5 ha were permeable green areas (slopes, green spaces, and ditches) within the road areas. The green areas were not expected to contribute considerable runoff to the collection pipe network and the stormwater treatment train downstream. In the event of moderate rain, the precipitation infiltrated directly into green areas and did not burden the facility. In heavier rains, however, the green areas could become temporarily saturated and a portion of the precipitation from these areas could burden the stormwater collection and treatment system.

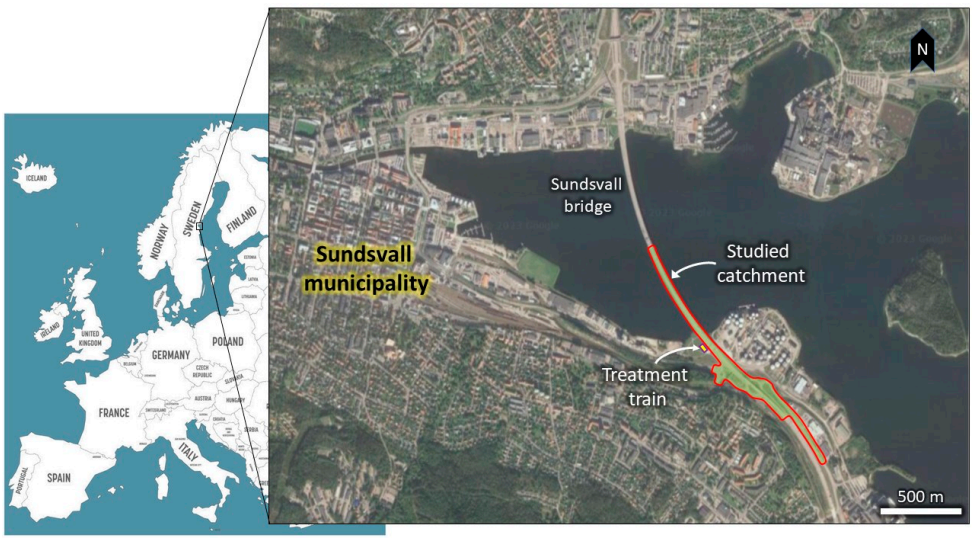


Figure 4. Field site map showing the studied catchment and treatment train location

Runoff from the catchment was collected and then transported through a 100 m underground pipe (slope 0.5% and diameter 0.8 m) to a stormwater treatment train facility. The facility's outlet/overflow then went to Sundsvall bay (*Sundsvallsfjärden*) near the facility. According to Water Information System in Sweden (VISS), Sundsvall bay experienced environmental problems related to environmental toxins including heavy metals and organic pollutants such as PAHs, dioxins, and poly-brominated diphenyl ethers (PBDEs) up to 2021 (VISS, 2022).

3.1.1.2. Stormwater treatment train

The stormwater treatment (TT) facility (Figure 5) was located next to the southern abutment of the bridge in order to treat the stormwater received from the catchment area (Figure 4). The TT was basically designed according to German stormwater biofilter guidelines for treatment of highway runoff (DWA-M 187, 2005). It was constructed in 2018, so was 2–3 years old at the time of the experiments.

At the end of the stormwater collection pipe, the stormwater enters a GPT that includes a sedimentation chamber and an oil separator. The stormwater in the GPT is then discharged through a stepwise valve-controlled siphon system (under hydrostatic pressure) to three parallel filter cells (Figure 6)). The valves are controlled by a floating balloon which triggers the valves depending on the water level in the GPT. According to these level meter measurements, the GPT's detention volume (active discharging capacity) during each charging and discharge step is about 23.3 m^3, which is discharged over approximately 4 minutes when the valves are opened. If the runoff inflow exceeds this capacity, the excess stormwater bypasses the whole TT at the GPT inlet.

The GPT outflow is evenly spread over the three filter cells through 12 distributor pipes (4 pipes/cell placed on top of each cell as shown in Figure 6) and vertically infiltrates through the filter media of the cells. All three filter cells share the same ponding zone (Figure 5), but an ethylene propylene diene terpolymer (EPDM) waterproofing fabric has been used to divide the filter into the three cells and also to protect the bottom of the filter bed. All three filter cells are made of the same sand-based filter material, however, one of the filter cells is non-vegetated (sand filter SF), and the other two are vegetated (biofilters BFC and BF). Additionally, the BFC filter media has been amended with 10% w/w crushed grey chalk ($CaCO_3$). The vegetation layer in BF and BFC is made of salt-tolerant meadow vegetation mats (Veg Tech AB, Sweden) with 17 different plant species pre-cultivated in a 3–4 cm deep sandy or silty-sandy soil with 2.5–5% w/w mulch (see Figure S2 in Paper II for more details). The treated stormwater drains from the cells through a gravel drain layer with embedded drainpipes underneath the filter material, into three sampling wells, before finally being collected and released to the downstream recipient, which is a bay. Technical information on sizes and hydraulic features of TT compartments are presented in Paper II, Table S1.

Figure 5. Photos illustrating filter cells with and without stormwater

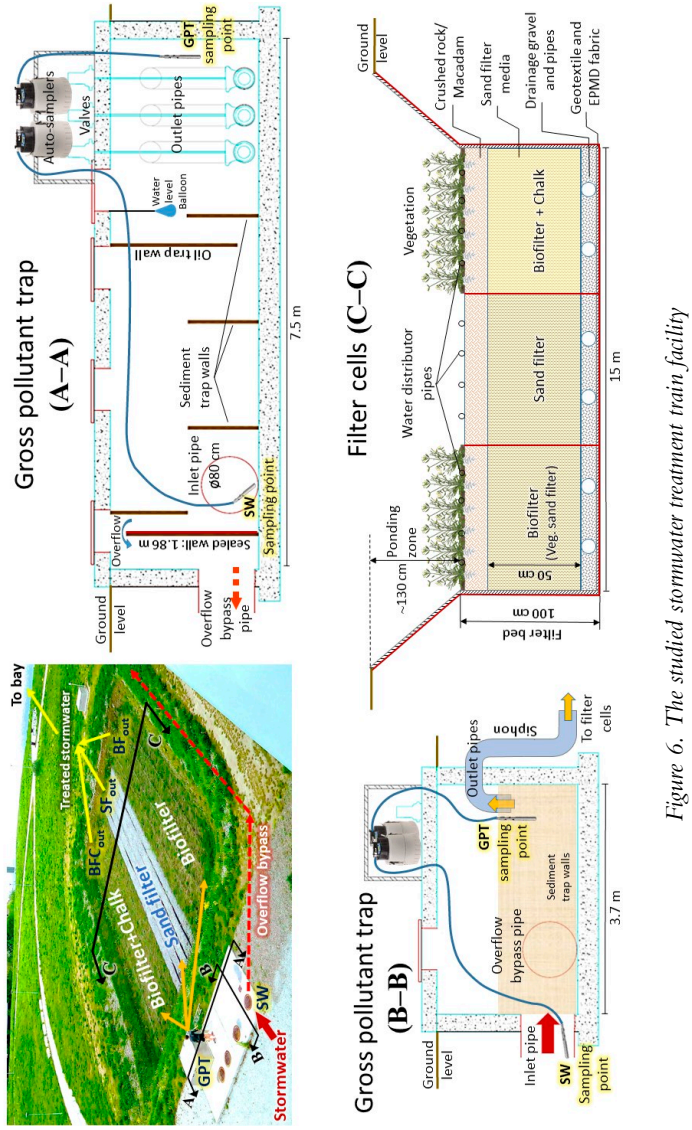


Figure 6. The studied stormwater treatment train facility

3.1.2. Sampling methods

The results described in this thesis are based on a total of 11 rain events, sampled between September 2020 and September 2021 (rain A to K). Table 1 shows which rain events were included for the different objectives investigated for the thesis and the appended papers (stormwater quality assessment, removal performance of TT units, inter-event and intra-events concentration variations, and environmental risk analysis, see Figure 1). Samples were collected from five sampling locations, as marked in Figure 6, with the following labels:

- **SW**: stormwater received at GPT inlet from the catchment
- **GPT_{out}**: gross pollutant trap outflow (inflow of the filter cells**)**
- **BFC_{out}**: chalk-amended, vegetated biofilter outflow
- **SF_{out}**: non-vegetated sand filter outflow
- **BF_{out}**: vegetated biofilter outflow

Samples during the rain events were taken volume-proportionally using automatic samplers. The samplers were programmed to collect a maximum of 8 volume-proportional subsamples (using Teflon PFA bags) at each point during each event. Rain characteristics (i.e. depth, peak and mean intensity (I_{peak} and I_{mean}), and antecedent dry period (ADP)), number of subsamples taken, and the total and sampled volumes at each sampling spot for all events are summarized in Table 1. Detailed information about the equipment used for sampling, rainfall and volume measurements at various sampling points, along with sample storage strategies, are described in Paper II, section 2.2.

3.2. Analytical methods

3.2.1. Selection and analysis of contaminants

OMP selection in this field study was carried out based on a number of criteria: 1) available literature on prioritized or most-frequently detected organic micropollutants in stormwater outlets/overflows or stormwater sediment ponds, 2) expected OMP toxicity, 3) OMPs relevant to road catchments, 4) practical feasibility (i.e. maximum number and volume of subsamples, sampling equipment material, organic compounds sensitive to storage conditions etc.), and 5) financial limitations (Flanagan et al., 2021; Gasperi et al., 2022; Lundy et al., 2012; Masoner et al., 2019; Müller et al., 2020; Mutzner et al., 2022). Based on these considerations, three groups were selected to be analyzed from the studied catchment and TT facility. The selected OMPs include nine phenolic substances (bisphenol A, 4-t-octylphenol (OP), nonylphenol (NP), octylphenol ethoxylates (OPnEO; n=1, 2, 3), nonylphenol ethoxylates (NPnEO; n=1, 2, 3)), sixteen PAHs, and four fractions of PHCs. A full list of the selected OMPs associated with their abbreviations and limit of quantifications (LoQs) is given in Table 2.

Table 1. Rain events characteristics, and sampling and flow volume information

Related thesis objectives (see section 1.1)	Related papers	Rain event characteristics							Total and sampled volumes at sampling spots									
									SW		GPT		BFC		SF		BF €	
		Rain event	Sampling date (2020-21)	Rain (mm)	Rain duration (hr)	ADP¥ (day)	Mean intensity: I_{mean} (mm/hr)	Peak intensity: I_{peak} (mm/hr)	Tot. vol. passed* (m3)	Vol. sampled (%)	Tot. vol. passed* (m3)	Vol. sampled (%)	Tot. vol. passed (m3)	Vol. sampled ** (%)	Tot. vol. passed (m3)	Vol. sampled ** (%)	Tot. vol. passed (m3)	Vol. sampled ** (%)
1, 2, 4	I, II	**A**	15 Sep	7.3	14.3	3	1.5	5.5	257	100	257	100	129.4	-	40.4	-	102.3	95
1, 2, 4	I, II	**B**	21 Oct	4.6	13.8	0.8	0.7	2.4	195	100	195	100	53.8	-	90	-	25.5	55
1, 2, 3, 4	I, II, III	**C**	17 May	7.8§	3.25§	1.7§	2.6§	12.0§	373	100	373	100	72.6	-	202.9	98	53.1	80
2, 4	II	**D**	12 Jun	4.1	6.5	25.3	2.9	7.5	-	-	-	-	71.2	78	28	68	44	98
2, 4	II	**E**	15 Jun	3.2	6.25	2.4	2.3	11.6	-	-	-	-	23.1	99	35.3	99	9.2	99
2, 4	II	**F**	20 Jun	7.5	10	4.5	2.0	6.1	-	-	-	-	100.3	92	119	99	65	95
1, 2, 4	I, II	**G**	30 Jun	3.8	18.6	6.7	2.3	8.6	128	83 $	128	83$	10.2	51	92.7	89	<0.1	-
1, 2, 4	I, II	**H**	11 Jul	8.3	13.7	10.5	9.4	32.7	280	100	280	100	141.5	99	80.6	99	106	99
1, 2, 3, 4	I, II, III	**I**	20 Aug	32.4	40.9	1	3.7	21.2	2353	79#	1921##	79#	680.6	98	628.2	99	611.4	91
1, 2, 3, 4	I, II, III	**J**	25 Aug	7.9	46.7	6.3	1.4	4.2	303	96	303	96	57.6	63	196.8	84	17.7	68
1, 2, 4	I, II	**K**	24 Sep	17.8	24.4	10.4	1.7	4.8	932	59	932	59	324.6	97	349.2	99	268.3	90

¥ Antecedent dry period (precipitations less than 1 mm were ignored)

€ One composite sample was taken from BF outflow except in rain events A and B with separate subsamples.

* Estimated using the number and volume of pulses (~23.3 m^3/pulse) received from the GPT discharge valve.

** The percentage of non-sampled outflow in BFC, SF, and BF is after sampling.

$ The first portion of inflow (~17%) was not sampled.

§ Due to missing data, the rain characteristics were reported from another weather station close to the catchment (1500 m away from the rain gauge next to the facility).

\# 21% of inflow was not sampled during the last quarter because of at least one of these reasons: bypassed overflow (16%), GPT's discharge valve stayed open due to a very high inflow (sending no new signal to the SW and GPT samplers in this mode), or the sampling program ended (final 5%).

16% of inflow bypassed during the last quarter. The bypassed volume was estimated from the total volume summation of BFC, SF, and BF.

Table 2. List of the studied organic micropollutants and corresponding abbreviations and LoQs (µg/L)

Phenolic substances	*Bisphenol-A*: **BPA** (0.05); *Nonylphenol, mixture of isomers*: **NP** (0.1–1.35*); *Nonylphenol monoethoxylate*: **NP1EO** (0.1–0.3*); *Nonylphenol diethoxylate*: **NP2EO** (0.1–2.54*); *Nonylphenol triethoxylate*: **NP3EO** (0.1–3.12*); *4-tert-octylphenol*: **OP** (0.01–0.25*); *Octylphenol monoethoxylate*: **OP1EO** (0.01–0.03*); *Octylphenol diethoxylate*: **OP2EO** (0.01–0.02*); *Octylphenol triethoxylate*: **NP3EO** (0.01–0.033*).
Polycyclic Aromatic Hydrocarbons (PAHs)	*Naphthalene*: **Nap** (0.03); *Acenaphthylene*: **Acyl** (0.01); *Acenaphthene*: **Acen** (0.01); *Fluorene*: **Flu** (0.01); *Phenanthrene*: **Phen** (0.02); *Anthracene*: **Anth** (0.01); *Fluoranthene*: **Flth** (0.01); *Pyrene*: **Pyr** (0.01); *Benz(a)anthracene*: **BaA** (0.01); *Chrysene*: **Chry** (0.01); *Benzo(b)fluoranthene*: **BbF** (0.01); *Benzo(k)fluoranthene*: **BkF** (0.01); *Benzo(a)pyrene*: **BaP** (0.01); *Dibenz(a.h)anthracene*: **DahA** (0.01); *Benzo(g.h.i)perylene*: **Bper** (0.01); *Indeno(1.2.3-cd)pyrene*: **InP** (0.01). *Sum of all*: **∑16 PAH**; *Carcinogenics*: **∑Car PAH** (Nap, BaA, Chry, BbF, BkF, BaP, BahA, Bper); *Non-carcinogenic*: **∑nonCar PAH** (Acyl, Acen, Flu, Phen, Anth, Flth, Pyr, InP); *Low molecular weight:* **∑LMW PAH** (Nap, Acyl, Acen, Flu, Phen, Anth); *Medium molecular weight:* **∑MMW PAH** (Flth, Pyr); and *High molecular weight*: **∑HMW PAH** (BaA, Chry, BbF, BkF, BaP, DahA, Bper, InP).
Petroleum Hydrocarbons (PHCs)	***Total PHCs*** *or* **C_{10}-C_{40}** (50); **C_{10}-C_{12}** (5); **C_{12}-C_{16}** (5); **C_{16}-C_{35}** (30); **C_{35}-C_{40}** (10).

* Upper limit of the range of LoQ includes a shift due to matrix interference during chemical analysis.

Apart from these OMPs, all samples were also analyzed for a number of other water quality parameters: total organic carbons (TOC), total suspended solids (TSS), turbidity, conductivity, pH, and temperature. The OMPs and TOC were analyzed by accredited ALS Czech Republic laboratory, and TSS by accredited ALS Scandinavia AB. It should be noted that the LoQs for phenolic substances (except BPA) were sometimes affected by matrix interference during chemical analysis, meaning that the LoQs varied over the experiments (see Table 1 in Paper II). Turbidity, conductivity, pH, and temperature were all measured during sampling events on-site. Table S2 in Paper II summarizes the analytical methods used.

Blank tests on sampling equipment were carried out to ensure that said equipment did not leach out the OMPs of concern (for more information, see section 2.3 in Paper I). Also, each bag was assigned to the same position in the identical automatic sampler to avoid cross-contamination throughout the experiments. Sampler bags were replaced with a new set of bags after the first 6 or 7 events.

3.3. Data analysis

After the sampling campaign and data collection, water quality parameters were used in different ways to obtain pollutographs and event mean concentrations for studying the removal efficiencies, and for environmental risk analysis. Figure 7 shows the flowchart of the data analysis procedure used for this thesis. In the subsequent sections 3.3.2 and 3.3.3, a brief overview of the applied methods to determine the removal efficiency and environmental risk is provided. However, for a more comprehensive understanding, readers are encouraged to refer to the appended papers for detailed information.

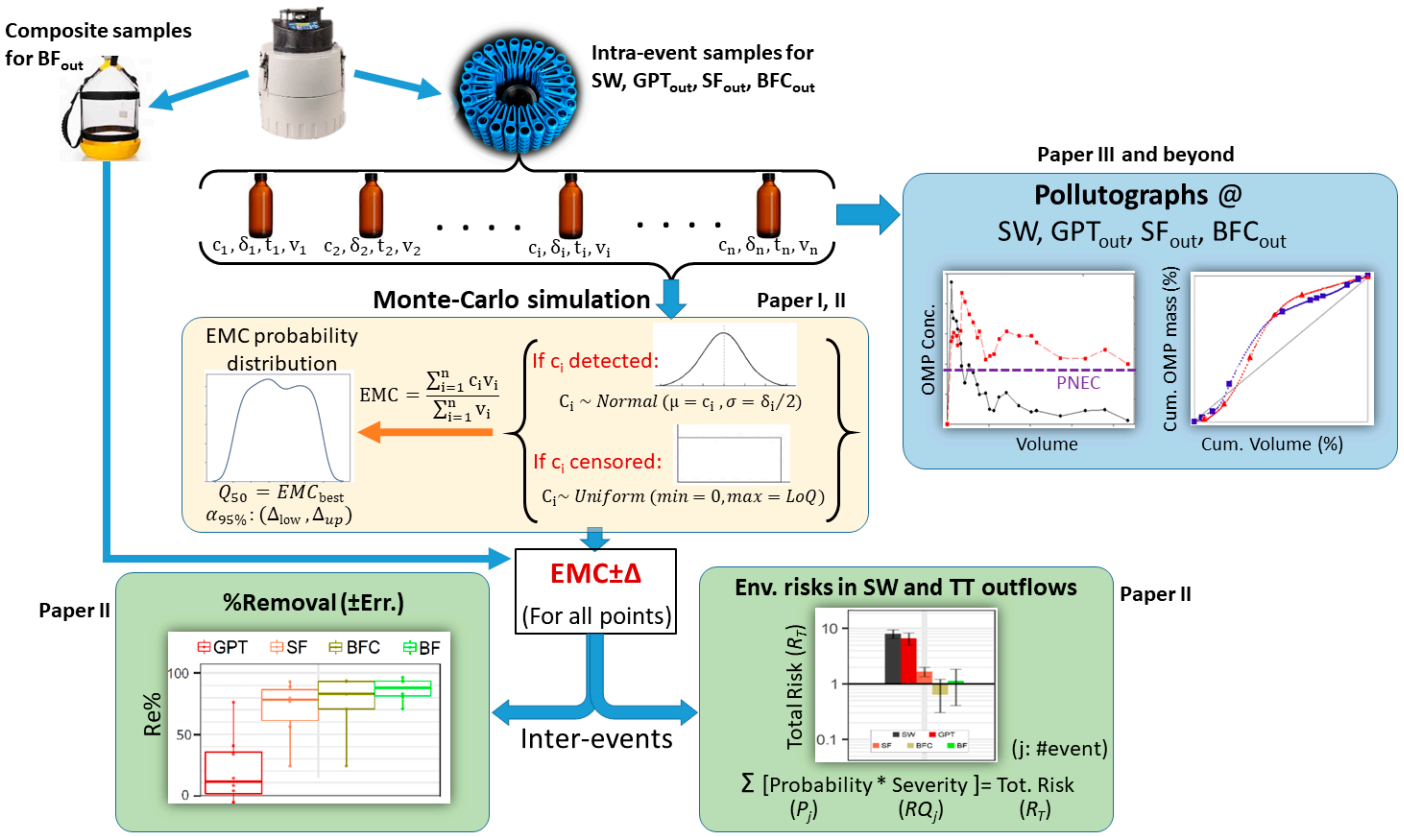


Figure 7. Flowchart of data elaborations and analyses

3.3.1. Evaluation of intra-event concentrations (IEC)

The data from the analyses of the intra-event subsamples was directly used to generate pollutographs and M-V curves. For a given OMP and a given event, the pollutograph shows the concentrations with respect to time or stormwater volume. Where the concentration of a given substance was too low to be quantified (non-detects), half the LoQ was used. The M-V curve is a dimensionless illustration of OMP cumulative mass with respect to cumulative volume (normally fitted to a power function $M=V^{\beta}$), generated from merging a pollutograph (C(t)) and a hydrograph (Q(t)). The lower the β, the higher proportion of pollutant mass is transported for a given volume discharged. Bertrand-Krajewski et al. (1998) proposed six zones for the M-V curve (Figure 8) as follows: zone 1: $0<\beta<0.185$, zone 2: $0.185<\beta<0.862$, zone 3: $0.862<\beta<1$, zone 4: $1<\beta<1.159$, zone 5: $1.159<\beta<5.395$, and zone 6: $5.395<\beta$. An M-V curve allows the analysis of the variation of the pollutant mass during storm events, so it is useful for identifying first flush events. According to Bertrand-Krajewski et al. (1998), a first flush is defined as an event where at least 80% of the total pollutant mass is transported in the first 30% of the volume discharged during the event (the so-called "30/80 first flush", which corresponds to values of β below 0.185 or zone 1). In this thesis, this definition was used to identify first flush events. In the events where the sampling did not cover the entire volume (Table 1), the concentration of the missed portion was assumed to be equal to the last subsample's concentration that could be calculated for the total mass conveyed to generate M-V graphs.

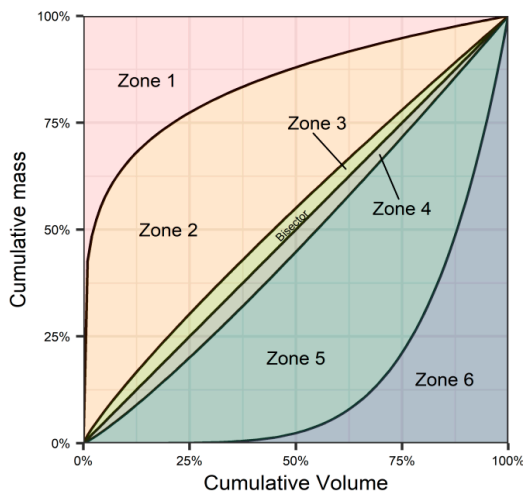


Figure 8. Zone classifications of M-V curve

3.3.2. Calculation of event mean concentrations (EMC)

To evaluate the treatment performance and the environmental risks over all events, first, the event mean concentration (EMC) of OMPs for a given event and sampling point

were calculated using the measured concentrations of the intra-event subsamples and their corresponding stormwater volumes passing the relevant sampling point. The EMC calculation shown in Equation 1 was adjusted for the events where the sampling duration did not cover the entire stormwater volume (see Table 1). In these cases, the missing volume can be attributed to the last subsample with the same concentration (or to the first subsample for rain event G at SW and GPT_{out}) to obtain a more accurate total EMC (Furuta et al., 2022).

$$EMC = \frac{M_T}{V_T} = \frac{\sum m_i}{\sum v_i} = \frac{\sum_{i=1}^{n} c_i v_i}{\sum_{i=1}^{n} v_i} \qquad \textit{Equation 1}$$

M_T: total mass transported during the entire event period
V_T: total stormwater volume at the given sampling point
m_i: pollutant mass transported during taking i^{th} subsample
n: number of subsamples
c_i: concentration of i^{th} subsample
v_i: corresponding stormwater volume passed

To attain the best estimation for EMCs (using Equation 1) and their associated uncertainties, a Monte-Carlo (MC) simulation was programmed in R. The main reason for choosing MC was that using such a stochastic model has shown promising results to account for measurement uncertainties (errors) in the data influencing final outcomes, as well as properly dealing with data that include a considerable number of censored values (c_i < LoQ) (Flanagan et al., 2019a). From the MC simulation, a distribution for each EMC at a given sampling point and a rain event can be generated (Figure 7). The median of the distribution is then considered as the best-estimated event mean concentration (EMC_{best}, referred to as EMC in the rest of the thesis), and the range between the 95% confidence interval (2.5% and 97.5% quantiles) as the lower and upper limits for EMC error (Δ_l, Δ_u). For further details about implementing MC simulation, refer to Paper I, section 2.4.2. Additionally, the EMCs of OMPs were compared with the lowest Predicted No-Effect Concentrations (PNECs) in freshwater (NORMAN, 2012) to assess the stormwater quality and environmental risk levels at different treatment stages (see section 3.3.3). Further statistical analyses of EMCs mentioned in the thesis are described in Paper I, section 2.4.3 and Paper II, section 2.4.4.

3.3.3. Removal efficiency calculations

The effectiveness of various treatment sections was determined by computing the removal efficiencies (Re%) using Equation 2.

$$Re\ (\%) = 100 \times \frac{EMC_{in} - EMC_{out}}{EMC_{in}} \qquad \textit{Equation 2}$$

Here, EMC_{in} and EMC_{out} denote the estimated EMC in the inflow and outflow of the relevant treatment unit, respectively. Equation 3, as defined by Taylor (1997), was also used to calculate the absolute removal error (Err_{Re}%) with the assumption that the

uncertainties in EMCs for the inflow and outflow (Δ_{in} and Δ_{out}) are independent. Notably, the MC method applied in this study showed that EMC_{best} for a censored EMC (concentrations of all subsamples were censored) was typically about half of LoQ. Nonetheless, if both inflow and outflow EMCs of an OMP were censored during an event, their calculated Re% and Err_{Re}% were excluded from the statistical analysis. Consequently, the number of data points considered for analyzing Re% and Err_{Re}% of OMPs ranged from 5 to 9.

$$\mathrm{Err_{Re}}(\%) = 100 \times \sqrt{\left(\Delta_{\mathrm{in}} \cdot \frac{\mathrm{EMC_{out}}}{\mathrm{EMC_{in}}^2}\right)^2 + \left(\Delta_{\mathrm{out}} \cdot \frac{1}{\mathrm{EMC_{in}}}\right)^2} \qquad \textit{Equation 3}$$

3.3.4. Environmental risk analysis

According to Skivington (1997), risk refers to the combination of the occurrence likelihood of a defined hazard (presence of OMP) and the magnitude of the occurrence consequences. Equation 4 was used to estimate the total environmental risk associated with an OMP at a particular sampling point during the entire experiment. The OMP's environmental hazard, or potential criticality, was assessed using the risk quotient (RQ_j), which is calculated by dividing the observed concentration of the OMP by the chronic environmental quality standard (EQS) for freshwater (Mutzner et al., 2022). Here, the EQS was derived from the PNEC value (if available) for the OMP which is based on an ecotoxicological database. The calculated R_Ts were then used to compare the risk posed by OMPs at different stages in stormwater. Additionally, OMPs with an R_T>1 were assumed to be potentially risky pollutants for the recipient, although the dilution effect in the recipient may mitigate the risks in reality.

$$R_T = \sum_j P_j . RQ_j = \sum_j P_j . (EMC \pm \Delta)_j / PNEC \qquad \textit{Equation 4}$$

j: rain event

R_T: total risk of an OMP at a given sampling point over the rain events

P_j: probability of OMP occurrence (event j), which equals 1 over the number of events included for the OMP

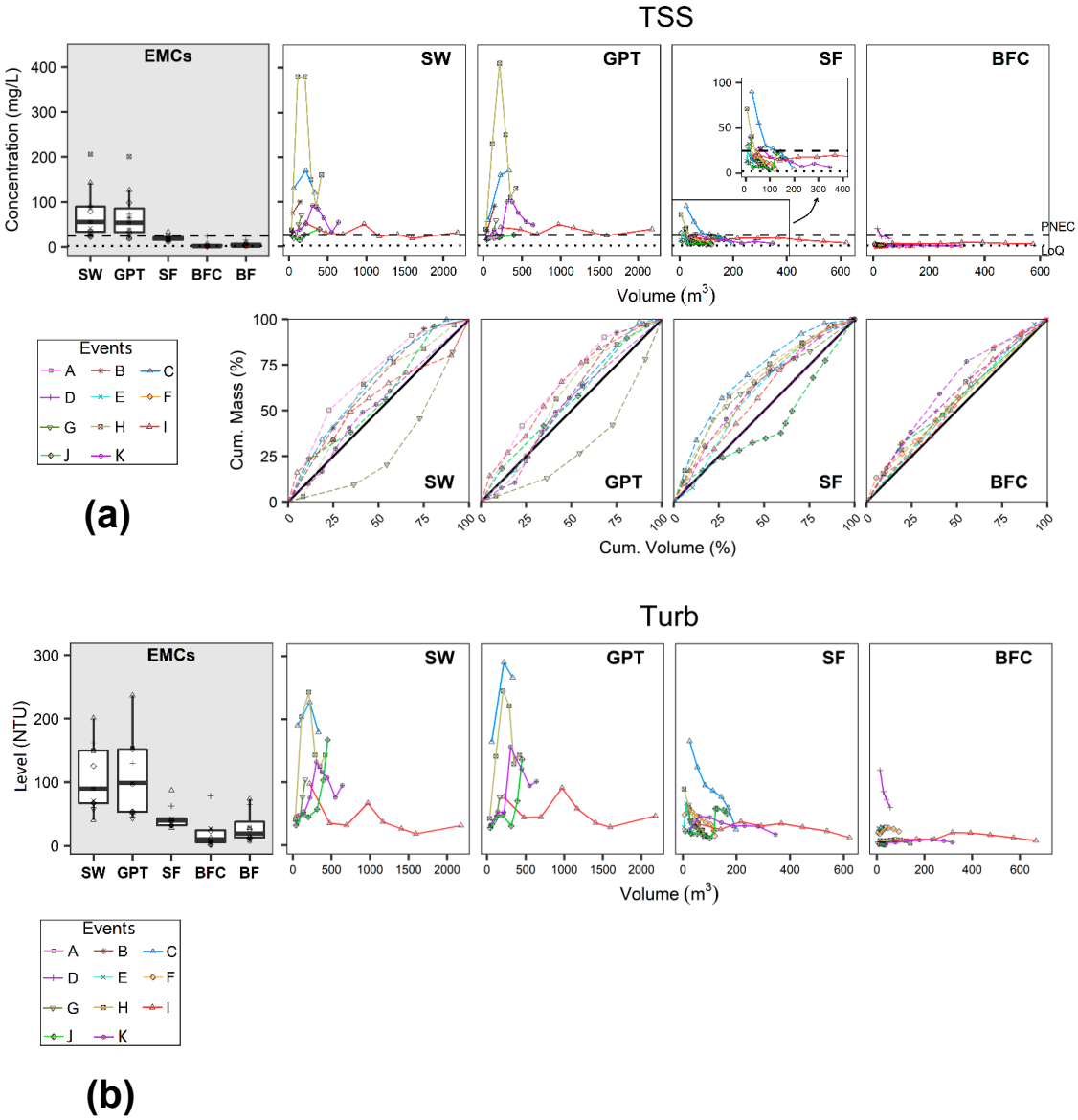
RQ_j: risk quotient of the OMP at event j

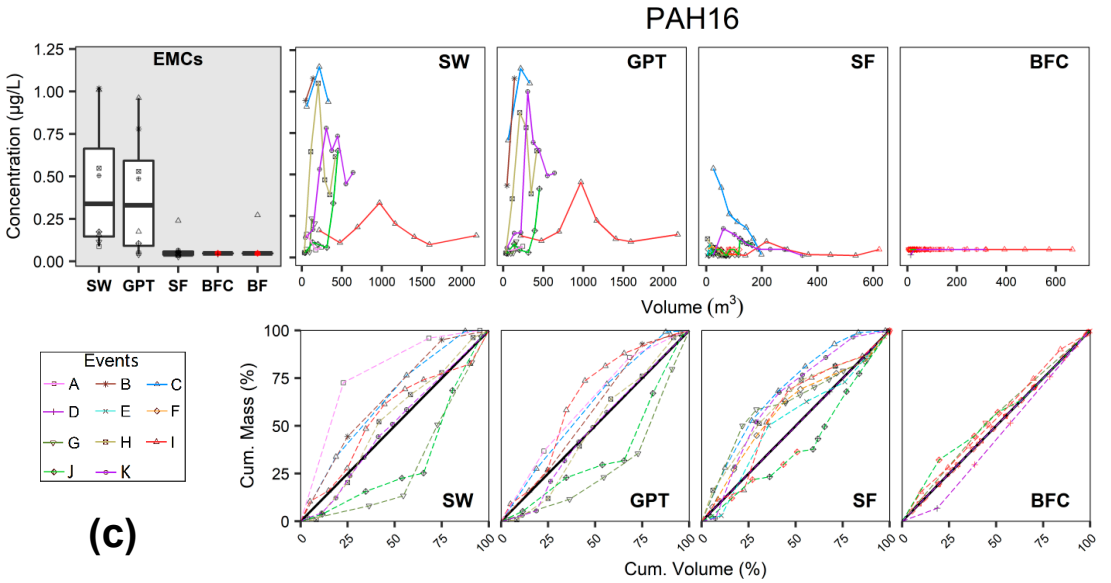
$(EMC \pm \Delta)_j$: OMP's event mean concentration and the associated error at event j

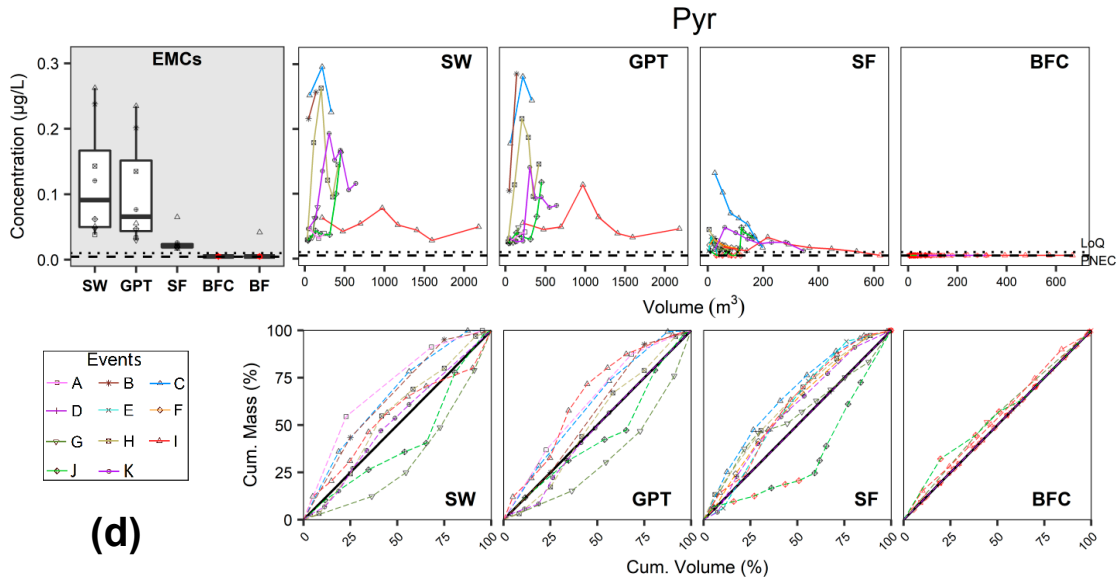
PNEC: predicted non-effect concentration for the OMP

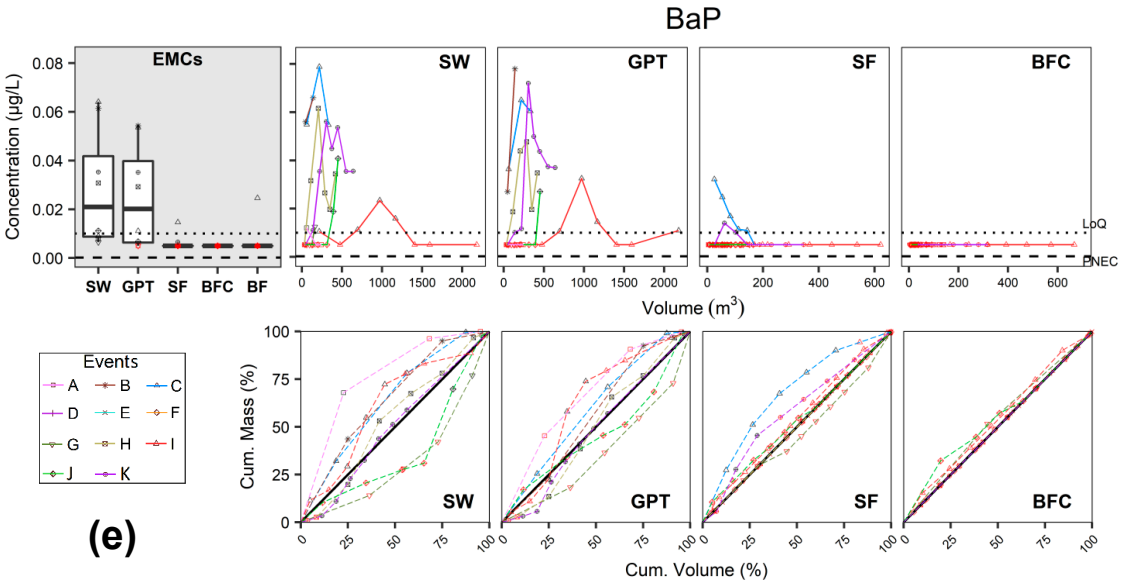
4. Results

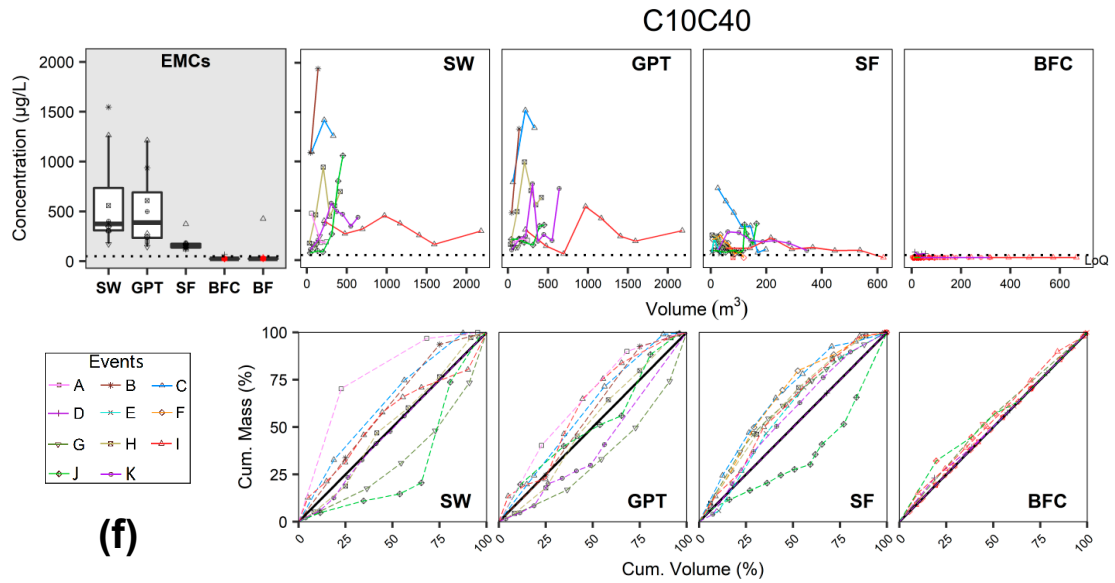
The estimated/measured EMCs were analyzed over the rain events for all sampling points. A statistical summary of the occurrence and EMC of all OMPs is presented in Table 3 and discussed below. Furthermore, IECs were investigated at SW, GPT_{out}, SF_{out}, and BFC_{out}. Figure 9 illustrates the inter-event and intra-event variations (i.e., EMC distributions, and IEC pollutographs and M-V curves) in both untreated and treated stormwater at different units' outflow. The variations are discussed in sections 4.1 and 4.2 for each individual parameter.

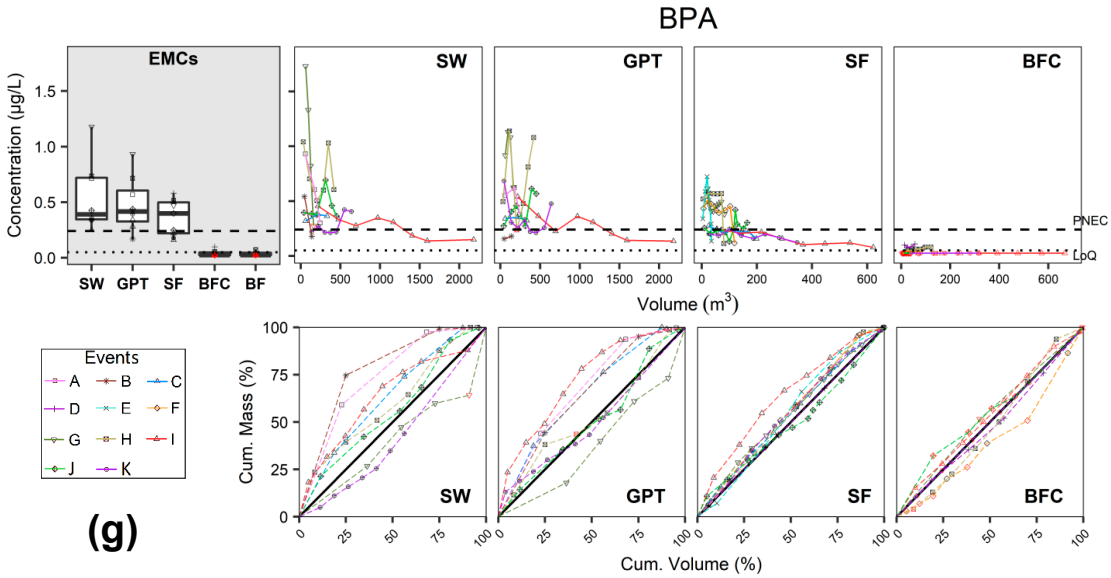



PAH16
EMCs
SW
GPT
SF
BFC
BF
Concentration (µg/L)
Volume (m3)
Events
A
B
C
D
E
F
G
H
I
J
K
Cum. Mass (%)
Cum. Volume (%)
(c)

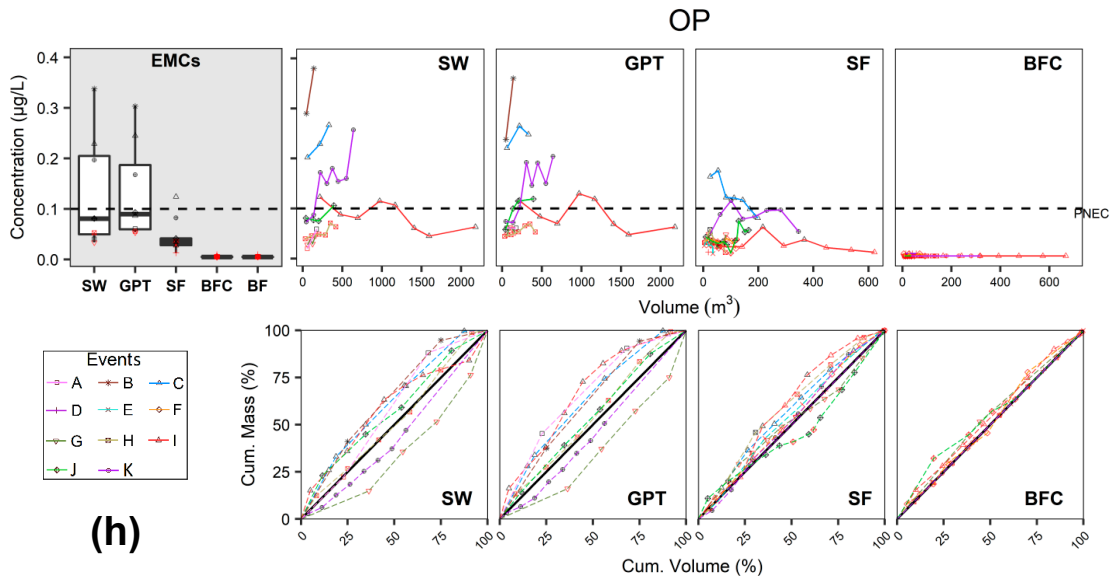

Pyr
EMCs
SW
GPT
SF
BFC
BF
Concentration (µg/L)
LoQ
PNEC
Volume (m3)
Events
A
B
C
D
E
F
G
H
I
J
K
Cum. Mass (%)
Cum. Volume (%)
(d)


BaP
EMCs
SW
GPT
SF
BFC
BF
Concentration (µg/L)
0.08
0.06
0.04
0.02
0.00
LoQ
PNEC
Volume (m3)
Events
A
B
C
D
E
F
G
H
I
J
K
Cum. Mass (%)
Cum. Volume (%)
(e)


C10C40
EMCs
SW
GPT
SF
BFC
BF
Concentration (µg/L)
2000
1500
1000
500
0
LoQ
Volume (m3)
Events
A
B
C
D
E
F
G
H
I
J
K
Cum. Mass (%)
Cum. Volume (%)
(f)


BPA
EMCs
SW
GPT
SF
BFC
Concentration (µg/L)
SW GPT SF BFC BF
PNEC
LoQ
Volume (m3)
Events
A B C
D E F
G H I
J K
Cum. Mass (%)
Cum. Volume (%)

(g)


OP
EMCs
SW
GPT
SF
BFC
Concentration (µg/L)
SW GPT SF BFC BF
PNEC
Volume (m3)
Events
A B C
D E F
G H I
J K
Cum. Mass (%)
Cum. Volume (%)

(h)

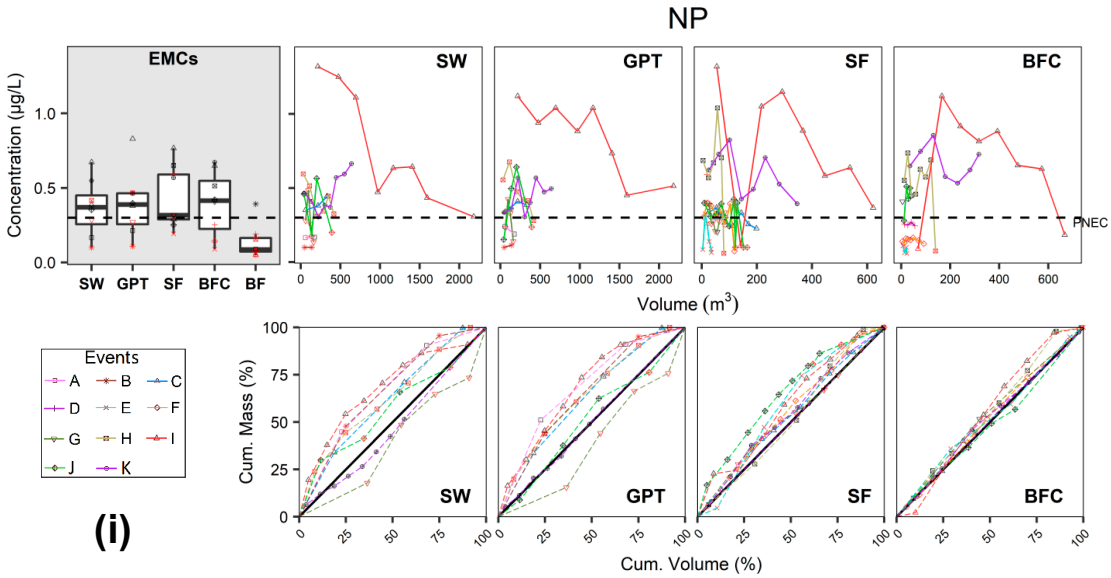


Figure 9. EMCs distributions, IECs, and M-V curves of selected parameters at different sampling points for the studied rain events (Black symbols: quantified values; Red symbols: censored values)

Table 3. Statistical summary (min, mean, max, SD) of EMCs over events (N= $n_{detected}$ + $n_{censored}$) at different sampling points

Parameter	SW						GPT						BFC						SF						BF						PNEC for freshwater
	n (quantified)	n (censored)	EMC_min	EMC_mean	EMC_max	SD	n (quantified)	n (censored)	EMC_min	EMC_mean	EMC_max	SD	n (quantified)	n (censored)	EMC_min	EMC_mean	EMC_max	SD	n (quantified)	n (censored)	EMC_min	EMC_mean	EMC_max	SD	n (quantified)	n (censored)	EMC_min	EMC_mean	EMC_max	SD	
Nap (µg/L)	**0**	**8**		100%<0.03		-	**0**	**8**		100%<0.03		-	**0**	**8**		100%<0.03		-	**0**	**9**		100%<0.03		-	**0**	**9**		100%<0.03		-	2
Acyl (µg/L)	**0**	**8**		100%<0.01		-	**0**	**8**		100%<0.01		-	**0**	**8**		100%<0.01		-	**0**	**9**		100%<0.01		-	**0**	**9**		100%<0.01		-	1.3
Acen (µg/L)	**0**	**8**		100%<0.01		-	**0**	**8**		100%<0.01		-	**0**	**8**		100%<0.01		-	**0**	**9**		100%<0.01		-	**0**	**9**		100%<0.01		-	3.7
Flu (µg/L)	**0**	**8**		100%<0.01		-	**1**	**7**	87.5%	<0.006	0.01	-	**0**	**8**		100%<0.01		-	**0**	**9**		100%<0.01		-	**0**	**9**		100%<0.01		-	0.25
Phen (µg/L)	**5**	**3**	<0.02	0.026	0.065	0.017	**4**	**4**	<0.02	0.027	0.058	0.012	**0**	**8**		100%<0.02		-	**0**	**9**		100%<0.02		-	**0**	**9**		100%<0.02		-	0.5
Anth (µg/L)	**0**	**8**		100%<0.01		-	**1**	**7**	87.5%	<0.009	0.01	-	**0**	**8**		100%<0.01		-	**0**	**9**		100%<0.01		-	**0**	**9**		100%<0.01		-	0.1
Flth (µg/L)	**8**	**0**	0.008	0.069	0.163	0.059	**7**	**1**	<0.007	0.062	0.142	0.053	**0**	**8**		100%<0.01		-	**5**	**4**	<0.005	0.01	0.033	0.008	**1**	**8**	88.9%	<0.01	0.027	-	0.0063
Pyr (µg/L)	**8**	**0**	0.038	0.12	0.262	0.088	**8**	**0**	0.03	0.102	0.235	0.08	**0**	**8**		100%<0.01		-	**9**	**0**	0.017	0.026	0.065	0.015	**1**	**8**	88.9%	<0.01	0.042	-	0.0046
BaA (µg/L)	**6**	**2**	<0.008	0.021	0.044	0.014	**6**	**2**	<0.006	0.02	0.038	0.012	**0**	**8**		100%<0.01		-	**2**	**7**	0.006	0.008	0.01	0.002	**1**	**8**	88.9%	<0.01	0.016	-	0.012
Chry (µg/L)	**7**	**1**	<0.009	0.029	0.069	0.023	**6**	**2**	<0.008	0.028	0.057	0.019	**0**	**8**		100%<0.01		-	**6**	**3**	0.005	0.008	0.017	0.003	**1**	**8**	88.9%	<0.01	0.024	-	0.0029
BbF (µg/L)	**8**	**0**	0.013	0.061	0.14	0.049	**8**	**0**	0.006	0.055	0.131	0.048	**0**	**8**		100%<0.01		-	**9**	**0**	0.008	0.013	0.037	0.009	**1**	**8**	88.9%	<0.01	0.045	-	0.017
BkF (µg/L)	**6**	**2**	<0.006	0.016	0.031	0.01	**6**	**2**	<0.006	0.015	0.031	0.01	**0**	**8**		100%<0.01		-	**1**	**8**	88.9%	<0.008	0.01	-	**1**	**8**	88.9%	<0.01	0.011	-	0.017
BaP (µg/L)	**8**	**0**	0.006	0.028	0.064	0.024	**6**	**2**	<0.007	0.025	0.054	0.019	**0**	**8**		100%<0.01		-	**2**	**7**	0.007	0.007	0.015	0.003	**1**	**8**	88.9%	<0.01	0.025	-	0.00017
DahA (µg/L)	**5**	**3**	0.006	0.011	0.027	0.006	**4**	**4**	<0.01	0.013	0.026	0.006	**0**	**8**		100%<0.01		-	**1**	**8**	88.9%	<0.008	0.01	-	**1**	**8**	88.9%	<0.01	0.011	-	0.0014
Bper (µg/L)	**8**	**0**	0.013	0.066	0.145	0.054	**8**	**0**	0.007	0.054	0.158	0.05	**1**	**7**	87.5%	<0.007	0.01	-	**9**	**0**	0.008	0.014	0.042	0.011	**1**	**8**	88.9%	<0.01	0.043	-	0.0082
IP (µg/L)	**7**	**1**	<0.006	0.029	0.072	0.023	**6**	**2**	<0.008	0.029	0.075	0.023	**0**	**8**		100%<0.01		-	**3**	**6**	<0.005	0.008	0.022	0.005	**1**	**8**	88.9%	<0.01	0.028	-	0.27
Σ16PAHs (µg/L)	**8**	**0**	0.165	0.507	1.052	0.372	**8**	**0**	0.127	0.455	0.997	0.34	**1**	**7**	87.5%	<0.04	0.095	-	**9**	**0**	0.114	0.143	0.301	0.062	**1**	**8**	88.9%	<0.095	0.317	-	-
ΣCar.PAHs (µg/L)	**8**	**0**	0.061	0.208	0.438	0.155	**8**	**0**	0.051	0.195	0.409	0.145	**0**	**8**		100%<0.035		-	**9**	**0**	0.052	0.065	0.131	0.025	**1**	**8**	88.9%	<0.035	0.175	-	-
Σnon-Car. PAHs (µg/L)	**8**	**0**	0.104	0.3	0.631	0.218	**8**	**0**	0.074	0.26	0.588	0.197	**1**	**7**	87.5%	<0.026	0.06	-	**9**	**0**	0.061	0.078	0.17	0.035	**1**	**8**	88.9%	<0.06	0.142	-	-
ΣLMW-PAHs (µg/L)	**8**	**0**	0.045	0.059	0.1	0.019	**8**	**0**	0.045	0.058	0.097	0.018	**0**	**8**		100%<0.025		-	**0**	**9**		100%<0.025		-	**0**	**9**		100%<0.025		-	-
ΣMMW-PAHs (µg/L)	**8**	**0**	0.047	0.19	0.41	0.147	**8**	**0**	0.037	0.163	0.377	0.135	**0**	**8**		100%<0.01		-	**9**	**0**	0.023	0.034	0.098	0.024	**1**	**8**	88.9%	<0.03	0.069	-	-
ΣHMW-PAHs (µg/L)	**8**	**0**	0.066	0.258	0.566	0.208	**8**	**0**	0.045	0.234	0.552	0.193	**1**	**7**	87.5%	<0.019	0.04	-	**9**	**0**	0.045	0.063	0.158	0.036	**1**	**8**	88.9%	<0.04	0.20	-	-

C_{10} – C_{40} (µg/L)	**8**	**0**	172.2	613.2	1545.6	506.1	**8**	**0**	144.5	514.9	1213.8	385.6	**1**	**7**	87.5%	<50	65.7	–	**9**	**0**	118.0	173.0	373.2	78.5	**1**	**9**	90%	<50	426	–	1000[¿]
C_{10} – C_{12} (µg/L)	**2**	**6**	<2.77	3.283	5	0.512	**1**	**7**	87.5%	<3.663	5	–	**0**	**8**		100%	<5	–	**0**	**9**		100%	<5	–	**0**	**10**		100%	<7.5	–	90[$]; 300[€]
C_{12} – C_{16} (µg/L)	**7**	**1**	<4.55	9.375	13.39	3.445	**7**	**1**	<3.913	7.707	13.34	3.328	**0**	**8**		100%	<5	–	**5**	**4**	<2.82	3.223	5	0.565	**0**	**10**		100%	<7.5	–	90[$]; 300[€]
C_{16} – C_{35} (µg/L)	**8**	**0**	138.6	471.0	1167.7	380.8	**8**	**0**	119.33	399.8	941.3	293.9	**1**	**7**	87.5%	<30	49.53	–	**9**	**0**	93.3	140.1	298.0	62.5	**2**	**8**	<30	59.55	319	86.50	90[$]
C_{35} – C_{40} (µg/L)	**8**	**0**	29.67	131.0	361.6	123.5	**8**	**0**	21.84	105.8	259.7	90.13	**1**	**7**	87.5%	<10	14.16	–	**9**	**0**	20.17	30.56	71.22	15.57	**2**	**8**	<10	19.24	102	27.58	–
OP (µg/L)	**6**	**2**	<0.04	0.131	0.338	0.104	**6**	**2**	<0.061	0.139	0.303	0.085	**0**	**8**		100%	<0.02	–	**5**	**4**	<0.026	0.049	0.124	0.032	**0**	**8**		100%	<0.02	–	0.1
OP1EO (µg/L)	**0**	**6**		100%	<0.024	–	**0**	**6**		100%	<0.01	–	**0**	**6**		100%	<0.02	–	**0**	**6**		100%	<0.01	–	**0**	**5**		100%	<0.01	–	0.9
OP2EO (µg/L)	**0**	**6**		100%	<0.45	–	**0**	**6**		100%	<0.01	–	**0**	**6**		100%	<0.02	–	**0**	**6**		100%	<0.01	–	**0**	**5**		100%	<0.01	–	0.91
OP3EO (µg/L)	**0**	**6**		100%	<0.033	–	**0**	**6**		100%	<0.028	–	**0**	**6**		100%	<0.02	–	**0**	**6**		100%	<0.04	–	**0**	**5**		100%	<0.011	–	0.91
NP (µg/L)	**5**	**3**	<0.166	0.374	1.19	0.181	**5**	**3**	<0.2	0.397	1.11	0.201	**5**	**3**	<0.22	0.428	0.673	0.167	**6**	**3**	<0.17	0.416	1.18	0.207	**2**	**6**	<0.1	0.127	0.39	0.1	0.3
NP1EO (µg/L)	**0**	**6**		100%	<0.18	–	**0**	**6**		100%	<0.22	–	**0**	**6**		100%	<0.2	–	**0**	**6**		100%	<0.18	–	**0**	**5**		100%	<0.15	–	0.64
NP2EO (µg/L)	**0**	**6**		100%	<2.54	–	**0**	**6**		100%	<1.49	–	**0**	**6**		100%	<0.36	–	**1**	**5**	83.3%	<0.067	1.66	–	**0**	**5**		100%	<0.38	–	0.37
NP3EO (µg/L)	**0**	**6**		100%	<1.27	–	**0**	**6**		100%	<1.49	–	**0**	**6**		100%	<0.42	–	**0**	**6**		100%	<3.54	–	**0**	**5**		100%	<0.74	–	0.3
BPA (µg/L)	**8**	**0**	0.247	0.542	1.179	0.314	**8**	**0**	0.169	0.48	0.933	0.249	**3**	**5**	<0.042	0.051	0.097	0.018	**9**	**0**	0.158	0.365	0.58	0.164	**3**	**7**	<0.05	0.054	0.07	0.008	0.24
TOC (mg/L)	**11**	**0**	2.34	10.06	23.03	7.08	**11**	**0**	2.06	10.56	24.96	7.50	**8**	**0**	2.95	8.9	19.30	6.618	**9**	**0**	2.963	11.19	22.4	7.096	**10**	**0**	1.51	8.978	19.1	6.652	12[¥]
TSS (mg/L)	**11**	**0**	22.42	74.34	205.8	56.95	**11**	**0**	18.87	69.03	200.8	55.11	**6**	**2**	<1.931	5.544	23.86	7.073	**9**	**0**	11.48	19.71	33.52	6.67	**5**	**3**	<2.5	5.59	15	4.06	25[¢]
Turb (NTU)	**9**	**0**	40.39	107.2	201.1	54.79	**9**	**0**	43.06	112.9	236.8	62.51	**8**	**0**	1.405	19.90	78.24	25.40	**9**	**0**	28.30	44.87	87.49	18.82	**8**	**0**	6.47	29.78	73.7	25.38	–
EC (µS/cm)	**9**	**0**	32.77	138.4	299.5	82.08	**9**	**0**	38.54	141.8	318.5	87.16	**8**	**0**	114.52	305.6	495.6	140.1	**9**	**0**	52.34	157.5	327	89.80	**8**	**0**	50.3	205.4	398	141.6	–
pH	**9**	**0**	6.799	7.148	7.308	0.156	**9**	**0**	7.026	7.148	7.409	0.11	**8**	**0**	7.543	7.867	8.135	0.181	**9**	**0**	6.965	7.109	7.22	0.098	**8**	**0**	5.62	7.083	7.8	0.646	–
Temp. (°C)	**9**	**0**	11.62	16.52	22.35	3.38	**9**	**0**	12.1	16.71	22.91	3.40	**8**	**0**	13.45	18.15	23.62	3.27	**9**	**0**	14.13	18.04	24.22	2.92	**8**	**0**	7.23	16.28	23.7	4.70	–

¿ Gothenburg's guideline value for aliphatic and aromatic hydrocarbons in stormwater (Miljöförvaltningen, 2013)

$ WHO's recommendation for aromatic PHCs in drinking water (WHO, 2008)

€ WHO's recommendation for aliphatic PHCs in drinking water (WHO, 2008)

¥ Gothenburg's stormwater annual average benchmark concentration at the point of discharge to receiving water body (Miljöförvaltningen, 2013)

¢ Protective threshold concentration against chronic effects on fish in freshwater (EC, 2006)

4.1. Highway runoff

In this section, the highway runoff quality was assessed from eight rainfall events A, B, C, G, H, I, J, K in respect of OMPs and conventional parameters.

4.1.1. Occurrence and event mean concentrations (EMCs)

TSS and turbidity: The EMC of TSS ranged from 22.4 to 206 mg/L (median: 54 mg/L) (Figure 9a). Onsite measurements also showed that the turbidity of samples ranged from 40.4 to 201.1 NTU for all rain events. The EMCs of TSS and turbidity were strongly correlated in SW (Spearman's R^2=0.9, p-value<0.05).

PAHs: MMW- and HMW-PAHs were frequently quantified in the highway stormwater samples: Flth, Pyr, BbF, BaP, and Bper were detected across all rain events in SW samples, while Chry and InP were detected in seven, BaA and BkF in six, and DahA in five of eight events (Table 3). Six out of eight carcinogenic PAHs had EMCs so high in SW that they exceeded PNECs for freshwater (i.e., BaP, BaA, Chry, BbF, DahA, and Bper). BaP, for example, the most potent carcinogenic PAH, was detected at EMCs between 0.006 and 0.064 μg/L (median 0.02 μg/L) which is 2-3 orders of magnitude larger than the PNEC (Figure 9e). Of the LMW-PAHs (including Nap, Acyl, Acen, Flu, Anth, Phen), only Phen was found in four of eight events in SW, but never exceeded the PNEC (0.3 μg/L). The EMCs of ∑16 PAH varied between 0.16 and 1.05 μg/L (median: 0.37 μg/L) (Figure 9c), around 42% of which were always attributed to carcinogenic PAHs.

PHCs: As shown in Figure 9f, the EMCs of total PHCs (C_{10}-C_{40}) in SW varied between 175 and 1539 μg/L (median: 385 μg/L). Lighter fractions, such as C_{10}-C_{12} and C_{12}-C_{16}, were rarely found in stormwater, while the heavier fractions, such as C_{16}-C_{35} and C_{35}-C_{40}, dominated the PHCs observed in highway runoff.

Phenolic substances: BPA, OP, and NP were detected in the runoff in eight, six, and five of eight rain events accounted for SW, respectively, while NPnEOs (n=1,2,3) and OPnEOs (n=1,2,3) were never quantified in SW samples (Table 3). The EMCs for BPA ranged between 0.247 and 1.179 μg/L (median: 0.39 μg/L). The range for NP was similar, varying from <0.166 to 1.19 μg/L (median: 0.34 μg/L), while the range for OP was lower, between <0.041 and 0.338 μg/L (median: 0.08 μg/L). PNEC values defined for BPA, NP, and OP (0.24, 0.3, and 0.1 μg/L, respectively) were exceeded eight, four, and three times across the eight studied rain events for SW, respectively.

4.1.2. Intra-event concentration (IEC) variations

The IECs of OMPs in stormwater were analyzed based on eight rain events A, B, C, G, H, I, J, and K (runoff quality data were missing for events D, E, and F). According to the OMP pollutographs shown in Figure 9, in general, all OMP concentrations in the stormwater runoff varied considerably during the rain events. However, no clear rising or falling trend was observed among all events. The most substantial IEC variations

in OMPs in runoff occurred during rainfall events C, H, I, J, and K (i,e. among events with relatively higher intensity variations, larger depth and I_P), while the smallest variations occurred during events A, B, and G (i.e. among events with lower intensity variations and smaller depth), except for BPA whose IEC variations during events A, B, and G were also comparable with the other events. In addition, the OMPs' pollutograph peaks occurred in all stages of the runoff inflow (Figure 9): for PAHs, PHCs, TSS, and turbidity, rain events C, H, I, and K were often identified with a peak at the middle phase, event A at the beginning, and event J at the end phase of the runoff. Phenolic substances, however, behaved differently. The IEC of BPA showed peaks also at the beginning phase of events G, H, and I, at the middle of event J, and at the end of storm event K (Figure 9g). For OP and NP, IECs showed peaks at the beginning phase of event I and at the end of events C and K (as well as A and H for OP) (Figure 9h-i).

Although discernible concentration peaks were observed for OMPs, M-V curves (Figure 9) revealed that the cumulative loads (M) of OMPs and TSS increased relatively proportional to the cumulative runoff volume (V), with small to moderate deviations from the bisector (β=1). For seven out of eight events, 80% of the OMPs load is transported in more than 60% of the volume, so the M-V curves often varied between zones 2 to 5 (as defined in Figure 8). Therefore, a "30/80 first flush" (as defined by Bertrand-Krajewski et al. (1998); see section 3.3) most often did not occur for the OMPs. Nonetheless, during event A (in which a concentration peak was observed at the beginning phase of runoff for most OMPs), the "30/80 first flush" occurred for BbF, Bper, ∑16PAH, and HMW-PAHs. Otherwise, the M-V curve fell at least into zone 2 (i.e. very close to first flush conditions) for TSS, Flth, BaP, ∑Car-PAH, ∑Non-car PAHs, C_{10}-C_{40}, C_{16}-C_{35}, C_{35}-C_{40}, and BPA. A "30/80 first flush" occurred also for BPA during event B, although a better interpretation of this event would probably require more subsamples. Moreover, most OMPs' M-V curves frequently fell into zone 2 during rain events B and C, and zone 5 during rain events G and J, as well as event K for phenolic substances. The M-V curves varied between zones 2, 3, and 4 during the rest of the rain events (i.e. H, I, J, K). Refer to Figure 9 for more details about the OMPs' mass load conveyance with respect to the stormwater volume passed.

It is worth noting that the analysis of IEC variations and M-V curves at SW during rain events A, B, C, and G was affected by the low numbers of subsamples (2-4) and thus, might be less accurate. Relatively higher uncertainties in OP and NP concentration measurements might also have influenced the investigation. It was not possible to explore the intra-event variations of LMW-PAHs and C_{10}-C_{12} since their concentrations were often below the LoQ.

4.2. Treatment train (TT) performance in OMP removal

Assessment of the OMP concentrations in the TT outflows included eight to ten rainfall events as shown in Table 1. This section presents the results of EMC and IEC analysis of the evaluated parameters for each TT unit as given in Figure 9 and Table 3, followed by a discussion of the removal efficiency and the effects of each treatment factor on the removal. The removal efficiencies of OMPs in a given unit were investigated over five to seven rainfall events depending on the number of events where the EMC data for both inflows and outflows were available.

The removal efficiency of the TT could not be calculated for Nap, Acyl, Acen, Flu, Anth, and OPnEO and NPnEO (n=1,2,3) as these were never quantified at SW or at any of the TT units' outflows (except for NP2EO and Flu which were only found in one subsample at SF_{out} and GPT_{out}, respectively). It was not possible to investigate the treatment of lighter PAH and PHC fractions in filter cell outflows properly because they were not often detected in the SW and GPT_{out}, probably due to partial loss by volatilization and more limited use of gasoline having lighter fractions than diesel fuel (Leroy et al., 2016). Therefore, the results and discussion of the removal efficiencies by the TT units, presented in Figure 10, will focus on the quantified parameter only.

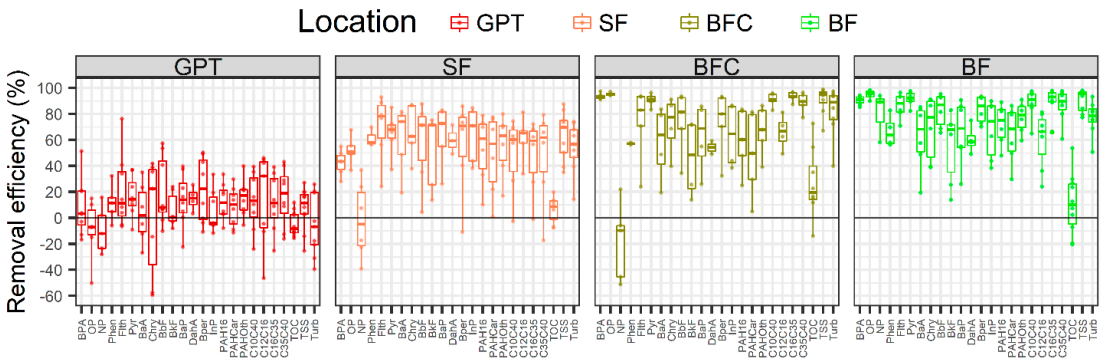


Figure 10. Removal efficiencies of TT units for selected parameters

4.2.1. Gross pollutant trap (GPT)

As can be implied from Figure 9 and Table 3, the occurrence, EMCs, and IECs of all OMPs, TSS and turbidity at GPT_{out} followed similar patterns as observed at SW. No statistically significant differences were found between SW and GPT_{out} quality for both EMC and IEC data. Thus, the same conclusions as for SW can be drawn regarding the inter- and intra-event variations of OMPs and other conventional parameters for GPT.

4.2.2. Non-vegetated sand filter (SF)

The EMC of OMPs at SF_{out} varied greatly. EMC levels of TSS at GPT_{out} significantly dropped, with a range of 10.4–35.0 mg/L (median=18.9±2.3), after being treated by the SF cell and rarely exceeded the protective threshold concentration of 25 mg/L against

chronic effects in freshwater (EC, 2006). Turbidity at SF_{out}, ranging between 18 and 90 NTU (median: 44.9), followed a similar inter-event and intra-event pattern of variations as obtained for TSS (Figure 9b). Consequently, median removal percentages of 70±8% for TSS and 57% for turbidity were achieved by the SF.

The EMCs and occurrence results at SF_{out} varied a good deal between the different PAH substances. Phen, the only substance of the LMW-PAHs found at SW and GPT_{out}, was never found at SF_{out}, indicating efficient removal. Both MMW-PAHs and HMW-PAHs, however, were found at SF_{out} during at least one up to nine out of nine events. Pyr, BbF, and Bper were found with the highest occurrence (nine events), Chry and Flth with a moderate occurrence (5–6 events), and IP, BaA, BaP, BkF, and DahA with the lowest (1–4 events). For some of the most dangerous PAHs found at SF_{out}, such as Pyr and Chry, EMCs were considerably higher than the PNEC values. Median PAH Re% at SF ranged between 60% and 80%, and among the substances, the medium and high weight molecules Flth, BbF, Bper, and InP showed higher Re% (median> 70%), while Phen and DahA had relatively lower Re% (median< 50%) (Figure 10).

PHCs were repeatedly found in the SF outlet (C_{10}-C_{40} median EMC: 148±19 µg/L but always below Gothenburg's guideline value of 1000 µg/L (Miljöförvaltningen, 2013)). C_{16}-C_{35} and C_{35}-C_{40} (i.e. heavier PHC molecules) were identified as the predominant PHC fractions in all samples, while C_{10}-C_{12} and C_{12}-C_{16} (i.e. lighter fractions) only accounted for a maximum of 4% of total PHC concentrations at different sampling points. SF removed 60±14% of the total PHCs and showed a similar Re% variation for C_{16}-C_{35}, and C_{35}-C_{40} fractions as for the total PHCs (Figure 10).

BPA was found in all samples at SF_{out}, while OP and NP were found in five and six out of nine rain events, respectively. Analysis of the EMCs at SF_{out} revealed that there was no significant difference in the EMCs of BPA and NP between GPT_{out} and SF_{out} so that the PNECs (0.24 and 0.3 µg/L, respectively) were still exceeded in seven of nine rain events for BPA and considering uncertainty, three to seven of nine events for NP. So, the median Re% by SF was limited to 43±22% for BPA and -5±46% for NP. In contrast, the EMCs of OP at SF_{out} were considerably reduced, having levels below PNEC (0.1 µg/L) with a median of 0.035±0.013 µg/L, which resulted in a 51±24% removal efficiency by the SF.

4.2.3. Vegetated biofilter (BF)

In general, the vegetated biofilter BF (and BFC) was able to treat a majority of the OMPs effectively. There were statistically significant differences between GPT_{out} and BF_{out} for the EMCs of phenolic substances, PAHs, PHC fractions, TSS, and turbidity, except for DahA due to large analytical uncertainties. Although the maximum removal for most OMPs reached a high percentage ranging between 70 and 98%, the Re% of most OMPs varied over a wide range and was highly affected by the ratio of influent EMC with respect to LoQ (discussed in Paper II, section 4.6).

The EMCs of TSS at BF_{out} were always below 26.7 mg/L with a median of 3.0±0.9 mg/L, which is far below the 25 mg/L threshold (EC, 2006). Moreover, turbidity was always below 73.7 NTU (median: 29.8 NTU) at BF_{out}. As a result, BF, on average, removed TSS by 95±3% and turbidity by 79%, both of which were statistically significantly higher than SF's removal performance (70±8% and 57%, respectively).

PAHs and PHCs were rarely found at BF_{out} (and BFC_{out}) which indicates efficient removal. Only during one event (rain C) did the outflow contain heavier fractions of MMW-PAHs, HMW-PAHs and C_{16}-C_{40}. In this rainfall event, the EMCs of PAHs were also observed at their maximum levels at SW and GPT_{out}. The median treatment efficiencies by the BF cell were 75±6% for Σ16PAHs, 69±19% for BaP, and 91±9% for C_{10}-C_{40}.

OP was never found in the vegetated biofilters outflows, so had been removed by the filter. However, BPA and NP were found at BF_{out} in three of ten and two of eight rain events, respectively. As shown in EMC distributions in Figure 9g-i, after BF, the EMCs of BPA, NP and OP decreased to below the PNEC values, resulting in a high median Re% of 91±7% for BPA, 95±6% for OP, and 74±19% for NP.

4.2.4. Chalk-amended vegetated biofilter (BFC)

Compared to BF cell, although the chalk amendment (10% w/w crashed limestone) in BFC caused an increase in the median event mean values of pH (for about 0.8) and EC (for about 100 μS/cm) (details in Table 3), the study found no significant difference between the performance of BF and BFC in removing OMPs, except for NP (which is discussed separately). Nevertheless, NP was the only OMP for which BFC and BF significantly differed regarding the observed outflow EMCs and obtained removal efficiencies. NP was found at BFC_{out} in five of eight rain events with the median EMC of 0.41±0.12 μg/L, which was comparable to the EMCs at SW and GPT_{out} (Re% of -10±66%). The removal efficiencies by BFC are summarized in Figure 10, but for more details about the BFC removal efficiencies, the reader is encouraged to refer to Paper II, section 3.2.3.

4.2.5. Intra-event concentration (IEC) variations in TT units' effluents

As illustrated in Figure 9, the IECs in GPT_{out} were associated with those observed for SW, so more or less the same interpretations as for SW can be made for GPT regarding the variations in pollutographs and M-V curves. Nonetheless, comparing the SW and GPT pollutographs showed that GPT can slightly attenuate the sharp peaks recorded in SW, randomly across the events. Again, the IEC observations highlighted the ineffectiveness and unreliability of GPT on the stormwater quality in the TT facility. The pollutographs for OMPs and TSS in BFC_{out} most often ranged below LoQs or showed small variations around LoQs when the concentrations were measured (which consequently led to an approximately proportional increase of cumulative mass with

cumulative volume (MV curves were very close to bisector)). The only exception for the IECs observed at BFC_{out} was NP with high, random variations which were related to leaching from the biofilter construction material. Thus, in the following, the results of IEC variations and M-V curves were presented only for the SF during nine rain events from C to K.

OMPs concentrations at the SF outflow generally varied over the course of events (Figure 9), unless the concentrations in subsamples were censored or very close to LoQ (often observed during events G, H, and I for Phen, Flth, Chry, BaA, BkF, DahA, InP, C_{10}−C_{16}, and OP). In contrast to the highway runoff and the GPT outflow, concentration peaks of all OMPs, TSS, and turbidity either occurred at the beginning of the effluent events within the first 100 m^3 of the effluent, or concentrations appeared relatively stable throughout the SF outflow, unless a sharp peak or rising concentration in the middle towards the end of the storm event occurred at SW/GPT_{out}. Again, the only exception for such an observation was NP due to the potential leaching from the facility's construction material. It is noteworthy that higher concentrations observed at SF_{out} during the events usually resulted in higher IEC variations whereas in the other events, generally low IECs close to LoQ affected the magnitude of the variations.

Further IEC analysis revealed that, in general, deviations from the bisector in the M-V curves of OMPs and TSS in SF_{out} were smaller than those observed in SW and GPT_{out} (Figure 9a-b) indicating that the pollutant loads were discharged relatively more evenly over the course of the outflow event. Moreover, deviations below the bisector (zones ≥4) were less common in the SF_{out}.. Event J was the only exception as illustrated in Figure 9, due to the event duration being longer than the filter cell's detention time making the SF's effluent load follow the GPT's pattern. Therefore, no "30/80 first flush" event was observed at SF_{out} and for over ~90% of the events, the M-V curves at SF_{out} fell into either zone 3 or zone 2 but still very close to zone 2. Nevertheless, the finding regarding the cumulative pollutant load discharged from SF remains unclear for the last part of events D, G, and J in which the collected subsamples did not cover the whole SF outflow event (10–30% of volume was not sampled) (Table 1). More specifically, after 30% of the total SF outflow volume, maximum 50–60% of the total mass of TSS, PAHs, and PHCs (except C_{10}-C_{12}) was discharged from the cell. For TSS, PAHs, and PHCs load discharge, the highest deviation from the bisector line was often identified in events C, J, and K, while for BPA, this happened in event I. This might be explained by either greater observed IEC variations of OMPs (during events C and K) or higher recorded outflow rates at SF_{out} (in events I and K).

4.3. Environmental risk analysis

Apart from the removal efficiencies, the environmental risks of OMPs in stormwater were considered in order to examine the TT performance for OMPs reduction. Total environmental risks (R_T) of selected OMPs over eight to eleven events were estimated

in runoff water and compared with those in the outflow of each treatment unit (Figure 11).

R_T of TSS and 11 OMPs (BPA, OP, NP, and eight PAHs: Flth, Pyr, BaA, Chry, BbF, BaP, DahA, Bper) at SW exceeded the potential risk level (R_T>1), while that was not the case for C_{10}-C_{40}, three PAHs (Phen, BkF, and InP), and probably NP (if considering NP's associated errors). Similarly, previous road runoff quality studies have also reported that the OMPs with the potential risk as previously mentioned are among the most frequently detected micropollutants in stormwater with concentrations higher than their EQSs (Mutzner et al., 2022).

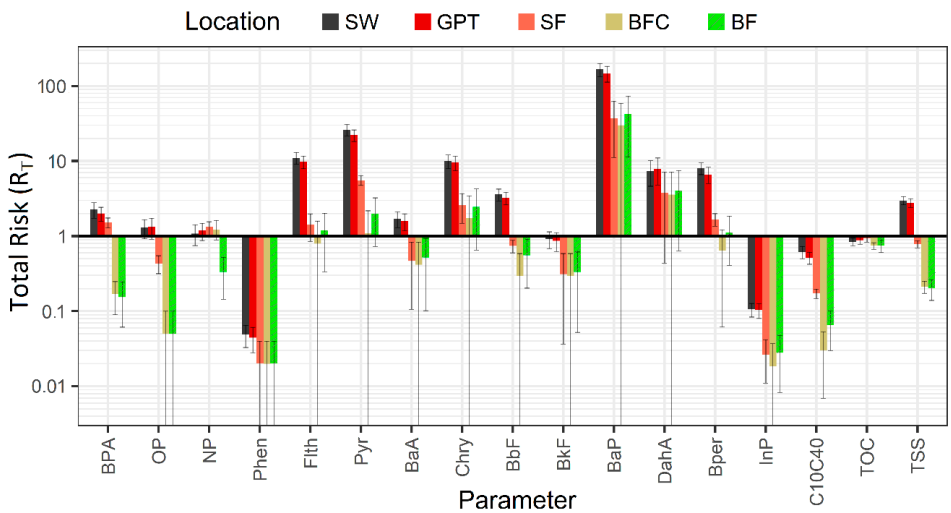


Figure 11. Total risk (and associated uncertainty) of selected parameters at different sampling locations

For the TT unit's outflows, GPT displayed a slightly lower but comparable R_T to that of SW, which was expected due to its inadequate OMP treatment. The SF cell, however, did reduce the risk of OMPs and TSS to some extent when compared to SW and GPT (excluding NP due to possible leaching). For TSS, OP, BaA, BbF, BkF, and probably Flth and DahA (if considering their associated errors), the SF section was quite effective, leading to their total risk falling to safe levels (R_T<1). However, the SF section was not successful in adequately reducing the environmental risks of BPA, Pyr, Chry, BaP, DahA, and Bper.

The vegetated biofilters BFC and BF were more effective in reducing OMP risk levels than SF. Both BFC and BF performed similarly in terms of environmental risk reduction, effectively lowering the risks of BPA, OP, Flth, BaA, BbF, Bper, and TSS to safe levels (R_T<1), which previously had high risk levels in SW and GPT_{out}. Nonetheless, it is unclear whether extremely hazardous OMPs, such as Pyr, Chry, BaP, and DahA, reach a safe level after BFC and BF treatment since the LoQ was above their very low PNECs.

5. Discussion

5.1. Highway runoff quality

5.1.1. Comparison of EMCs with other studies

5.1.1.1. TSS and turbidity

Although the EMCs of TSS were near the low end of globally-observed mean values for major roads (110–5700 mg/L according to Lundy et al. (2012)), they still exceeded the European quality objective of 25 mg/L (the protective threshold against chronic effects in freshwater (EC, 2006)) in six out of eight rain events. The EMCs of TSS were comparable with those reported in scientific literature describing studies of runoff quality from Swedish/European/North-American motorways (see Paper I, Table 4), but noticeably lower than those reported for some roads with higher traffic loads (Flanagan et al., 2018; Gasperi et al., 2014; Kayhanian et al., 2012), and lower than the levels previously observed by Lange et al. (2022) (158 mg/L) for the same catchment. Meanwhile, we must also assume that the 50-meter-long transportation pipe at this site may have attenuated stormwater TSS load to some degree before the runoff reached the SW sampling point; this would be especially relevant during less intense rainfall.

5.1.1.2. PAHs

Similarly, Mutzner et al. (2022) concluded that MMW- and HMW-PAHs are among the most commonly detected and dangerous substances, not only among all PAHs but also across a wider range of micropollutants in stormwater flows. The results for LMW-PAHs agreed with other studies; these are less likely to be detected in stormwater (Järlskog et al., 2021), since they have much greater volatility and relatively smaller sediment adsorption coefficients (K_{OC}) than other PAH fractions (Hawthorne et al., 2006; Khodadoust et al., 2005) (see Paper II, Table S2 for more details). The EMC range of ∑16 PAH observed in this study fell within the range typically expected for major roads (0.03–6 μg/L) according to Lundy et al. (2012). However, the concentrations were lower than those reported in other studies of road catchments listed in Table 4, Paper I, regardless of traffic load. Given that MMW- and HMW-PAHs are predominantly found in the particulate phase (Markiewicz et al., 2017) (as the EMCs of TSS and ∑16 PAHs in SW were significantly correlated in this study too; Spearman's R^2=0.74 and p-value<0.05), it is possible that the relatively low TSS levels recorded in this study contributed to the finding. The low TSS levels might be partly explained by the partial deposition of stormwater sediments along the transport pipe (which had a low slope of 0.5%) from the catchment to the facility downstream.

5.1.1.3. PHCs

The observed median EMC of total PHCs was similar to previous reports by Gasperi et al. (2022) and Leroy et al. (2016), but lower by one-half to one order of magnitude than

those observed from roads with either lower or higher traffic loads compared to this site (Järlskog et al., 2021; Kayhanian et al., 2007; Zhang et al., 2014) (refer to Paper I, Table 4). The predominance of the heavier PHC fractions is because the lighter fractions have higher volatility and much lower Koc than heavier fractions (>C_{16}) (refer to Paper II, Table S2). Aromatic/aliphatic compounds above C_{20} are neither volatile nor soluble in the aquatic phase and are thus likely to be absorbed by suspended solids (Reed & Stemer, 2002). As evidence, there were strong to very strong correlations between TSS and C_{16}-C_{35} and C_{35}-C_{40}, statistically (R^2>0.69, p-value<0.05). Moreover, the observed concentrations of total PHCs often fell below the city of Gothenburg's local guideline maximum threshold of 1000 μg/L for releasing PHC-contaminated stormwater to freshwater (Järlskog et al., 2021; Miljöförvaltningen, 2013). However, this threshold was exceeded by the EMC in two of eight rain events.

5.1.1.4. Phenolic substances

The median EMCs of BPA and NP in the runoff from major roads in this study were often similar to, or sometimes lower than, those measured in previous studies carried out in Sweden and Germany (see Paper I, Table 4). The observed differences in EMCs can be attributed to variations in traffic load, which is a primary factor affecting the release of phenolic substances (Kalmykova et al., 2013). Although catchments in urban areas compared to highways are expected to include more sources emitting phenolic substances (e.g. surface coating paints, building roof materials, PVC gutters, etc.), the EMCs of OP in the stormwater were found to be higher than those previously reported in diverse urban catchments (Bressy et al., 2012; Gasperi et al., 2014). This is likely due to the primary source of OP being tire wear particles (Flanagan et al., 2019a; Lamprea et al., 2018), which are more prevalent on highways carrying heavier and/or faster vehicles. Additionally, the stormwater collection pipes made of high-density polyethylene (HDPE) in the catchment, so may also release phenolic substances, including OP, into the stormwater. Further details on the observed levels of phenolic substances and their potential sources in the catchment are discussed in Paper I, section 3.1.1.

5.1.2. Intra-event concentration variations in runoff

The M-V curves were very variable and dispersed for each OMP and for the series of rainfall events. These variations may be due to the different pollutant characteristics, changes in the availability and transport of pollutants on the pavement surface, as well as rain characteristics such as changes in the runoff volume, flow rate, and ADP (Bertrand-Krajewski et al., 1998; Christian et al., 2020; Deletic, 1998). The preliminary investigations of the rain characteristics showed that in this study, the IEC variation of OMPs was reasonably associated with rain intensity (and flow rate) variation as depicted in Figure 12 and Figure 13. However, given the very large number of factors affecting pollutant accumulation on surfaces and subsequent transport with stormwater runoff, a larger number of rainfall events would have been required to produce a representative

set of pollutographs to obtain generally applicable relationships to rain characteristics. Furthermore, in the case of events A, B, C, G, and J during which M-V curves of OMPs (except phenolic substances) fell into zones 1, 2, or 5, (due to an elevated concentration either at the beginning or end phase of the storm), the rain hyetograph showed a few clear peaks at those phases (Figure 12). But in other events such as I and K, several flow peaks were observed in the hyetograph, which led to M-V curves of OMPs closer to bisector, as other studies have concluded (Bertrand-Krajewski et al., 1998). However, this was not the case for BPA in events G and J, and for NP and OP in event J.

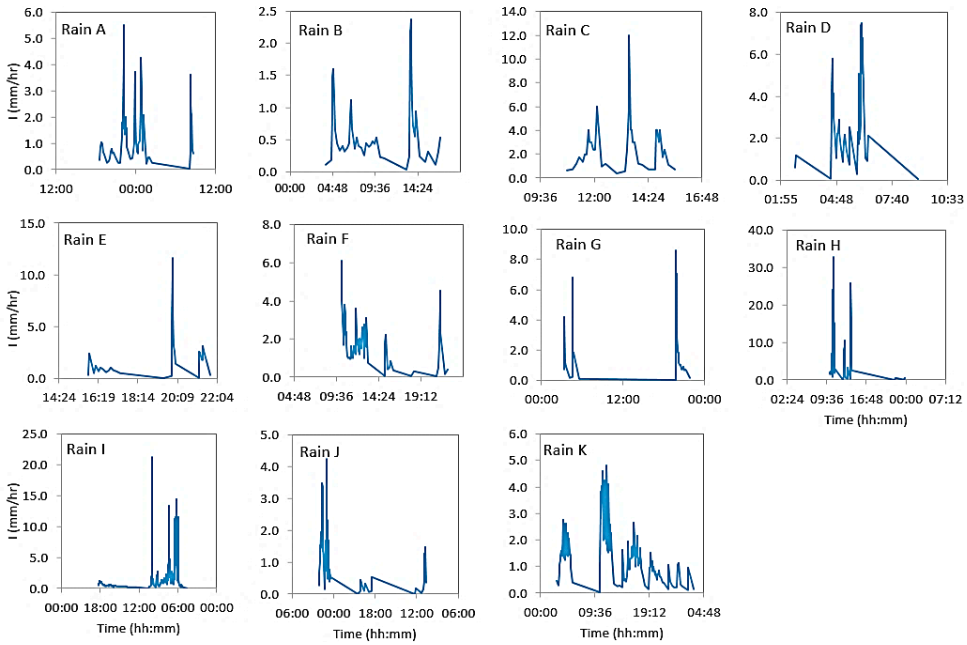


Figure 12. Rain intensity variations during the events (hyetographs with a resolution of 0.1 mm)

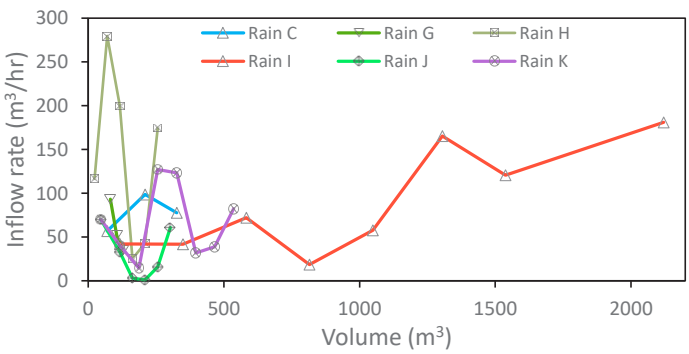


Figure 13. Inflow rate variations during the events (hydrographs with respect to volume)

Although it is believed that a first flush event is more likely to happen for smaller catchments (Lee et al., 2002), "30/80 first flush" was rarely observed for the small catchment evaluated in this study, which again emphasis on the complexity of flush phenomena and the fact that many explanatory variables such as rain characteristics, spatial characteristics, climatic and traffic load variations are needed to adequately describe the behavior of MV curves (Reinholdt Jensen et al., 2022).

Another finding was that the IEC of quantified PAHs and heavier PHCs (but not phenolic substances) were strongly associated with both/either TSS and/or turbidity during the rain events (except for those events having a few intra-event data points) so that Spearman's correlations with ranks above 0.7 ($p<0.05$) were obtained during events H, I, J, and K (events identified with ≥5 data points). This was expected for pollutants that are predominantly particle-bound and/ or in the particulate phase (Galfi et al., 2016; Lange et al., 2022). The correlation also highlights the importance of the availability and transport of particles in the road catchment during the event. The TSS/turbidity intra-event variations are linked to the rain intensity and inflow rate, as earlier studies have suggested (Deletic, 1998; Galfi et al., 2016), while some others are not (Ly et al., 2019). During events I and J, the aforementioned OMPs were only correlated with turbidity, and not with TSS. These two rain events had a relatively long rain duration (>40 hr, which resulted in a lower mean rain intensity).

Although some studies of TSS, metals, nutrients, and microbes such as coliforms have reported concentrations peaking early during the storm and then falling over time with commonly-seen first flush events (Cho & Lee, 2017; Galfi et al., 2016; D. Li et al., 2015; Maniquiz-Redillas & Kim, 2014), in this study, early-phase peaks and first flush were rarely observed for the OMPs. The observation was in line with the findings of Lange et al. (2022) about the IECs of total metals (which was correlated with TSS) in the same catchment. The IECs of BPA, however, were also elevated during the initial phase of 50% of events, which can be related to somewhat different characteristics of BPA compared with PAHs and PHCs. Other studies have also reported early-phase peaks more commonly seen for dissolved fractions of metals (Lange et al., 2022; Nicolau et al., 2012; Sansalone & Cristina, 2004). Since BPA can be found in stormwater in colloidal/dissolved forms at comparable levels to its particle-bound form due to its relatively lower affinity to organic carbon in solid phases (Flanagan et al., 2018), such a decreasing pattern of IEC for BPA can probably be explained by dilution effects during the runoff, as suggested by Nicolau et al. (2012), associated with the fact that higher colloidal/dissoluble pollutants are more available and transportable at the beginning of the storm.

5.2. Treatment train functionality

5.2.1. Pretreatment performance by the GPT

In general, GPT did not contribute to the stormwater treatment significantly (median Re% of OMPs did not exceed 20%), which is in line with the results of previous studies of similar sedimentation basins for TSS and PAHs (Pettersson et al., 2005) and NPs (Björklund et al., 2009). In addition, no removal effect by the same GPT has been shown before for trace metals (Fahlbeck Carlsson, 2021) and microplastics (Lange et al., 2021, 2022) at this site. The ineffectiveness of the studied GPT can be linked to its undersized design (with respect to the catchment area) (Lieske et al., 2021, Lange et al., 2021, 2022), pulse outflow (instead of a constant outflow, as described in the methods section, which may cause turbulent flows and particle resuspension in the chamber during the discharge), and a generally inefficient removal of finer particles, usually found abundantly in stormwater (Pamuru et al., 2022), by such relatively small sedimentation facilities.

5.2.2. Non-vegetated sand filter (SF)

Overall, the SF cell exhibited considerable improvements in the quality of GPT outflow (and, thus, also the stormwater SW). However, its performance varied based on the physiochemical properties of the different OMPs. Apart from NP's negative Re% which was probably linked to possible leaching from the TT construction material (most probably drainage pipes and EPDM fabrics; see Paper II, section 4.5), SF was generally less efficient for BPA and OP, compared with quantified PAHs, PHCs, and TSS. MWH- and HWH-PAHs, and C_{16}-C_{40} fractions have a higher partitioning to suspended solids compared with phenolic substances. This is due to their lower water solubility, greater hydrophobicity (larger K_{OW}) and greater tendency to adsorb to the organic carbon in sediments/filter media and Fe particles (larger K_{OC}) (Andersson et al., 2018; Diblasi et al., 2009; Gasperi et al., 2022; Leroy et al., 2016). Thus, these particle-bound PAHs and PHCs detected in the study were more likely to be retained in the SF medium through particle filtration processes compared to phenolic substances (David et al., 2015; Furén et al., 2022). This idea was supported by the strong correlation between the removal efficiencies (Re%) of most PAHs and heavier PHC fractions (C16-C35 and C35-C40) and the Re% of TSS and turbidity by the SF cell. However, none of the phenolic substance removals were statistically correlated to TSS and turbidity. These findings are consistent with previous studies that have suggested sand filters may not be effective for treating soluble OMPs, such as triazine herbicides, biocides, and triclosan-methyl (Spahr et al., 2019), as the primary mechanisms responsible for removal in sand-based filters are physical particle straining and colloidal attachment to the filter medium.

5.2.3. Vegetated biofilter (BF)

In general, the vegetated biofilter (BF) performed better than the non-vegetated filter (SF) with the same filter material. The presence of vegetation (including a finer root-soil

layer on top) resulted in significantly increased Re% (compared to SF) for BPA, OP, NP (in BF only), and also to a lesser extent for Pyr, C_{16}-C_{40}, and TSS (Re% for BF reached above 90%, being at least 30% higher than those for SF), but not as great as for the rest of PAHs substances and PHCs fractions. One of the reasons for the positive effect of vegetation on OMP treatment can be related to the enhanced filtration processes by the (finer) 3–4 cm topsoil layer and/or greater amount of accumulated particles on the vegetated filters. During the filtration processes of particle-bound pollutants, a vegetation layer (and the previously accumulated particles) can greatly contribute to the removal of OMPs by trapping particles in that topsoil layer (especially larger ones (Chu et al., 2021)). Two additional studies carried out at the same facility, by Lange et al. (2021) and Fahlbeck Carlsson (2021), provided further evidence to support the efficacy of vegetated biofilters (BF and BFC). It was observed that these biofilters were also more effective than the SF in removing microplastics and (total and dissolved) metals. The improved performance was attributed to the enhanced particulate filtration capacity of the vegetation soil layer.

In addition, the soil layer containing vegetation had been enhanced with 2.5–5% organic mulch (to promote plant growth), which may aid in the absorption of BPA, OP, NP, and colloidal/dissolved fractions of MMW-PAHs, HMW-PAHs and C_{16}-C_{40} (Duan et al., 2015; Furén et al., 2022; Hong et al., 2006).

It is important to note that plant-related processes such as uptake are likely to be unimportant during the rain events since most of the found OMPs were categorized as low soluble and hydrophobic organic compounds (log K_{OW} >4), rendering them unavailable for plant uptake. Nevertheless, they can still be retained and stabilized in the root epidermis (Leroy et al., 2015b; Ruppelt et al., 2020).

5.2.4. Chalk-amended vegetated biofilter (BFC)

The results suggest that chalk may not have much practical importance in sand-based biofilter media for OMP removal. Originally, adding chalk to the filter material was recommended to enhance metal removal (DWA-M 187, 2005). However, it is important to note that this single study cannot be used to draw a definitive conclusion about the preference for chalk amendment in OMP treatment.

Considering the relatively high NP removal efficiency achieved by the BF cell, the negative Re% of NP in BFC was related to a potential leaching from the filter cell construction materials (i.e. EPDM fabrics, geotextile membranes, and drainage pipes, illustrated in Figure 6). Previous leaching studies have reported that EPDM rubber fabrics, geotextile membranes made of polypropylene and HDPE plastic drainage pipes can be a source of trace phenolic substances which are used as additive compounds in such materials for soil-water systems (Flanagan et al., 2019a; Gromaire et al., 2014; Magnusson & Mácsik, 2017; Nilsson et al., 2008). A detailed discussion about the NP leaching is provided in Paper II, section 4.5.

5.2.5. Intra-event concentration variations in the filter cells

As mentioned before, since many concentrations in BFC_{out} subsamples were censored or measured at very low levels around LoQs, the IECs of OMPs and TSS did not vary considerably (except for NP due to the potential leaching). The following discussion, thus, focuses on the results of the intra-event variations obtained for the SF outflow.

Compared to highway stormwater, concentrations appeared relatively stable throughout the SF outflow events. Since the cumulative volume of SF effluent in all the rain events was higher than the SF's pore volume (~30 m^3), and also the GPT_{out} hydraulic load (~2.12 m/hr) was higher than the filters' saturated infiltration rate (maximum of 0.36 m/hr, according to technical design info; table S1 in Paper II), ponding occurred on the top of the filter cells after a few GPT discharge pulses. Therefore, an IEC variation attenuation in pollutographs is expected through the mixing effect of the inflow water on top of the filter during the detention time. As a result, smaller deviations from the bisector of the M-V curves were often observed for SF effluent events than those observed for highway stormwater and GPT effluent. The exceptions for such behavior were events I and J, for which the incoming storm duration (>40 hr) exceeded the detention time of the filter cells (~24 hr for 20 mm of rain). It is also worth noting that no significant difference was observed between phenolic substances and PAHs/PHCs regarding such concentration stabilization effect in the SF.

Although no "30/80 first flush" was observed for any parameters at SF_{out}, the concentration of OMPs and TSS frequently increased during the early phase of the SF's effluent events and then was stabilized towards the end provided that the concentrations were at levels sufficiently greater than the LoQ (bigger than 4×LoQ, according to the findings in Paper II, section 4.6.2). A similar variation pattern of IECs peaking at the beginning and then decreasing during the effluent event has been reported by other field studies of trace levels of total/dissolved metal concentration in the biofilter outflows (Davis, 2007; Hatt et al., 2009; Lange et al., 2022), specially Lange et al. (2022) who investigated one of the vegetated biofilters (BFC) in the same facility. In addition, mesocosm experiments by Ulrich et al. (2015) on the transport of trace levels of organic pollutants (incl. prometon, atrazine, tris(3-chloro-2-propyl)phosphate, benzotriazole, and diuron) in biochar-amended biofilter basins also showed that concentrations peaks at the beginning phase of single-loading events (for 100 pore volume) during the first 50-100 pore volume followed by a decreasing trend. In general, the observed trend of OMPs at the SF effluent might be described by at least one of the following processes: **1)** flush of the fine particles (so the particle-bound OMPs) retained in the filter media between the events by the wetting front of the new event causing particle resuspension and aggregate breakup (Subramaniam et al., 2015), **2)** higher remobilization potential of dissolved/colloidal OMPs previously adsorbed and accumulated in the filter material that have low organic matter content (as with the studied SF cell) in the beginning phase of

the event (Tedoldi et al., 2016), **3)** early-phase OMP concentration peaks discharged from GPT outlet (specially in events C, I, and sometimes J), which might reflect the effect of high initial inflow rate (or rain intensity), as suggested by Deletic (1998), **4)** greater amount of OMP dilution in the detention pond of the filters coupled with more settling of particulate/particle-bound OMPs (before reaching the filter media) towards the end of the infiltration event (especially for heavier fractions of PAHs and PHCs), **5)** higher OMP volatilization, biodegradation, and/or photodegradation during the detention time in the pond and filter media towards the end of the infiltration event (especially important for lighter fractions of PAHs and PHCs and phenolic substances), **6)** faster infiltration rate of the wetting front at the beginning of the event before saturation conditions, resulting in faster transport of OMPs (more relevant to dissolved/colloidal fractions of OMPs and/or OMP ligands absorbed on mobile dissolved organic carbon/metal ions (Schwab et al., 2008; Tedoldi et al., 2016)).

5.3. Further discoveries by the environmental risk analysis

TT reduced the risk of OMPs at different levels, depending on the OMP and the type of treatment unit. Regarding the evaluated factors' impact level (i.e. pretreatment, sand filtration, vegetation, and chalk amendment), in general, the same outcomes as the removal efficiency study were achieved in terms of risk reduction. However, Re% alone might not be enough to provide a comprehensive understanding of the SCMs' functionality concerning the environmental impacts of the actual concentration levels in the outlet. If inflow concentrations are very high, even with a high removal percentage, outflow concentrations can still exceed environmentally relevant concentrations. Consequently, for some OMPs, there were differences between removal efficiency results and the risk ranking. For instance, the EMCs might have the potential to pose a risk in the outflows (R_T>1), while a high Re% was often observed for them at a given treatment unit. This was the case for Flth and BaP in all filter cells and Pyr in BFC and BF. Conversely, Re% can be low and considered insufficient, while the outflow concentrations may not be a concern from an ecotoxicological perspective. This was the case for Phen and BaA in all cells, NP in BF, as well as OP, BbF, C_{10}-C_{40}, and possibly TSS in SF. Other than these two situations, a similar conclusion was reached for OMPs in both methods, indicating that a low Re% agreed with a high risk ranking and vice versa. Nevertheless, to improve confidence in the risk analysis results, (as always) sampling more rain events would have been beneficial to obtain more accurate occurrence probabilities and to cover a wider range of rain depths and intensities, especially when the TT cannot handle the excess water which is bypassed during heavy rainfall events in which the OMPs environmental risks in the outflow are as high as in stormwater.

In addition, OMP pollutographs could provide valuable information about the intra-event PNEC exceedance. Since the IECs of most OMPs at SW and GPT_{out} (except Phen, InP, and C_{10}-C_{40}) varied above PNECs, so the intra-event risk quotients varied proportionally to the measured concentrations. Thus, in this case, the EMC analysis could

sufficiently identify the overall potential risks over the course of the events. However, comparison of the IECs in the SF effluent with the corresponding PNECs revealed that the elevated IECs of TSS, Flth, BaA, BbF, BaP, Bper, BPA, and OP at the beginning phase of SF effluent frequently exceeded the PNECs, while the range and median of EMCs over the series of events did not reflect that clearly (if at all). This may suggest a need for further control strategies to protect the water recipients (or recipients for water reuse applications) from the potential risks posed by the OMPs discharged during the beginning phase of the SF effluent event, which is, according to the results of this research as well as the study by Lange et al. (2022) of the same facility, equivalent to approximately the first 100 m^3 of the effluent (or the first three pore volumes of the SF cell).

6. Conclusion

The work described in this thesis showed that organic micropollutants (OMPs) are of concern in highway runoff. EMC analysis revealed that the runoff contained considerable amounts of phenolic substances, including BPA, OP, and NP, with concentrations above or around PNECs for freshwater. More common OMPs, such as PAHs and PHCs, were also identified in the runoff (mainly in the form of heavier weight fractions), although the observed concentrations often fell below the ranges reported in other studies carried out under similar conditions. Nevertheless, EMCs of MWM-PAHs and HWM-PAHs still exceeded the corresponding PNECs across most rain events. Five PAH substances (BaP, BaA, Chry, BbF, and DahA), classified as extremely or possibly carcinogenic, were observed among the potentially risky PAHs for aquatic environments (EMC>PNEC).

The performance of a stormwater treatment train (TT) facility comprising a GPT and three parallel filter cells with various design features (SF, BF, and BFC) downstream of the catchment was also investigated. The GPT did not significantly contribute to the stormwater treatment so that the OMP median removal did not exceed 20%. In contrast, the filter cells significantly improved the quality of stormwater received from the GPT outflow at different levels, depending on the cells' design features and OMP types. Of the filters, both vegetated filters (i.e. BF and BFC) performed better than non-vegetated filter (SF). There was a significant difference in the removal efficiency of BPA, OP, NP (in BF only), Pyr, C_{16}-C_{40}, and TSS between vegetated and non-vegetated cells, with BFC and BF having an at least 30% higher Re% than SF (Re%>90% in BFC and BF). The reason behind this difference is likely due to the vegetation's topsoil layer, which improves physiochemical filtration processes and increases absorption capacity with its organic carbon content. However, the difference was not as large for other PAHs substances and PHCs fractions. Further statistical tests showed no significant difference between BFC (with chalk in filter media) and BF (without chalk) performance for all OMPs studied, except NP (due to potential leaching), meaning that the chalk-amendment has likely no significant effect on OMP removal. However, this requires further study since the good efficiency of vegetation, in addition to generally low inflow concentrations of OMPs, might influence the results to observe the effect of chalk on removals clearly.

An intra-event stormwater quality assessment using a total of 40 intra-event subsamples collected over eight events revealed that the OMP concentrations in the highway stormwater noticeably varied and no straightforward pattern could explain the IECs and load conveyance of all OMPs along the course of the stormwater events. Nevertheless, the IECs and M-V curves for TSS, MMW-PAHs and HMW-PAHs, and C_{16}-C_{40} (the heavier PHC fractions) in runoff were rather similar, while different behaviors of those were observed for phenolic substances (especially BPA). Studying the M-V curves indicated that "30/80 first flush" did not occur frequently for any parameter (only once

out of eight events), but the mass transport of OMPs with respect to the conveyed volume considerably varied from one event to another, which resulted in some deviations from the M-V curves being relatively deviated from (5–6 events) with results very close to the bisector (2-3 events). Preliminary explorations identified the flowrate (or rainfall intensity) as a key factor controlling the IEC variations.

Further intra-event investigations into TT units' effluent concentrations using 155 subsamples collected over eleven events, revealed that the concentrations of TSS and OMPs in the effluent of SF also varied during the events. However, the magnitude of the variations (so the deviations of the cumulative mass transport with respect to the cumulative conveyed volume) were smaller compared to those in runoff (and GPT outflow). Thus, no "30/80 first flush" was observed in the SF's effluent and the pollutant loads were discharged more evenly during the outflow event. Nevertheless, the IECs peaks in the SF outflow often occurred at the beginning (within the first 100 m^3 out of maximum record of ~600 m^3) of the effluent events, followed by a concentration stabilization towards the end of the event. In the early phase of storm, elevated concentrations of TSS, Flth, BaA, BbF, BaP, Bper, BPA, and OP exceeded the PNECs, a fact that was not shown by the EMC-based analysis, thus highlighting the advantage of the IEC analysis. Moreover, the GPT had no significant effect on IEC variations of OMPs, so similar patterns to those in the corresponding highway stormwater were observed in the GPT effluent. The IECs of OMPs in the effluent of the BFC were mostly below LoQs.

The pollutant risk analysis provided a more comprehensive tool for stormwater quality assessment. According to the risk rankings, the overall treatment performance of the TT was reliable/adequate ($R_T<<1$) and robust (>90% risk reduction) for InP and C_{10}-C_{40}, moderate ($R_T<1$ but probably not adequate enough risk reduction) for OP (only in SF_{out}), BaA, BbF, BkF, and TSS (only in SF_{out}), but insufficient ($R_T>1$) or unreliable (low risk reduction) for BPA (only in SF_{out}), NP, Flth, Pyr, Chry, BaP, DahA, and Bper. Including risk analyses in future stormwater treatment research is highly recommended for a better understanding of the potential environmental risks of OMPs, in scenarios where the removal efficiency analysis alone does not present such information.

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Paper I

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Occurrence and concentrations of organic micropollutants (OMPs) in highway stormwater: A comparative field study in Sweden

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Occurrence and concentrations of organic micropollutants (OMPs) in highway stormwater: A comparative field study in Sweden

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Abstract

This study details the occurrence and concentrations of organic micropollutants (OMPs) in stormwater collected from a highway bridge catchment in Sweden. The prioritized OMPs were bisphenol-A (BPA), eight alkylphenols, sixteen polycyclic aromatic hydrocarbons (PAHs), and four fractions of petroleum hydrocarbons (PHCs), along with other global parameters, namely, total organic carbon (TOC), total suspended solids (TSS), turbidity, and conductivity (EC). A Monte Carlo (MC) simulation was applied to estimate the event mean concentrations (EMC) of OMPs based on intra-event subsamples during eight rain events, and analyze the associated uncertainties. Assessing the occurrence of all OMPs in the catchment and comparing the EMC values with corresponding environmental quality standards (EQSs) revealed that BPA, octylphenol (OP), nonylphenol (NP), five carcinogenic and four non-carcinogenic PAHs, and C_{16}-C_{40} fractions of PHCs can be problematic for freshwater. On the other hand, alkylphenol ethoxylates (OPnEO and NPnEO), six low molecule weight PAHs, and lighter fractions of PHCs (C_{10}-C_{16}) do not occur at levels that are expected to pose an environmental risk. Our data analysis revealed that turbidity has a strong correlation with PAHs, PHCs, and TSS; and TOC and EC highly associated with BPA concentrations. Furthermore, the EMC error analysis showed that high uncertainty in OMP data can influence the final interpretation of EMC values. As such, some of the challenges that were experienced in the presented research yielded suggestions for future monitoring programs to obtain more reliable data acquisition and analysis.

Keywords: Road runoff, Quality monitoring, Monte-Carlo simulation, Uncertainty analysis, Censored data, Correlated parameters

Highlights

- Organic micropollutants in Swedish highway runoff compared to European countries
- Most phenolic substances, PAHs, and PHCs were frequently detected and exceeded EQSs
- Monte-Carlo model: a reliable method to estimate event mean concentrations (EMCs)
- Uncertainties in OMP data and in the interpretation of the EMCs can be high

1. Introduction

Stormwater runoff is a primary source of toxic organic substances in urban surface waters and near-shore sediments (Barbosa et al., 2012; Launay et al., 2016; Luo et al., 2014). Among different types of urban catchments, roads represent one of the most important sources of certain carcinogenic trace organic compounds, such as polycyclic aromatic hydrocarbons (PAHs) (Diblasi et al., 2009; Wicke et al., 2021). However, traffic-related activities can also release many other types of organic pollutants which may be resistant to environmental degradation, demonstrate bioaccumulation tendencies, and potentially cause long-term detrimental effects on aquatic life (Diblasi et al., 2009; Markiewicz et al., 2017). Recent studies by Wicke et al. (2021) and Gasperi et al. (2022) showed that five and seven organic micropollutants (OMPs), respectively, including phthalates, alkylphenols, and PAHs, can be found in stormwater road runoff at levels that exceed European environmental quality standards (EQS) for surface waters. Mutzner et al. (2022) also revealed that seven traffic-related organic substances (all PAHs) are among the top ten top micropollutants that pose an environmental risk in urban wet-weather flows, which occurred in >92% of stormwater sampling sites around the world. Although OMP

concentrations in receiving bodies are often expected to be lower than acute toxic levels of concern (due to dilution), OMPs can nevertheless cause long-term chronic negative effects, either directly or after interacting with other substances (Gerbersdorf et al., 2015; Rehrl, 2019). For instance, a recent eco-toxicological field study confirmed that hydrophilic trace organic substances found in stormwater runoff exert adverse acute and chronic effects on some aquatic species in the receiving surface water (Spahr et al., 2019).

Nevertheless, there are some clear differences in how certain runoff pollutants are represented in the highway stormwater quality database. Previous studies have extensively characterized contamination arising from trace metals, nutrients, oil and grease, COD, and TSS, among others. However, despite the importance of the OMPs described above, there is still limited information about the levels at which these compounds are found in road runoff (Gasperi et al., 2022; Mutzner et al., 2022). Research into this area has increased on a global level in recent years, but prior studies have mainly focused on polycyclic aromatic hydrocarbons (PAHs) while largely ignoring emerging substances, such as phenolic substances, despite their potential environmental risks. Given the importance of OMPs in road runoff, the present work aims to investigate the occurrence of poorly studied organic substances (bisphenol-A (BPA), 4-t-Octylphenol (OP), Nonylphenol (NP), and OP- and NP-ethoxylates) as well as common OMPs (sixteen PAHs and four fractions of petroleum hydrocarbons (PHCs)). More in-depth knowledge of OMP sources and concentrations can signal the risk that these compounds pose for receiving waters and, subsequently, contribute to the development of road runoff quality management strategies both in the forms of source control and treatment in specific catchments.

Another important aspect to study is the associations between different stormwater organic contaminants (especially new emerging OMPs), as well as how the levels of OMPs are associated with conventional water quality parameters (e.g., suspended solids, organic carbons, turbidity, and conductivity). The associations may reveal novel information about identifying potential conventional indicator parameters that can be used to follow the trends of the studied OMPs with similar environmental fates and transport behaviors (Mutzner et al., 2020), although establishing such parameters using correlations requires extensive investigations and would be site-specific. For example, one application can be that the concentrations of specific OMPs are continuously evaluated at high time-resolution using a relatively small set of constituent parameters in certain stormwater monitoring programs on this site. This complementary information can eventually be useful for runoff pollutant prioritization, source identification, reducing analytical costs, improving economic water quality monitoring programs, monitoring the effectiveness of best management practices (BMPs), as well as determining further treatment possibilities.

The first objective of this study was to monitor the occurrence and concentration levels of target OMPs in road runoff from a highway bridge catchment in Sweden. Regarding this objective, the event mean concentrations (EMCs) were compared with highway/road runoff characteristics reported in the literature and surface water quality objectives (WQO) to determine the possible risks of the detected OMPs. The second objective was to identify the association of conventional water quality parameters with the selected OMPs for future monitoring purposes at this specific site.

2. Methodology

2.1. Study site

The field study was carried out in Sundsvall, Sweden, which has a continental subarctic climate (Dfc) and cool summers. The impervious catchment area comprises 4.7 ha, of which 1.9 ha are included in a highway bridge (E4) with an average traffic load of 13,000 vehicles/day (Figure S1). The rest of the area consists of a highway exit, an acceleration ramp entering the highway, main roads associated with two roundabout, and sidewalk paths.

Sundsvall E4 bridge was built and opened to public in 2014. The pavement surface asphalt was constructed using a polymer-modified bitumen (PMB20) product (Endura F2), especially designed for bridge applications, for which the wearing course of the pavement is made of polymer modified stone mastic asphalt (ABS 11) (Lu et al., 2016; Nynas.com, 2018). The PMB product has excellent aging resistance and high elasticity and exceptional flexibility, resulting in sustaining large strains/stresses at a wide range of temperatures (Lu et al., 2016). The pavement surface was in a good condition. According to the Swedish Pavement Management System (PMSv3), some rutting tests

on another part of E4 highway pavement under the similar conditions (i.e., same asphalt mixture, climate region, and traffic load as for this study) showed that the rutting development for the PMB20 is very insignificant over 8 years (Lu et al., 2016), meaning that the damage to the asphalt concrete is expected to be very low at the time of experiment, but the residual pavement wear particles might still be a source of organic pollutants in the runoff.

2.2. Sampling procedure and strategies

The number of events needed to reliably estimate mean OMP concentrations in the stormwater outlets of a study site depends on local conditions, along with the characteristics and variability of each micropollutant. A metastudy on stormwater outlets across 55 sites found the median number of selected events to be six (with Q10 and Q90 quantiles of 1 and 25 events) (Mutzner et al., 2022). Also, studies on micropollutants typically sample between 1 and 12 events (Spahr et al., 2020). In the present study, we investigated stormwater quality for eight rain events (referred to as rains A to H) between September 2020 and September 2021 (Table 1). As shown in Table 1, the sampling events only covered the warmer seasons and none of them was performed during winter conditions or snow-melting periods, so the effect of de-icing salt and pollution accumulation in snow deposits were not investigated in this study.

All of the samples were collected from the end of a storm sewer pipe (length: ~100 m; diameter: 800 mm; slope: 0.5%) which was downstream of the highway catchment. Rainfall data were recorded using a tipping bucket rain gauge (ISCO 674; Teledyne ISCO, Lincoln, NE) that was situated directly beside the highway. An ISCO-6712 automatic sampler (Teledyne ISCO) was used to collect volume proportional samples during the rain events.

Flow volume at the sampling point was measured by counting the signals sent by discharge valves of a gross pollutant trap chamber (GPT chamber) located downstream of the pipe outlet to the sampler. Every 23.3 m^3, a balloon-type floating switch in the GPT chamber sent a signal to the GPT discharge valves to open/close and, at the same time, triggered the automatic sampler to take a subsample. Based on forecasted precipitation, the sampler was programmed to collect a maximum of eight volume-proportional subsamples. Table 1 summarizes the precipitation characteristics and flow information at the sampling point for all events. For some rain events, we could not cover the entire runoff volume due to practical limitations such as rain depth, duration uncertainties, and time constraints in delivering the samples.

The sampler was equipped with 24 Teflon bags (lay flat PFA bag, Welch Fluorocarbon, Dover, NH), with every three bags represented one subsample. The Teflon bags were washed thoroughly with tap water before sampling. After the sampling procedure, the samples were delivered to the laboratory within one day. In case of delivery time lag (e.g., weekends), all OMP samples were stored in a dark and cool place ($1 - 4\,^{\circ}C$), except for TOC samples, which were stored in a freezer (< -15˚C).

2.3. Water quality analysis

All of the samples were analyzed for the OMPs listed in Table 2 and global parameters, including total organic carbon (TOC), total suspended solids (TSS), turbidity, conductivity, pH, DO, and temperature. OMPs and TOC were analyzed by the ALS Czech Republic laboratory (Prague, Czechia; accredited by the Czech Accreditation Institute) and TSS by ALS Scandinavia AB (Luleå, Sweden; holding Swedac accreditation). Gas chromatography with MS or MS/MS detection was used for analyzing the OMPs present in samples. According to the lab reports, the chemical analyses included matrix interference between alkylphenol substances, which occasionally affected the limits of quantification (LoQ) (Table 2). In addition, other global parameters, including turbidity, conductivity, pH, and temperature, were measured for each subsample. Further information about the analytical methods and equipment are provided in Table S1.

Batch leaching tests were conducted to investigate whether OMPs could have leached from the sampling equipment (the Teflon bags and sampler suction line). The suction line has two parts: a 1.3 m silicon rubber hose at the sampler's pumping head and a 13.5 m Teflon-lined LDPE tube attached to a stainless-steel strainer at the other end. First, tap water was pumped through the sampler (through the tubes described above) and poured into both a new and a used Teflon bag. The water was then kept in the Teflon bags for 24 h. Next, the water was analyzed for OMPs of concern. Comparisons of the concentrations of certain analytes in the reference batch water

and water that had been kept in the Teflon bags for 24h revealed that the sampling equipment did not leach phenolic substances. However, TOC concentrations increased from below LoQ (0.5 mg/L) to 0.52–1.36 mg/L (less than 10% of the mean TOC value measured in this study). Field pretests on grab samples also showed that the sampling equipment did not become contaminated by either PAHs or TPHs. Nevertheless, the Teflon bags were replaced after the first 6 to 7 events. Moreover, each bag was assigned to the same position in an identical sampler to avoid cross-contamination throughout the experiment.

Table 1. Rain event characteristics, sampling, and flow volume information

Rain event characteristics							Total volume conveyed and the percentage sampled	
Rain event	Sampling date (2020–21)	Depth (mm)	Duration (hr)	ADP¥ (day)	Mean intensity or I_{mean} (mm/hr)	Peak intensity or I_{peak} (mm/hr)	Tot. volume passed* (m^3)	Tot. volume sampled (%)
A	15 Sep	7.3	14.3	3	1.5	5.5	257	100%
B	21 Oct	4.6	13.8	0.8	0.7	2.4	195	100%
C	17 May	7.8§	3.25§	1.7§	2.6§	12.0§	373	100%
D	30 Jun	3.8	18.6	6.7	2.3	8.6	128	83% $
E	11 Jul	8.3	13.7	10.5	9.4	32.7	280	100%
F	20 Aug	32.4	40.9	1	3.7	21.2	2353	79%#
G	25 Aug	7.9	46.7	6.3	1.4	4.2	303	96%
H	24 Sep	17.8	24.4	10.4	1.7	4.8	932	59%

¥ Antecedent dry period (events with total precipitation <1 mm were excluded)

* Estimated by the number and volume of pulses (~23.3 m^3/pulse) received from the GPT discharge valve.

$ The first portion of the inflow was not sampled.

§ Reported by the nearest station to the catchment (1500 m away from the rain gauge at the facility).

21% of inflow was not sampled during the last quarter because of at least one of the following reasons: bypassed overflow (16%); GPT discharge valve stayed open due to a very high inflow (no new signal to the SW and GPT sampler was sent in this mode); or the sampling program had ended (final 5%).

Table 2. List of organic micropollutants (OMPs) analyzed in the stormwater samples

	Organic substances, abbreviations, and limits of quantification (LoQs in µg/L)
Phenolic substances	*Bisphenol-A*: **BPA** (0.05); *Nonylphenol, mixture of isomers*: **NP** (0.1–1.35*); *Nonylphenol monoethoxylate*: **NP1EO** (0.1–0.3*); *Nonylphenol diethoxylate*: **NP2EO** (0.1–2.54*); *Nonylphenol triethoxylate*: **NP3EO** (0.1–3.12*); *4-tert-octylphenol*: **OP** (0.01–0.25*); *Octylphenol monoethoxylate*: **OP1EO** (0.01–0.03*); *Octylphenol diethoxylate*: **OP2EO** (0.01–0.02*); *Octylphenol triethoxylate*: **NP3EO** (0.01–0.033*).
Polycyclic Aromatic Hydrocarbons (PAHs)	Substances: *Naphthalene*: **Nap** (0.03); *Acenaphthylene*: **Acyl** (0.01); *Acenaphthene*: **Acen** (0.01); *Fluorene*: **Flu** (0.01); *Phenanthrene*: **Phen** (0.02); *Anthracene*: **Anth** (0.01); *Fluoranthene*: **Flth** (0.01); *Pyrene*: **Pyr** (0.01); *Benz(a)anthracene*: **BaA** (0.01); *Chrysene*: **Chry** (0.01); *Benzo(b)fluoranthene*: **BbF** (0.01); *Benzo(k)fluoranthene*: **BkF** (0.01); *Benzo(a)pyrene*: **BaP** (0.01); *Dibenz(a.h)anthracene*: **DahA** (0.01); *Benzo(g.h.i)perylene*: **Bper** (0.01); *Indeno(1.2.3-cd)pyrene*: **InP** (0.01). Fractions: *Sum of all*: ∑**16 PAH**; *Carcinogenics*: ∑**Car PAH** (Nap, BaA, Chry, BbF, BkF, BaP, BahA, Bper); *Non-carcinogenic*: ∑**nonCar PAH** (Acyl, Acen, Flu, Phen, Anth, Flth, Pyr, InP); *Low-weight molecules:* ∑**LMW PAH** (Nap, Acyl, Acen, Flu, Phen, Anth); *Medium-weight molecules:* ∑**MMW PAH** (Flth, Pyr); and *High-weight molecules*: ∑**HMW PAH** (BaA, Chry, BbF, BkF, BaP, DahA, Bper, InP).
Petroleum Hydrocarbons (PHCs)	Fractions: *Total PHCs or* **C_{10}-C_{40}** (50); **C_{10}-C_{12}** (5); **C_{12}-C_{16}** (5); **C_{16}-C_{35}** (30); **C_{35}-C_{40}** (10).

* The upper limit of the range includes a shift in the limit of quantification (LoQ) due to matrix interferences during chemical analysis.

2.4. Data analysis

2.4.1. Event mean concentration (EMC)

The EMC for each OMP was calculated based on subsample concentrations and flow data. The EMC represents the total pollutant mass (M_T) conveyed by the total runoff volume (V_T) during the entire sampling period of each rain event (Equation 1). However, for events in which the subsamples do not cover the whole stormwater volume, the EMC represents a partial mean concentration for the sampled portion of the rain event. A majority of the instances in which the subsamples do not cover the entire rain event were missing the end of the event (Table 1), with the exception of rain event D, for which the first 17% of stormwater was not sampled. Therefore, a decision was made to use suggestions from Furuta et al. (2022) to more accurately estimate total EMC by attributing the missing volume to the volume of the last subsample under the assumption that the concentrations between the missing volume and final subsample are equivalent. Similarly, the missing period of rain event D was attributed to the first subsample in the total EMC calculation.

$$EMC = \frac{M_T}{V_T} = \frac{\sum m_i}{\sum v_i} = \frac{\sum_{i=1}^{n} c_i v_i}{\sum_{i=1}^{n} v_i} \qquad \text{Equation 1}$$

where EMC is the stormwater event mean concentration; n is the number of subsamples; m_i is the mass of pollutant conveyed in the period during which the i^{th} subsample was taken; c_i and v_i represent the concentration measured in the i^{th} subsample and the corresponding volume of stormwater, respectively.

The calculated EMC values were briefly compared with the lowest Predicted No-Effect Concentrations (PNEC) reported in the NORMAN Ecotoxicology Database and/or with annual average Environmental Quality Standards (AA-EQS) prioritized by the European Union Water Framework Directive (2013/39/EU); both serve as water quality reference points for freshwater.

2.4.2. EMC estimation and uncertainty propagation using a Monte-Carlo method

A Monte-Carlo (MC) method was applied to estimate the EMC, along with the uncertainty associated with each EMC value (Bertrand-Krajewski et al., 2021). MC uncertainty propagation is easy to interpret and can be used to assign various uncertainty distributions to different data types (Albert, 2020). One source of uncertainty in input variables is the analytical measurement uncertainties ($\pm\delta_i$) of subsample concentrations (c_i). The laboratory reported the δ_i values as extended uncertainties (JCGM 100, 2008) with a coverage factor of two (covering a ~95% confidence level) only for quantified substances with concentrations above the LoQ. In this case, the uncertainty distribution for each c_i was assumed to be *normal* for detected substances. When a substance was not quantified in a subsample (i.e., the concentration was left-censored), the uncertainty distribution was assumed to be a uniform distribution between zero and the LoQ, as shown in ***Equation 2***. The volume that passed in the first subsamples (v_1) was also assumed to have a *uniform* distribution due to the possible presence of runoff in the GPT chamber before the start of the event. We expected a negative uncertainty in the 21 m^3 of water (90% of the GPT chamber's discharging volume) that passed during the first subsample period (v_1). For the subsequent subsamples, we assumed that the uncertainty of v_i values calculated by the number of valve opening pulses and the known GPT chamber's discharging volume (23.3 m^3) would be insignificant.

$$\begin{cases} C_i \sim N(\mu = c_i\,, \sigma = \delta_i/2) \quad if \;\; C_i \; detected \\ C_i \sim U(min = 0, max = LoQ) \quad if \;\; C_i \; censored \\ V_1 \sim U\left(min = v_1 - 21^{(m^3)}\,, max = v_1\right) \end{cases} \qquad \text{Equation 2}$$

In the MC method, Equation 1 was used to obtain the EMC. The first EMC value was calculated via random sampling from the specified uncertainty distributions of all n input values in ***Equation 2*** under the assumption that the uncertainties are independent. Then, this calculation procedure was repeated 10^5 times with new drawings at each iteration. According to the rules of the MC method, the distribution generated by many random trials can directly indicate the best estimation for EMC and the associated distribution parameters (mean, standard deviation or SD, and confidence intervals or CI). The median of the trial EMC values was referred to as EMC_{best}, while the 2.5% and 97.5% quantiles represent the lower (Δ_l) and upper (Δ_u) uncertainty levels, respectively, for EMC ($\Delta_l \leq$

191 $EMC \leq \Delta_u$ with CI 95%). The SD of the randomly-generated EMC values was also reported as a statistical
192 parameter of the resulting distribution (with $\mu=EMC_{best}$). In the case that all of the subsample concentrations were
193 censored, the EMC was reported as occurring between zero and the maximum LoQ observed.

194 The described MC method was applied twice to estimate the EMC values and analyze the uncertainties for six
195 different fraction groups of PAHs (PAH-16Sum, PAH-Car, PAH-nonCar, PAH-LMW, PAH-MMW, PAH-
196 HMW). In the first step, concentration distributions for the fraction groups in each subsample were generated
197 using single PAH substances data. Next, these distributions were used to estimate the EMC_{best} and uncertainty
198 levels of the fraction groups.

199 *2.4.3. Statistical and censored data analysis*

200 All of the EMC value estimations, including uncertainty analysis and statistical tests, were carried out in R
201 software (V4.1.3). In addition, the *NADA* (Nondetects and Data Analysis for Environmental Data) package in R
202 was used for the statistical analysis of EMC datasets which contained nondetects. After MC calculations, a non-
203 exceedance probability (NEP) plot of the EMCs for all rain events was generated to evaluate EMC estimation
204 error and statistical distribution among all events. In NEP plots, the y-axis represents the cumulative probability
205 of the calculated EMCs (shown on the x-axis) using the Kaplan-Maier method, which is commonly applied for
206 censored data analysis (Helsel, 2010). *EnvStats* (V2.3.0), a comprehensive R package for environmental statistics,
207 was used to calculate the cumulative probabilities through the Kaplan-Maier method. The calculated EMCs were
208 briefly compared with the lowest Predicted No-Effect Concentrations (PNEC) reported in the NORMAN
209 Ecotoxicology Database and/or annual average Environmental Quality Standards (AA-EQS) prioritized by the
210 European Union Water Framework Directive (2013/39/EU); both serve as water quality reference points for
211 freshwater.

212 The correlations between all parameters, including the EMC of OMPs and global parameters and rain
213 characteristics (rain depth, mean intensity or I_{mean}, peak intensity or I_{peak}, and antecedent dry period), were
214 evaluated using non-parametric pairwise Spearman's rank correlation or Kendall's tau test with $N=\delta$ (number of
215 events). Given that most parameters over the rain events did not follow a normal distribution (according to a
216 Shapiro-Wilk normality test), the first test (Spearman's rank correlation) was used for the detected data sets.
217 Therefore, the latter test was applied to determine correlations between two data sets of which at least one included
218 left-censored data. The resulting correlation coefficients were then classified as very strong, strong, moderate,
219 weak, and very weak (>0.9, >0.7, >0.3, >0.1, <0.1, respectively, for Spearman's rank correlation; >0.7, >0.5, >0.2,
220 >0.1, <0.1, respectively, for Kendall's tau test). The statistical significance of association was accepted if the p-
221 value ≤ 0.05 in both tests (H_0: There is no true correlation between the two parameters).

222 ## 3. Results and discussion

223 ### 3.1. The occurrence and concentrations of OMPs

224 A statistical summary (min, mean, max, SD, number of detects and nondetects) of the best EMCs of various OMPs
225 in stormwater is presented in Table 3 for all rain events. Also, the distributions of EMCs are depicted in Figure 1
226 (a)−(e).

227 According to the results of stormwater quality analysis for eight rain events, BPA, OP, and NP were detected in
228 the runoff from 100%, 75%, and 66% of all rain events (Table 3), respectively. In rain events C, F, G, and H,
229 these three phenolic substances were detected simultaneously. Among the phenolic substances, the EMCs of BPA
230 and NP were higher than what was measured for OP (Figure 1 (a)). The EMC of BPA varied from 0.247 and 1.179
231 µg/L, with a median concentration of 0.39 µg/L. The EMC values of NP were in a similar range (<0.166–1.19
232 µg/L, with a median concentration of 0.34 µg/L). The corresponding values for OP were <0.041–0.338 µg/L
233 (median: 0.08 µg/L). Unlike phenolic substances, nonylphenol and octylphenol ethoxylates (NPnEO and
234 OPnEOs; n=1,2,3) were never quantified in the road stormwater samples analyzed in this study (always
235 ∑NPnEO< 2.54 and ∑OPnEO< 0.45 µg/L; see Table 3 for more details).

236 PAHs were frequently quantified in the highway stormwater samples. Some PAH substances, including Flth, Pyr,
237 BbF, BaP, and Bper, were detected across all rain events, while Chry and InP were detected in 87%, BaA and
238 BkF in 75%, DahA in 62%, and Phen in 50% of events (Table 3). On the other hand, Nap, Acy, Ace, Anth, and

Flu (all among LMW PAHs) were never quantified in the assessed stormwater samples (Table 3). The ∑16 PAH concentrations varied between 0.165 and 1.052 µg/L, with a median EMC of 0.37 µg/L. Carcinogenic PAHs contributed to 41% of the total PAHs. BaP, considered as the most potent carcinogenic PAH, was detected across all events at concentrations between 0.006–0.064 µg/L, with a median concentration of 0.019 (SD= 0.024) µg/L. Of the 59% of total PAHs that were non-carcinogens, about 38% was attributed to Flth and Pyr (equivalent to ∑MMW-PAHs).

Table 3. A statistical summary of the calculated EMC values for all events (N = $n_{detected}$ + $n_{censored}$)

Parameter	Unit	N (Tot.)	n (detected)	n (censored)	EMC_min	EMC_mean	EMC_max	SD	Water quality objective (WQO)*	Num. of EMCs certainly above WQO	Num. of EMCs uncertainly above WQO
Nap	µg/L	**8**	**0**	**8**			100%<0.03	–	2	0	0
Acyl	µg/L	**8**	**0**	**8**			100%<0.01	–	1.3	0	0
Acen	µg/L	**8**	**0**	**8**			100%<0.01	–	3.7	0	0
Flu	µg/L	**8**	**0**	**8**			100%<0.01	–	0.25	0	0
Phen	µg/L	**8**	**5**	**3**	<0.015	0.026	0.065	0.017	0.5	0	0
Anth	µg/L	**8**	**0**	**8**			100%<0.01	–	0.1	0	0
Flth	µg/L	**8**	**8**	**0**	0.008	0.069	0.163	0.059	0.0063	7	**1**
Pyr	µg/L	**8**	**8**	**0**	0.038	0.12	0.262	0.088	0.0046	8	0
BaA	µg/L	**8**	**6**	**2**	<0.008	0.021	0.044	0.014	0.012	4	0
Chry	µg/L	**8**	**7**	**1**	<0.009	0.029	0.069	0.023	0.0029	7	**1** (censored)
BbF	µg/L	**8**	**8**	**0**	0.013	0.061	0.14	0.049	0.017	6	**2**
BkF	µg/L	**8**	**6**	**2**	<0.006	0.016	0.031	0.01	0.017	3	**1**
BaP	µg/L	**8**	**8**	**0**	0.006	0.028	0.064	0.024	0.00017	8	0
DahA	µg/L	**8**	**5**	**3**	<0.006	0.011	0.027	0.006	0.0014	5	**3** (censored)
Bper	µg/L	**8**	**8**	**0**	0.013	0.066	0.145	0.054	0.0082	8	0
InP	µg/L	**8**	**7**	**1**	<0.006	0.029	0.072	0.023	0.27	0	0
∑16 PAHs	µg/L	**8**	**8**	**0**	0.165	0.507	1.052	0.372	–	–	–
∑Car-PAHs	µg/L	**8**	**8**	**0**	0.061	0.208	0.438	0.155	–	–	–
∑non-Car-PAHs	µg/L	**8**	**8**	**0**	0.104	0.3	0.631	0.218	–	–	–
∑LMW-PAHs	µg/L	**8**	**8**	**0**	0.045	0.059	0.1	0.019	–	–	–
∑MMW-PAHs	µg/L	**8**	**8**	**0**	0.047	0.19	0.41	0.147	–	–	–
∑HMW-PAHs	µg/L	**8**	**8**	**0**	0.066	0.258	0.566	0.208	–	–	–
BPA	µg/L	**8**	**8**	**0**	0.247	0.542	1.179	0.314	0.24	7	**1**
OP	µg/L	**8**	**6**	**2**	<0.041	0.131	0.338	0.104	0.1	3	0
OP1EO	µg/L	**6**	**0**	**6**			100%<0.024	–	0.9	–	–
OP2EO	µg/L	**6**	**0**	**6**			100%<0.45	–	0.91	–	–
OP3EO	µg/L	**6**	**0**	**6**			100%<0.033	–	0.91	–	–
NP	µg/L	**8**	**5**	**3**	<0.166	0.374	1.19	0.181	0.3	3	**3** (2 censored)
NP1EO	µg/L	**6**	**0**	**6**			100%<0.18	–	0.64	–	–
NP2EO	µg/L	**6**	**0**	**6**			100%<2.54	–	0.37	–	–
NP3EO	µg/L	**6**	**0**	**6**			100%<1.27	–	0.3	–	–
C_{10}–C_{40}	µg/L	**8**	**8**	**0**	172.18	613.19	1545.56	506.12	1000¥	–	–
C_{10}–C_{12}	µg/L	**8**	**2**	**6**	<2.772	3.283	5	0.512	900$ (Arom.), 300$ (Aliph.)	–	–
C_{12}–C_{16}	µg/L	**8**	**7**	**1**	<4.551	9.375	13.392	3.445	900$ (Arom.), 300$ (Aliph.)	–	–
C_{16}–C_{35}	µg/L	**8**	**8**	**0**	138.6	470.96	1167.74	380.85	900$ (Arom.)	–	–
C_{35}–C_{40}	µg/L	**8**	**8**	**0**	29.67	131.00	361.55	123.47	–	–	–
TOC	mg/L	**8**	**8**	**0**	2.34	10.06	23.03	7.08	12¥	8	0
TSS	mg/L	**8**	**8**	**0**	2.37	66.51	205.70	60.60	25¥	9	**2**
Turb	NTU	**8**	**8**	**0**	40.39	107.17	201.11	54.79	–	–	–
EC	µS/cm	**8**	**8**	**0**	32.77	138.39	299.49	82.08	–	–	–
pH	-	**8**	**8**	**0**	6.799	7.148	7.308	0.156	6.5-9¥	–	–
Temp.	°C	**8**	**8**	**0**	11.62	16.52	22.35	3.38	–	–	–

* The water quality objectives refer to the lowest Predicted No-Effect Concentrations (PNEC) in the NORMAN Ecotoxicology Database and/or the Annual Average Environmental Quality Standards (AA EQS) in the European Union Water Framework Directive (2013/39/EU;WFD); both serve as established standards for freshwater quality unless another guideline is mentioned.
¥ Gothenburg's stormwater guideline for water recipients
$ WHO's guideline for aromatic (Arom.) and aliphatic (Aliph.) PHCs in drinking water (WHO, 2008)

C_{16}-C_{35} and C_{35}-C_{40} were the dominant fractions of PHCs observed in the highway stormwater (Figure 1 (b)). The concentrations of all PHCs (C_{10}-C_{40}) ranged from 175 and 1539 µg/L, with a median EMC of 385 µg/L. The fractions C_{10}-C_{12} and C_{12}-C_{16} (i.e., lighter PHC molecules) were rarely found in the stormwater samples, with relatively low maximum concentrations of 5 and 13 µg/L, respectively.

Finally, the analysis of global parameters in the sampled stormwater revealed that TSS ranged from 2.4 to 206 mg/L (median: 54 mg/L), while TOC ranged from 2.3 to 23.0 mg/L (median: 7.1 mg/L). The pH value of the

stormwater remained in the neutral range of 6.7–7.3, as was expected. Onsite measurements also showed that the turbidity of samples ranged from 40.4 to 201.1 NTU for all rain events.

The following section will describe the observed stormwater quality by comparing our results with the measured levels of OMP reported in other similar studies as well as water quality objectives.

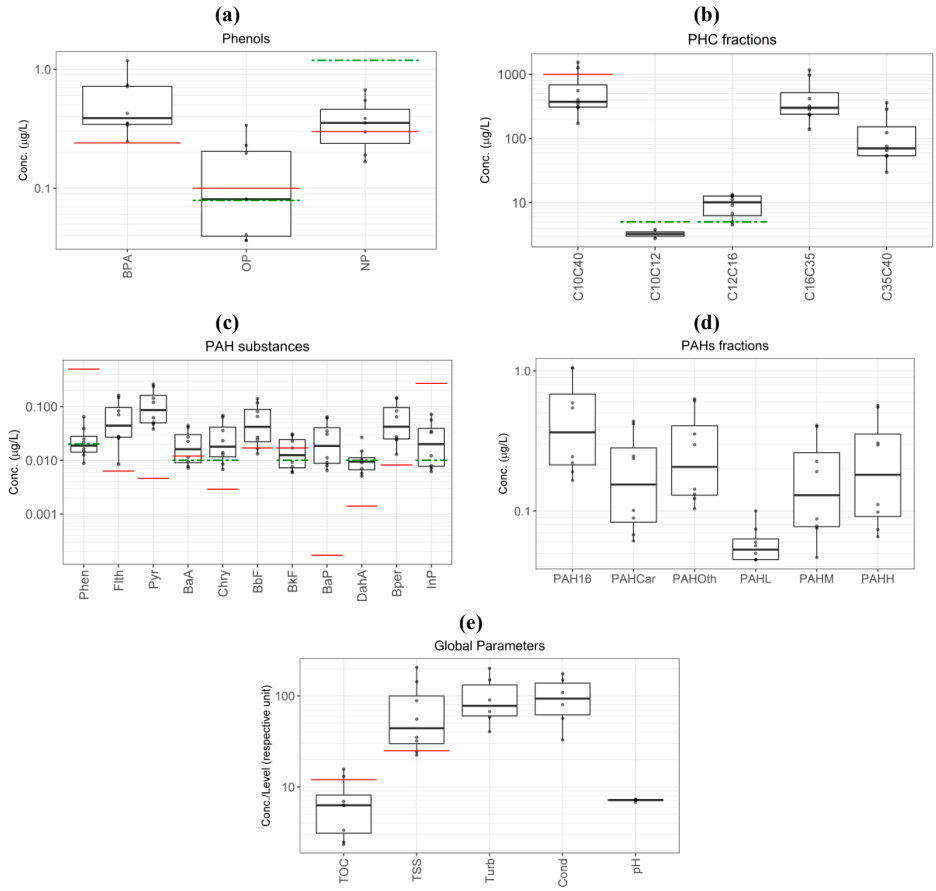

Figure 1. Stormwater quality parameters during all rain events (Boxplots show the 2.5, 25, 50, 75, and 97.5 percentiles of all calculated EMCs); Red lines represent the water quality objectives (WQOs) while green dotdashed lines illustrate the maximum censored level (if any) for the OMPs. TOC and TSS in mg/L; Conductivity (Cond) in µS/cm; and turbidity (Turb) in NTU.

3.1.1. Phenolic substances

Phenolic substances were often quantified in the highway stormwater, with BPA being the most frequently observed substance, followed by OP and NP. Although the variable LoQs for OP and NP caused some uncertainties in the results (discussed in section 3.2), both of these compounds were detected in more than two-thirds of the rain events. Similarly, a recent metastudy on micropollutants also demonstrated that BPA and OP are often detected in >75% of stormwater flows, whereas NP is observed less frequently, but demonstrates a higher risk according to Mutzner et al. (2022). The median EMC estimated for BPA was either similar or approximately half of what has previously been measured by other researchers in runoff from major roads (see Table 4). The EMC values of NP and OP were often similar to, or slightly lower than, what has been observed in other road catchments, but distinctly lower than what was reported by Gasperi et al. (2022) (see Table 4). The primary sources

of BPA, NP, and OP in roadways are traffic-related materials (brake fluids, car bodies and tires) and infrastructural chemicals (asphalt modifiers and road paints (Lamprea et al., 2018; Markiewicz et al., 2017). Accordingly, the observed concentration differences between our study and two prior studies can be explained by a higher traffic load (1.7–3 times), which would cause a higher pollutant load than what was experienced in the two other studies; the noticeable differences in TSS levels (see Table 4) also support this hypothesis. Secondly, additional sources of NPs (e.g., varnishes, lacquers, water paints, floor coatings, coated metal surfaces, polymeric compounds) might exist in one of the catchments with mixed urban runoff studied by Gasperi et al. (2022) relative to a mere roadway catchment.

The observed EMC values of NP and OP were also lower than what was previously reported for Swedish and German highways. The larger daily traffic load (five times larger than the present study) in the prior Swedish study (Kalmykova et al., 2013) was probably the primary reason for the discrepancy. In the case of the German study, which investigated a road with a similar traffic load (Stachel et al., 2010), the discrepancy may be explained by the decreased use of phenolic compounds after these substances were identified as priority pollutants by the EU WFD (2013). In contrast, the OP concentrations measured in the present study were higher than what has previously been reported for diverse urban catchments (Bressy et al., 2012; Gasperi et al., 2014). This may be explained by the fact that tire wear is the primary source of OP (Flanagan et al., 2019b; Hannouche et al., 2017). The high observed OP levels may also raise the question of additional sources at the study site, such as collection pipes made of high density polyethylene (HDPE), which may release phenolic substances, including OP, into the stormwater. Further investigation is needed to clarify this discrepancy in OP concentrations. Concerning the surface WQOs based on European guidelines, the AA EQS and PNEC defined for BPA, NP, and OP (0.24, 0.3, and 0.1 µg/L, respectively) were exceeded eight, four, and three times across the eight studied rain events.

In contrast to previous studies (including those conducted in Sweden; Table 4), NPnEOs and OPnEOs (n=1,2,3) were not detected in the runoff. A potential explanation could be matrix interference during chemical analysis, which adversely affected the LoQs; subsequently, we could not compare the actual concentrations with those reported by other researchers (Table 4). The reported LoQs of NPnOEs (up to ~20 times greater than the initial report limit in the analysis package) were affected more than the LoQs of OPnOEs (up to ~3 times larger). Another possible explanation is that these compounds are far more rare in roadways than in mixed urban catchments. This hypothesis is supported by the levels reported in Table 4 for these two distinct catchment types. In roads, NP- and OP-ethoxylates are mainly emitted by fuel and lubricant oils, car bodies, modified bitumen membranes, and concrete sidewalks, while in urban areas these compounds could also be released from PVC materials and polymeric resins used as lacquers, varnishes, and paints for roofing, building facade, and corrosion protection (Lamprea et al., 2018). From the perspective of freshwater quality objectives, all of the maximum levels reported for OPnEOs and NPnEOs were sufficiently below the lowest PNEC, except for NP2EO and NP3EO, with the NP2EO concentrations more of a concern (Table 3).

3.1.2. Polycyclic Aromatic Hydrocarbons (PAHs)

All MMW-PAHs and most HMW-PAHs were detected in at least 50% of the rain events, while most LMW-PAHs were not detected. Similarly, Mutzner et al. (2022) concluded that the PAHs observed in the present study are not only the most common and risky substances among all PAHs, but also present at noticeable levels among a wider range of micropollutants in various stormwater flows. Our results agreed with other studies in that LMW-PAHs are less likely to be detected in stormwater (Järlskog et al., 2021). The LMW-PAHs that were not detected may have degraded after being released into the environment due to their natural characteristics. These compounds have much greater volatility at warmer temperatures (10^{-3}< vapor pressure< 10 Pa at 25 $^{\circ}$C) and relatively smaller sediment adsorption coefficients (2.5< Log K_{OC}< 3.7) than other PAH fractions (Hawthorne et al., 2006; Khodadoust et al., 2005) (see Table S2 for more info). Therefore, they are less likely to exist in runoff water after being released. The ∑16 PAH concentrations fell within the range expected for major roads (0.03−6 µg/L) that was previously presented by Lundy et al. (2012). Järlskog et al. (2021) also found that LMW-PAHs in stormwater are temperature-dependent, which means that they readily evaporate into the atmosphere during warmer sessions (i.e., the sampling period in this study).

However, the range of ∑16 PAHs was less than what has been reported in other studies of road catchments, either with high or lower traffic loads (see Table 4). Since most PAHs are predominantly found in the solid phase or

absorbed by sediments (Markiewicz et al., 2017; Nielsen et al., 2015), it could be that the relatively low TSS levels observed in this study are an explanation for the result. This may be partly explained by the partial deposition of stormwater sediments along the transport pipe (low slope of 0.5%) from the catchment to the facility downstream. Among the detected PAHs, only Nap and InP were measured at levels that consistently fell below the lowest PNEC (AA EQS). The other PAHs were always detected at concentrations that exceeded the guideline quality objectives for freshwaters; exceptions were BaA, BbF, and BkF, which exceeded quality objectives in 50%, 20%, and 40% of rain events, respectively.

In the studied catchment, the PAHs most likely originated from vehicular traffic (brake lines, tire wear, exhaust gases/particles, and engine oil (Burant et al., 2018; Kose et al., 2008; Markiewicz et al., 2017)) and the abrasion of pavement material by tires and runoff water on the old asphalt road and sidewalks (Crane, 2014; Müller et al., 2020). However, regarding the pavement surface wear, it should be noted that the usage of tar coal asphalt (containing PAHs) has been legally forbidden in Sweden since 1973. So, the worn asphalt concrete material of the E4 highway bride (built in 2014) should not be a source of PAHs itself. Besides, assuming the maximum EMC for Phen (the only LMW-PAH detected) and the minimum and maximum concentration values for ∑HMW-PAHs, the results revealed a PAH diagnostic ratio Σ(LMW)/Σ(HMW) between 0.04 and 0.1, which is much lower than one. This means that PAHs in the road stormwater are more likely to originate from pyrogenic (vehicular emissions from exhaust after petroleum or liquid fossil fuel combustion) rather than petrogenic (e.g., brakes, vehicle tire debris, and spilled engine oil) sources. This finding agrees with previous literature on road runoff quality (Li & Kamens, 1993; Markiewicz et al., 2017; Szopińska et al., 2019; J. Zhang et al., 2017).

Moreover, rain events B, C, E, and H demonstrated the highest load of PAH pollution, both in terms of diversity and concentration of PAHs. No particular rain characteristics (given in Table 1) could explain the PAH concentrations observed during these rain events. Rain events B and C with the highest observed PAHs levels occurred in the time periods before and after winter conditions at which vehicles having winter tires (with more grip) may hypothetically cause greater tire wear particles on the roads with no ice/snow cover. However, further evidence and research are needed to demonstrate this.

3.1.3. Petroleum Hydrocarbons (PHCs)

The EMC range for total PHCs (C_{10}-C_{40}) was similar as what was reported by Gasperi et al. (2022) and Leroy et al. (2016), yet half to one order of magnitude lower than what was observed in runoff from roads with low and high traffic loads, respectively (Järlskog et al., 2021; Kayhanian et al., 2007; K. Zhang et al., 2014) (see Table 4). Heavier PHC fractions, namely, C_{16}-C_{35} and C_{35}-C_{40}, dominated the measured PHCs. The low-weight PHC molecules were most likely found at lower levels relative to heavier PHC molecules because aromatic/aliphatic C_{10}-C_{16} have higher volatility and much lower Koc than heavier counterparts (>C_{16}). On the other hand, aromatic/aliphatic compounds above C20 are neither volatile nor soluble in the aquatic phase and are thus likely to be absorbed by suspended solids (Reed & Stemer, 2002). However, higher-weight PHC molecules are usually considered to be less toxic for organisms, which means that >C_{20} compounds in the runoff represent a lower health risk. The observed EMCs for total PHCs often fell below 1000 µg/L, which is the city of Gothenburg's local guideline recommendation for releasing waters polluted with aliphatic and aromatic C_{10}-C_{40} (Järlskog et al., 2021; Miljöförvaltningen, 2013); this threshold was exceeded in 25% of rain events. However, the levels are still a matter of concern given WHO drinking water standards (WHO, 2008) (Table 3).

The two most frequently PHC fractions (C_{16}-C_{35} and C_{35}-C_{40}) were detected across all rain events, but the highest concentrations occurred during events B, C, E, and H; these rain events also demonstrated the highest levels of PAHs. Similarly, the highest PHCs concentrations were recorded at rain events B and C. Again, this might be related to the presence of more winter tire (with/without stud) and asphalt wear particles at those times of the year when no ice/snow has covered the road surfaces. Though, this hypothesis requires further investigations.

3.1.4. Global parameters

Although the EMCs of TSS were near the low end of globally-observed mean values on major roads (110–5700 mg/L according to Lundy et al. (2012)), they still surpassed the European quality objective of 25 mg/L (the protective threshold against chronic effects on fish life in freshwater (EC, 2006)) across 80% of the rain events. When compared to the scientific literature (Table 4), the TSS and TOC values were comparable with what has been observed in runoff from Swedish/European/North-American motorways, but noticeably lower than what has

been reported for some roads with higher traffic loads (Flanagan et al., 2018; Gasperi et al., 2014; Kayhanian et al., 2012). The notable difference may be explained by site-specific conditions (e.g., an extended acceleration zone, a higher proportion of heavy trucks, and lower precipitation over the study period), which would cause high wear particle production and more concentrated runoff (Flanagan et al., 2018). Meanwhile, we must also assume that the 50-m-long transportation pipe in our site may have attenuated stormwater TSS load to a certain degree before the runoff reached the SW sampling point; this would be especially relevant during less intense rainfall.

3.2. Uncertainty analysis of EMC calculations using a MC method

The recalculation of EMC values through MC simulation involved uncertainty analysis to get a reliable picture of OMP levels. As previously mentioned, each calculated EMC is associated with uncertainties due to analytical and sampling constraints; these uncertainties may influence data accuracy and interpretation. Analytical errors are a significant source of uncertainty for research into micropollutants because these compounds usually exist at low concentrations (Flanagan et al., 2018). Before the start of a rain event, the stormwater present in the downstream GPT chamber (which was used to calculate flow volume at the study site) was another source of uncertainty as it affected the first sampled volume (i.e., the first 23.3 m^3 or v_1). However, the relatively large total number of subsamples or sub-subsamples (smaller portions of a single subsample taken by a number of serial pulses) collected during the whole event decreased the influence of v_1 on EMC errors. In the case of rain events A, B, C, and D (which comprised fewer total number of subsamples than the other four rain events), at least five pulses were received from the discharging valve during the first sample collection (5 sub-subsamples for c_1; total #no. pulses >10). The total number of received pulses during rain events E, F, G, and H exceeded 12. Therefore, EMC errors due to v_1 were negligible compared with those due to analytical uncertainty, which was the primary source of uncertainty in the present study.

To assess EMC errors and their impact on data interpretation, non-exceedance probability (NEP) plots were generated for the EMC values of each OMP. A NEP plot does not only indicate the distribution of best-estimated EMCs across all rain events, but also visualizes the EMC ranges (EMC$-\Delta_l$, EMC$+\Delta_u$) resulting from uncertainty propagation in the MC method. The NEP plots for selected OMPs are presented in Figure 2 (a) to (i) (the rest shown in Figure S2 (a) to (t)). The NEP plots also revealed which EMCs might have reached the corresponding PNEC levels (WQOs) due to uncertainties (the number of rain events during which the threshold was exceeded due to uncertainty is shown for each OMP in Table 3). This was the case for BPA, NP, Flth, BbF, BkF, and TSS at one or two events (Figure 3). There were also a few events during which the censored concentrations of NP, Chry, and DahA (censoring as the only uncertainty factor) might have exceeded PNECs (see Figure 3).

To further assess uncertainty levels, a statistical summary of relative EMC errors among all of the rain events is shown in Figure 3 for OMPs, TSS, and TOC. An evaluation of the lower and upper uncertainties of the calculated EMCs revealed that all EMCs possessed approximately symmetric distribution (<1% difference between left and right EMC errors), which predominantly followed the symmetric behavior of the *normal* distribution of analytical uncertainties. Therefore, the reported errors in Figure 3 represent the EMC errors for both sides ($|\pm\Delta|$ (%)).

Table 4. Comparison of the concentration ranges of stormwater OMPs (min-median-max) observed in this study and other field studies

	Reference	Catchment type	Traffic load (veh/d)	∑16PAHs (µg/L)	PHCs (mg/L)	BPA (µg/L)	NP (µg/L)	OP (µg/L)	∑NPnEOs (µg/L)	∑OPnEOs (µg/L)	TSS (mg/L)	TOC (mg/L)
Sweden	**This study**	E4 highway/ major road	13000	(0.16-0.37-1.1)	(0.17-0.4-1.5)	(0.25-0.39-1.2)	(<0.17-0.34-1.2)	(<0.04-0.08-0.34)	(<4)	(<0.51)	(2.4-54-206)	(2.3-7.1-23)
	(Markiewicz et al., 2017)	Motorway	NA[$]	max available: 9-190 (≈5.8-29 kg/ha.yr)	–	–	–	–	–	–	–	–
	(Nielsen et al., 2015)	Motorway	40000	(3.2-139)	–	–	–	–	–	–	(130-150-170)	–
	(Kalmykova et al., 2013)	Motorway + industrial + landfill	85000 (motorway)	(0.02-0.32-12.1) (LMW >80%)	–	(<0.01-0.5-107)	(<0.1-0.3-7.3)	(<0.01-0.23-1.3)	(<0.1-<0.1-3.6)	(<0.01-0.03-5.3)	(2-820)	10-11
	(Kalmykova et al., 2013)	Only motorway	85000	mean: 0.3 In 2005: (0.97-2.8)	–	mean: 0.827	mean: 1.1	mean: 0.82	<0.01	mean: 9.64	9.5-350	14-20
	(Björklund et al., 2009)	E6 highway	85700	–	–	–	(<0.1-0.26-1.2)	–	(0.2-1.3-2.2)	–	(97-150-310)	(7-11-16) (DOC>85%)
	(Pettersson et al., 2005)	Motorway	NA	2.6 and 6.9	–	–	–	–	–	–	–	–
France	**(Gasperi et al., 2022)**	Urban road (dense area)	40000	~(0.8-3.2-9.5)	~(0.4-1.7-2.9)	~(0.7-2.4-7)	~(0.6-2-6)	~(0.1-0.8-1.8)	~(0.13-0.82-4.04)	~(0.07-0.23-0.95)	(26-223-1620)	DOC: (4-15-95)
	(Gasperi et al., 2022)	Suburban road	22000	~(1.2-5.5-13)	~(0.11-1.4-4.7)	~(0.2-0.4-1.1)	~(0.4-1.9-5.3)	~(0.18-0.5-0.7)			(54-210-933)	DOC: (2-6-15)
	(Flanagan et al., 2019, 2018)	Highway in industrial zone	22000	(1.3-4.9-11.5)	(0.3-1.1-4)	(0.2-1-4.1)	(0.9-1.6-5.8)	(0.2-0.4-1.5)	(0.21-0.59-3.57)	(0.03-0.06-0.35)	(70-291-933)	(14-49-111) (DOC:13%)
	(Leroy et al., 2016)	Roads in commercial area	2500	(0-3.2-6.5) (20% Phen)	(<0.05-0.6-1.3)	–	–	–	–	–	(75-290-774)	(13-37.6-109)*
	(Gasperi et al., 2014)	Major roads in urban areas	10000-60000	mean: 0.9-1.4	–	(0.2-0.55-0.8)	(0.2-0.4-0.5)	(0.04-0.06-0.07)	(0.12-0.51-0.57)	(0.013-0.036)	mean: 100-150	(10-32-56) (DOC<20%)
	(Bressy et al., 2012)	Mixed urban area	NA (<2000)	(0.55-1.1-2.2)	–	–	(0.16-0.5-0.9)	(0.01-0.04-0.07)	–	–	(15-26-64)	(9-14-35) (DOC: 50%)
	(Zgheib et al., 2012)	Big, dense urban area	NA (>15000)	(0.67-1.3-6.5)	–	–	(0.3-0.75-9.2)	(<0.05-0.1-0.26)	–	–	(11-106-430)	(2-27-104)*
Germany	**(J. Zhang et al., 2017)**	Roadway	13600-15000	mean: 0.27-0.66 (≈15.9 µg/m^2)	–	–	–	–	–	–	(41-85) (≈1-5 g/m^2)	–
	(Wicke et al., 2021)	Major road	>7500	(0.05-4.1-11)	–	<0.2	–	<0.4	–	–	(1-368-1330)	(25-79-98)*
	(Stachel et al., 2010)	Highways	63000-101000	(1.1-2.3-5.1)	C10-C13: <0.50	(0.24-1.4-2.5)	(0.2-0.8-3.6)	(0.15-0.3-1.9)	–	–	mean: 12	–
USA	**(Masoner et al., 2019)**	Mixed urban area	NA	(0.01-1.0-10)	–	(0.05-0.3-2.0)	–	–	–	–	–	–
	(David et al., 2015)	Parking lot+ public area	–	(0.67-2.3-4.6)	–	–	–	–	–	–	(2.9-21-43)	–
	(Diblasi et al., 2009)	Roadway+ parking lot	NA (<2000)	(0.67-2.3-4.6)	–	–	–	–	–	–	(16-33-68)	–

[*] Estimated from COD concentrations

[$] Not Available

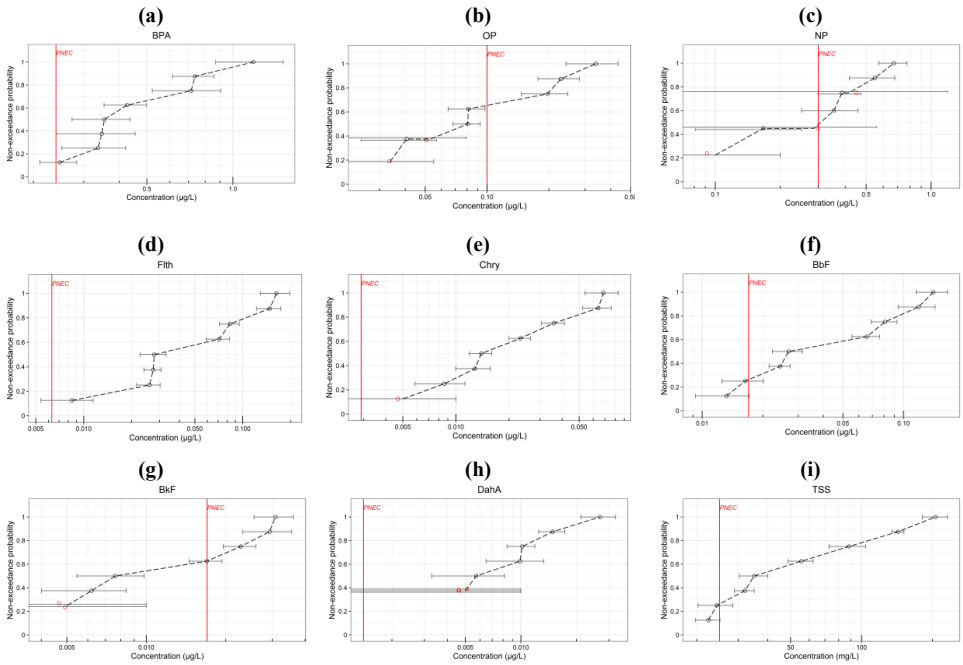

Figure 2. Non-exceedance probability (NEP) plots of the estimated EMCs for each OMP (Black points are detects and red points censored data (non-detects); Error bars show EMC errors (uncertainties); Red lines represent the lowest PNEC levels for freshwater, based on water quality objectives (WQOs))

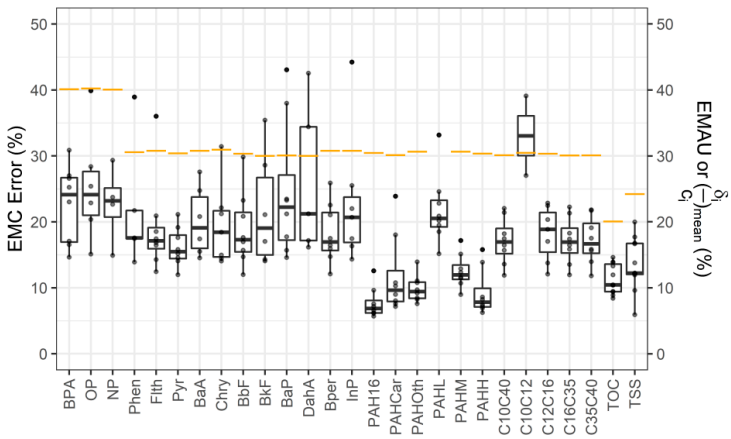

Figure 3. Statistical analysis of EMC estimation errors (boxplots: min, $Q_{25\%}$, $Q_{50\%}$, $Q_{75\%}$, and max of relative EMC errors over N=8 events) (Orange bars: mean of relative analytical uncertainty observed for all events (EMAU or $(\delta_i/c_i)_{mean}$))

The MC method-facilitated analysis of errors generally showed that the EMC errors for OMPs can vary between 5 and 45% (median errors between 10 and 25%, with the exception of 35% for C_{10}-C_{12}). Comparing different groups of OMPs (Figure 3) also revealed that phenolic substances had the highest EMC error range (23−25%), which means that the reported levels of these compounds in the studied stormwater are associated with less reliability. The median EMC errors for PAH substances and PHCs were in between the range of 17−23% (except

for C_{10}-C_{12} due to censored data). We also observed that the EMCs of TOC and TSS were associated with the smallest errors (10% and 12%, respectively). The observed differences in errors can be linked to differences in the corresponding analytical uncertainties (δ_i); in this way, higher δ_i values resulted in larger EMC errors. To compare the levels of such uncertainties among the investigated OMPs, all-events-mean relative analytical uncertainty (EMAU or $(\delta_i/c_i)_{mean}$, i= subsample number) was calculated and defined as an analytical uncertainty index for each OMP (orange bars in Figure 3). So, as implied in Figure 3, EMC error boxplots can change proportionally to EMAUs variations. Furthermore, the median EMC errors were considerably less than the calculated EMAU values; this indicates how the original measurement uncertainties (δ_i) affected the calculations, i.e., in the EMC_{best} estimation using MC, the EMC error (or the standard error of the mean, which is a function of subsample standard deviations ($\sim\delta_i/2$)) declines based on the square root of the number of subsamples (Feiguin, 2009). It should also be noted that the errors of the HMW-PAH and MMW-PAH fractions (median: 12−15%, except LMW-PAH) were lower than those for PAH substances (median: 17−23%), although both showed similar EMAU. This was expected, as the EMCs for PAH fractions were estimated from the substance concentrations after applying the MC method twice (see section 2.4.2).

Thus, our error analysis revealed a considerable degree of uncertainty in the organic pollutant data; this is important to keep in mind when interpreting the data of other studies. We also found that, as expected, increasing the amount of censored data among subsamples increased the EMC error (see e.g., BkF, DahA, LMW-PAH, C_{10}-C_{12}, OP, and NP in Figure 3), which makes it hard to draw an appropriate conclusion regarding the EMC levels in those cases. Besides, it should be noted that although the applied MC simulation approach attenuated uncertainty in the actual measurements by about 10 to 15% (towards more optimistic results), this approach can be used as a simple and reliable method for estimating the EMCs of OMPs.

3.3. Correlated water quality parameters

Using statistical correlation analyses, we attempted to understand the mathematical relationships between the studied parameters with the objective of possibly identifying correlated conventional water quality parameters and rain characteristics that alongside monitoring campaigns, can help predict various highway runoff OMPs in this specific site. So, continuously measuring those conventional parameters could potentially complement data from monitoring programs in which long-term, high-resolution time series are of interest. The results of correlation analyses for all parameters are summarized in Table 5. Only the correlation coefficients (*rho* or *tau*) that demonstrated statistical significance (p-value ≤ 0.05) are included in this table. The entire correlation matrix, including confidence levels, can be found in Table S4.

The results did not reveal any correlations between TOC and TSS concentrations, which suggests that organic carbon in road runoff is mainly dissolved. Other DOC and TOC measurements at the same site before our sampling period (Lange et al., 2022) support this hypothesis. This result also agrees with what was reported in previous studies from Swedish and North-American highways (Björklund et al., 2009; Kayhanian et al., 2012), but disagrees with findings reported for major roads in France (Bressy et al., 2012; Flanagan et al., 2018; Gasperi et al., 2014). An abundance of suspended particles, which readily absorb organic carbon, might be responsible for the contradictory partitioning in these studies (Flanagan et al., 2018). Furthermore, TOC was strongly correlated with conductivity, which may support the assumption that organic carbon mainly exists in the dissolved phase. TOC was also associated with rain depth and I_{peak}.

Among phenolic pollutants, BPA was highly associated with TOC. Considering the previous hypothesis about TOC, this association suggests that BPA is more likely to exist in dissolved or colloidal forms in stormwater, i.e., less likely to be absorbed by suspended particles, which agrees with what was stated by Flanagan et al. (2019a) and Gasperi et al. (2022). However, Shehab et al. (2020) and Markiewicz et al. (2017) proposed contradictory dynamics. OP was strongly correlated with most PAHs, C_{16}-C_{35}, and Total PHCs, but not with turbidity or TSS. This may suggest that OP is released from similar sources as PAHs and heavier PHCs (e.g., tire particles), but then undergoes a different partitioning pathway (leaching in dissolved form) and/or does not attach to suspended solids, especially larger particles, as some other studies suggest (Gasperi et al., 2014; Kalmykova et al., 2013; Shehab et al., 2020). On the other hand, NP did not show any association with other parameters, which can be, in our study, related to the number of non-detected values (three out of eight events) with different levels of

censoring. The lack of an association between OP and NP also supports the idea that the sources of these two compounds differ.

Table 5. Summary of significantly correlated parameters

OMP categories	Correlated parameters	Correlation coefficient	Statistical test
Phenolic substances	BPA & TOC	+0.88	Spearman
	OP & some PAHs*	+(0.61–0.68)	Kendall's tau
	OP & 16PAHs	+0.86	Kendall's tau
	OP & Tot. PHCs	+0.68	Kendall's tau
	OP & C_{16}-C_{35}	+0.68	Kendall's tau
	NP & I_P	+0.5	Kendall's tau
PAHs	Pairs of PAHs	+(0.74–0.98)	Spearman
		+(0.57–0.74)	Kendall's tau
	LMW-PAH & MMW-PAH	+0.86	Spearman
	LMW-PAH & HMW-PAH	+0.81	Spearman
	MMW-PAH & HMW-PAH	+0.98	Spearman
	Car-PAH & Non-car-PAH	+0.95	Spearman
	Some PAHs₹ & Turbidity	+(0.83−0.94)	Spearman
	Some PAHs¥ & Turbidity	+(0.73−0.8)	Kendall's tau
	Some PAHs€ & TSS	+(0.76–0.88)	Spearman
	Phen & TSS	+0.57	Kendall's tau
	Car-PAH & Turbidity	+0.89	Spearman
	16PAHs & Turbidity	+0.94	Spearman
	16PAHs & TSS	+0.74	Spearman
PHCs	Tot. PHCs & C_{16}-C_{35}	+1	Spearman
	Tot. PHCs & C_{35}-C_{40}	+0.91	Spearman
	C_{16}-C_{35} & C_{35}-C_{40}	+0.91	Spearman
	Tot. PHCs£ & some PAHs$	+(0.68–0.82)	Kendall's tau
	Tot. PHCs£ & some PAHs #	+(0.79–0.98)	Spearman
	Tot. PHCs & Turbidity	+0.94	Spearman
	C_{16}-C_{35} & Turbidity	+0.94	Spearman
	C_{35}-C_{40} & Turbidity	+0.84	Spearman
	C_{35}-C_{40} & TSS	+0.74	Spearman
Global	TSS & Turbidity	+0.9	Spearman
	TOC & EC	+0.78	Spearman
	TOC & ADP	+0.65	Spearman

* Pyr, BaA, Chry, BbF, BaP, InP
₹ Flth, Pyr, BbF, BaP, Bper, Inp
¥ Phen, BaA, BkF
€ Flth, Pyr, BbF
$ Phen, BaA, Chry, BkF, DahA, InP
# Flth, Pyr, BbF, BaP, Bper
£ Predominantly C_{16}-C_{35} and C_{35}-C_{40} fractions

Within PAHs, the EMC values of all regularly detected substances and fractions (excluding Nap, Acy, Ace, Anth, and Flu, which were rarely detected) were highly associated with each other and turbidity and somewhat associated with TSS. As discussed before, this finding may support that many PAH fractions have similar sources and transport pathways in stormwater (Järlskog et al., 2021). Similarly, regarding PHC fractions, heavier fractions (including C_{16}-C_{35} and C_{35}-C_{40}, Total PHCs (C_{10}-C_{40}), TSS, and turbidity) were strongly correlated with each other. These fractions also demonstrated strong associations with PAH substances/fractions, which may suggest similar sources and/or environmental fates in stormwater. In contrast, no meaningful correlations were observed between the EMCs of lighter PHCs (C_{10}-C_{12} and C_{12}-C_{16}) and the investigated parameters or other PHC fractions. This could be explained by either a high proportion of censored data (less precise statistical relationship) or lower concentrations for lighter fractions relative to heavier C fractions, which may adversely influence the peak response during analysis. The investigated PAHs and PHCs showed a higher degree of correlation with turbidity than with TSS, which means that turbidity could be a better indicator for particulate/particle-bound OMP pollution loads in stormwater than TSS. This finding may explain that the particulate PAHs and PHCs tend to stay suspended longer (finer/lighter/more stabilized particles), whereas TSS contains dense, inorganic particles which

rapidly sediment from stormwater. Another reason for this result may be that PAHs and PHCs have high affiliation for finer suspended soil particles due to higher surface charge and/or higher surface area.

Although other studies have found that rain characteristics can influence the event mean concentrations of common pollutants such as metals (Kayhanian et al., 2007), our results did not show any significant correlations between rain characteristics (depth, ADP, I_{mean}, I_{peak}) and OMP levels. While it was expected that turbidity and TSS, and possibly OMP loads, are dependent upon event runoff volume or intensity (Murphy et al., 2015), we did not observe any significant correlations between TSS and rain depth, $I_{mean,}$ and I_{peak}; a plausible explanation for the lack of significant correlations could be the limited number of rain events included in this study (Lange et al., 2021). Thus, the impact of rain characteristics on the EMC values of organic micropollutants remains unclear and requires further investigation.

The relationships among all studied parameters have been depicted in Figure 4. What these correlations suggest is that turbidity has the potential to be used as a conventional indicator parameter for estimating the contamination levels of PAHs, total PHCs, and heavier fractions of PHCs at this specific site. However, further studies are needed to establish a surrogate parameter based on these correlations. In the same way, TOC and EC could also serve as complementary quality parameters for indicating BPA levels at this site. Within the PAHs category, Pyr and BaP can also be decent indicators for non-carcinogenic and carcinogenic PAHs, respectively. Moreover, our results did not identify any correlated conventional parameters to lighter PHCs, OP, NP, and OP- and NP-ethoxylates (due to their low concentrations around LoQs).

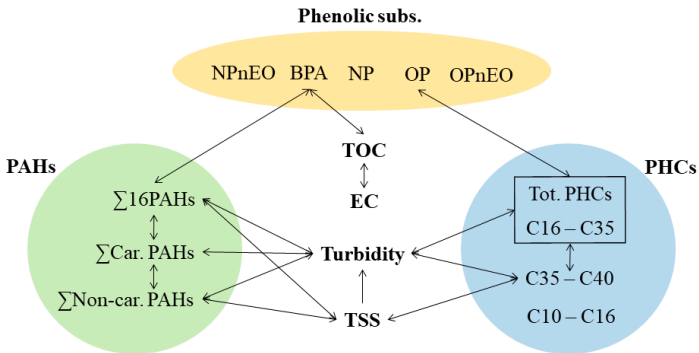

Figure 4 Highly correlated parameters with OMPs in the studied catchment

4. Conclusion

This field monitoring study demonstrated that organic micropollutants are a concern in highway stormwater runoff. The reported EMC values revealed that the runoff contained considerable amounts of phenolic substances, including BPA, OP, and NP (but not alkylphenol ethoxylates; OPnEO and NPnEO), with concentrations above or around corresponding EQSs for freshwater. For example, BPA was found in all of the samples within the same concentration range that was reported by other researchers. At the same time, OP and NP were detected in >65% of samples, but often at levels lower than what have been reported in other studies around Europe. The analysis and interpretation of data concerning OP and NP were slightly affected by different censoring levels and high measurement uncertainties caused by matrix interference during laboratory analysis. The data analysis revealed that BPA was correlated with TOC (predominantly dissolved and associated with EC), while OP was found to be associated with PAH levels and the concentration of total PHCs. This finding suggests that phenolic substances may have different sources or fractionation pathways and, thus, different environmental fates and transport in road runoff.

Regarding the more common OMPs, PAHs and PHCs were also identified in the runoff (mainly in the form of heavier weight fractions), although the observed concentrations often fell below the ranges reported in other studies performed under similar conditions. Nevertheless, the mean concentrations of MMW- and HMW-PAHs still significantly exceeded the corresponding freshwater quality objectives across most rain events. Five PAH

substances (BaP, BaA, Chry, BbF, and DahA), classified as extremely or possibly carcinogenic, were observed among the risky PAHs (EMC > EQS). A diagnostic ratio analysis showed that PAHs at the studied catchment probably originate from pyrogenic sources (vehicular emissions after combustion). Statistical correlation analyses supported the fact that PAHs and PHCs (heavier fractions), which are characterized by low solubility and high stability in different phases, are associated with the levels of suspended solids (especially finer particles) in stormwater runoff.

Further statistical analyses suggested that three conventional water quality parameters, including turbidity, TOC, and EC, are strongly associated with OMPs: turbidity with PAHs, PHC, and TSS and TOC and EC with BPA. This indicates that these parameters have the potential to be used as surrogates, though such a relationship requires further work to establish and would be also site-specific.

The presented research, which provides an approach for calculating reliable EMC values and analyzing data to face future monitoring challenges, yielded several additional lessons for researchers:

- In the case that a certain OMP has a high proportion of censored data, a greater number of events shall be monitored, especially when the EQS is below the LoQ.
- Highly accurate chemical analysis is needed to detect analytically-sensitive OMPs, e.g., phenolic substances with variable LoQs.
- Understanding the fractionation of OMPs (particulate, colloidal, and dissolved) is beneficial, especially when choosing proper quality treatment practices.
- More in-depth research on the current sources of the OMPs in the study catchment would benefit future source management.
- Although collecting a composite sample for an entire rain event would be a better approach in such studies, MC simulation can be used to reliably estimate EMC values and the associated uncertainty from subsamples' concentration and volume datasets.

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Statements and Declarations

Data Availability

All the data generated/analysed in this study are included in the manuscript, supplementary information. The processed dataset and the code used to generate the dataset is available at https://doi.org/10.5878/nny1-2045.

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Authors' contributions

Ali Beryani: Conceptualization, Methodology, Field investigation, Validation, Formal analysis, Visualization, Writing– original draft & review & editing. **Kelsey Flanagan**: Conceptualization, Validation, Formal analysis, Writing– review & editing. **Maria Viklander**: Supervision, Writing– review & editing, Project administration, Funding acquisition. **Godecke-Tobias Blecken**: Conceptualization, Methodology, Validation, Writing– review & editing, Supervision, Project administration, Funding acquisition.

Competing interest

There is no conflict of interest in this research.

Ethics declaration

Ethical approval and consent to participate are not applicable in this study.

Supplementary information

Occurrence and concentrations of organic micropollutants (OMPs) in highway stormwater: A comparative field study in Sweden

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Figure S1. Site plan of the catchment area (denoted in green) in Sundsvall, Sweden

Table S1. Standard analytical methods used for determining the concentrations of organic substances and other parameters

Parameter	Analytical method
PAHs	Determination of semi-volatile organic compounds by gas chromatography with MS or MS/MS detection according to methods US EPA 8270D, US EPA 8082A, CSN EN ISO 6468, and US EPA 8000D. Samples were prepared as per CZ_SOP_D06_03_P01 chap. 9.1, 9.4.1. ($LOR^{\$} \equiv LoQ^{\#}$)= 3*$LOD^{£}$ **LORs:** • Naphthalene: 0.03 µg/L; Benzo(a)pyrene: 0.005 µg/L; Phenanthrene: 0.02 µg/L; the rest of the parameters: 0.01 µg/L. • The upper limit depends a lot on the nature of the sample – The lab would roughly estimate it to be around hundreds of mg/L. **CRM*:** (standards and suppliers) • CLP Priority Pollutant Internal Standards (CLP PPIS): Absolute Standard • PAH Mix TCL: Sigma-Aldrich • PAH-Mix 9: Dr. Ehrenstorfer • Dibenz(a.h.)antracene-D14: Dr. Ehrenstorfer • Dibenz(a.h.)antracene-D14: Dr. Ehrenstorfer • 2-fluorobiphenyl: Sigma-Aldrich • p-Terphenyl-D14: Sigma-Aldrich

PHCs	Determination of extractable compounds in the range of hydrocarbons C10−C40, fractions were calculated from the measured values by gas chromatography with FID detection according to the following methods: CSN EN ISO 9377-2; US EPA 8015; US EPA 3510; TNRCC Method 1006. (LOR ≡ LoQ)= 3*LOD The tested measurement range was 10 to 1000 µg/ml of extract, which corresponds, when using a 200ml sample, to a range of 42 to 4170 µg/L sample. In this range, the calibration is linear. **CRM*:** (standards and suppliers) • two-component standard of diesel with oil, suitable presence of prystan and phytan, e.g. catalogue number BAM-K010; supplier: Chromservis. • standard, which contains mixture of n-alkanes (C_8-C_{40}), e.g. Alkanes-Mix 17, manufacturer: Dr. Ehrenstorfer. **RM****: • n-decane (C10), e.g., n-decane; manufacturer: Dr. Ehrenstorfer; supplier Chromservis • n-tetracontane (C40), e.g., n-tetracontane; manufacturer: Dr. Ehrenstorfer; supplier: Chromservis
BPA and Alkylphenols (APs)	Determination of alkylphenols and alkylphenol ethoxylates by gas chromatography with MS or MS/MS detection according to method CSN EN ISO 18857-2. Total alkylphenols and alkylphenol ethoxylates were calculated based on the measured values. (LOR ≡ LoQ)= 3*LOD **LORs:** • Nonylphenols: 0.05 µg/L; Octylphenols: 0.01 µg/L; Bisphenol A: 0.05 µg/L. • The upper limit, according to the lab estimations, would be around hundreds of mg/L. **CRM:** (standards and suppliers) • Custom mixture of Phenol Ethoxylates: CHIRON AS • 4-n-Nonylphenol D4: Neochema • 4-n-Nonylphenol diethoxylate: Chiron AS • Bisphenol A D16: Sigma-Aldrich
TOC	Total organic carbon (TOC) was determined by IR detection according to methods CSN EN 1484 and SM 5310.
TSS	Gravimetrical determination of suspended solids according to method SS-EN 872-2:2005.
Turbidity	Determined with a 2100Q IS Portable Turbidimeter, HACH (Loveland, CO), calibrated with Formazin primary StablCal Standards.
Conductivity and temperature	Determined with pHenomenal® Conductivity/TDS/°C Meter, Handheld, CO 3100 H, VWR (Radnor, PA), calibrated using the control standard KCl solution.
pH	Determined with a pH 330i meter, Handheld, WTW GmbH (Weilheim, Germany), calibrated by buffer solutions.

* Certified Reference Materials (CRM)
** Reference Materials (RM)
$ Limit of Reporting (LOR)
# Limit of Quantification (LoQ)
£ Limit of Detection (LOD)

Table S2. Characteristics of various Polycyclic Aromatic Hydrocarbons (PAHs)

PAH	Abbr.	Molecular mass$ (Daltons)	No. of rings	fraction	Carcino-genicity group*	Water solubility¥ (mg/L at 25 ° C)	Vapor pressure# (Pa at 25 ° C)	Log $K_{ow}$$	Log K_{oc} (calc.) £
Naphthalene	Nap	128	2	LWM	2B	31.6	10.4	3.37	2.95
Acephthylene	Acyl	152	3	LWM	–	16	9.0e-1	4.00	3.13
Acephthene	Acen	154	3	LWM	3	4.5	30e-1	3.92	3.46
Fluorene	Flu	166	3	LWM	3	1.8	9.0e-2	4.18	3.71
Phenthrene	Phen	178	3	LWM	3	1.3	2.0e-2	4.57	3.79
Anthracene	Anth	178	3	LWM	3	0.07	1.0e-3	4.54	4.57
Fluoranthene	Flth	202	4	MWM	3	0.24	1.2e-3	5.22	4.24

Pyrene	Pyr	202	4	MWM	3	0.14	6.0e-4	5.18	4.39
Benz(a) anthracene	BaA	228	4	HWM	2B	0.01	2.8e-5	5.91	5.09
Chrysene	Chry	228	4	HWM	2B	0.003	5.7e-7	1.65	5.41
Benzo(b) fluoranthene	BbF	252	5	HWM	2B	<0.001	–	5.80	5.70 <
Benzo(k) fluoranthene	BkF	252	5	HWM	2B	<0.001	5.2e-8	6.00	5.70 <
Benzo(a)pyrene	BaP	252	5	HWM	1	<0.001	7.0e-7	6.04	5.70 <
Dibenz(a.h) anthracene	DahA	278	5	HWM	2A	<0.001	3.7e-10	6.75	5.70 <
Benzo(g.h.i) perylene	Bper	276	6	HWM	3	<0.001	–	6.50	5.70 <
Indeno(1.2.3.cd) pyrene	InP	276	6	HWM	2B	<0.001	6e-8	6.58	5.70 <

¥ (Monaco et al., 2017)
(Joa et al., 2009)
$ K_{ow}: Octanol-water partition coefficient (Joa et al., 2009)
£ K_{oc}: Sediment organic carbon-water partition coefficient (Khodadoust et al., 2005)
* (1): carcinogenic to humans; (2A): probably carcinogenic to humans; (2B): possibly carcinogenic to humans; (3): not classifiable as carcinogenic to humans (IARC Working Group, 2010).

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Table S3. Characteristics of various Petroleum Hydrocarbons (PHCs) (Reed & Stemer, 2002)

Petroleum Hydrocarbons (only C10< fractions)	Molecular Weight	Water solubility¥ (mg/L at 25 ˚C)	Vapor pressure$ (Pa at 25 ˚C)	Boiling point (˚C)	Log K_{oc} (calc.) £
Aliphatic					
C_{10}–C_{12}	160	0.026	7.9e+1	200	5.4
C_{12}–C_{16}	200	5.9e-4	3.5	260	6.7
C_{16}–C_{21}	270	1.0e-6	1.7e-1	320	8.8
Aromatic					
C_{10}–C_{12}	130	25	7.8e+1	200	3.4
C_{12}–C_{16}	150	5.8	3.5	260	3.7
C_{16}–C_{21}	190	0.51	1.7e-1	320	4.2
C_{21}–C_{35}	240	0.0066	7.9e-4	340	5.1

Note: Values are based on pure substances; behaviour may differ in complex mixtures.
£ K_{oc}: Sediment organic carbon-water partition coefficient

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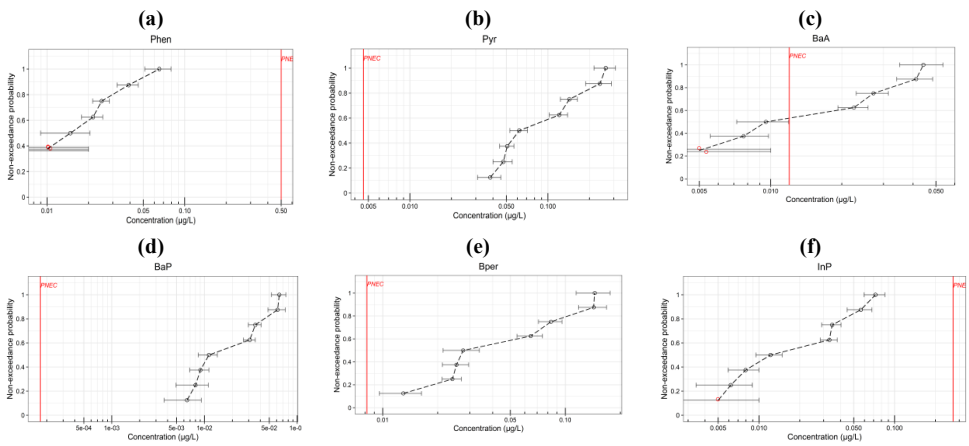

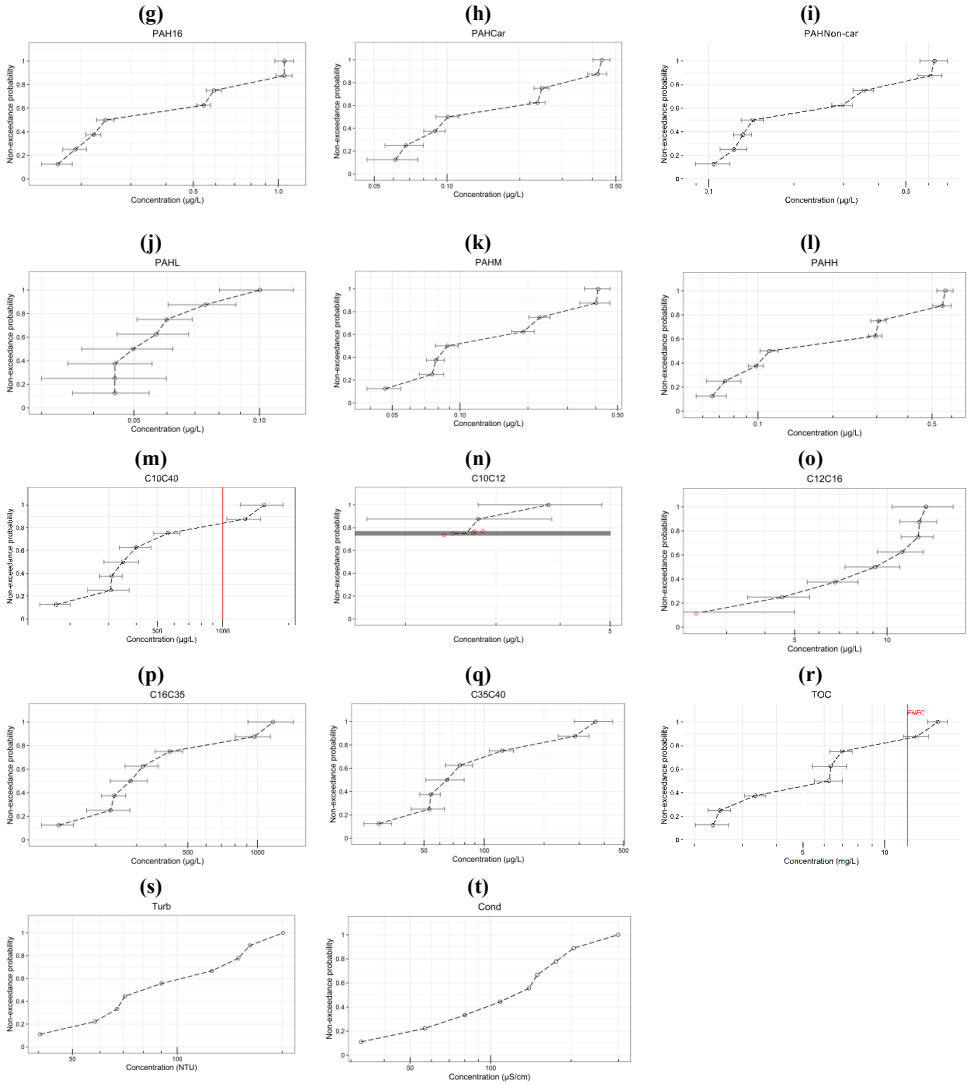

Figure S2. Non-exceedance probability (NEP) plots based on the estimated EMC values for each OMP (Black points are detects and red points censored data (non-detects); Error bars show EMC errors (uncertainties); Red lines represent lowest PNEC levels for freshwater based on water quality objectives (WQOs))

Table S4. Correlation coefficients matrix for all parameters (Kendall's Tau ranks are underlined while Spearman's correlation ranks are not) (Dark green: very strong; Green: strong; Yellow: moderate; Orange: weak; Red: very weak). The values shown in black are statistically significant (p-value < 0.05), while those in grey are not.

Phen	Flth	Pyr	BaA	Chry	BbF	BkF	BaP	DahA	Bper	InP	PAH16	PAHCar	PAHNon-car	PAHL	PAHM	PAHH	OP	NP	BPA	C_{10}-C_{40}	C_{10}-C_{12}	C12-C_{16}	C_{16}-C_{35}	C_{35}-C_{40}	TOC	TSS	Turb	Cond	pH	Depth	ADP	I_{mean}	I_{peak}	
0.79	0.79	0.71	0.71	0.71	0.71	0.64	0.64	0.71	0.79	0.64	0.79	0.64	0.79	0.79	0.71	0.71	0.50	-0.11	-0.14	0.79	0.04	0.39	0.79	0.79	-0.21	0.57	0.80	0.40	0.00	-0.14	-0.07	0.21	-0.07	Phen
	1.00	0.88	0.68	0.75	0.88	0.61	0.79	0.71	0.76	0.57	0.91	0.86	0.91	0.93	0.88	0.81	0.46	-0.04	-0.17	0.83	0.04	0.39	0.83	0.79	-0.29	0.88	0.83	0.60	-0.20	-0.14	-0.14	0.31	-0.19	Flth
		1.00	0.68	0.75	1.00	0.75	0.95	0.71	0.83	0.86	0.98	0.98	0.98	0.86	1.00	0.98	0.61	0.04	-0.29	0.95	0.04	0.39	0.95	0.81	-0.26	0.76	0.94	0.37	0.14	0.10	-0.14	0.38	0.10	Pyr
			0.82	0.75	0.68	0.75	0.75	0.62	0.75	0.75	0.75	0.75	0.75	0.75	0.68	0.68	0.61	-0.14	-0.18	0.75	0.04	0.29	0.75	0.68	-0.25	0.46	0.73	0.33	0.20	-0.11	-0.11	0.25	-0.18	BaA
				0.96	0.75	0.68	0.82	0.62	0.68	0.79	0.82	0.82	0.82	0.61	0.75	0.75	0.68	0.04	-0.39	0.82	0.04	0.50	0.82	0.75	-0.39	0.46	0.77	0.14	0.09	0.11	-0.25	0.32	0.04	Chry
					1.00	0.75	0.95	0.71	0.83	0.86	0.98	0.98	0.98	0.86	1.00	0.98	0.61	0.04	-0.29	0.95	0.04	0.39	0.95	0.81	-0.26	0.76	0.94	0.37	0.14	0.10	-0.14	0.38	0.09	BbF
						0.82	0.82	0.62	0.68	0.82	0.68	0.82	0.68	0.68	0.75	0.75	0.54	-0.07	-0.11	0.68	0.04	0.21	0.68	0.61	-0.18	0.54	0.73	0.33	0.20	-0.04	-0.04	0.32	-0.11	BkF
							1.00	0.62	0.88	0.93	0.93	0.98	0.93	0.79	0.95	0.98	0.68	0.04	-0.45	0.95	0.04	0.39	0.95	0.86	-0.43	0.64	0.89	0.26	0.31	0.17	-0.21	0.45	0.10	BaP
								0.71	0.71	0.62	0.71	0.62	0.71	0.71	0.71	0.71	0.33	-0.10	-0.05	0.71	0.05	0.38	0.71	0.71	-0.14	0.62	0.70	0.10	-0.30	-0.05	0.14	0.05	-0.05	DahA*
									1.00	0.71	0.86	0.81	0.86	0.83	0.83	0.91	0.54	-0.18	-0.21	0.93	0.04	0.39	0.93	0.98	-0.33	0.69	0.94	0.37	0.14	-0.07	-0.21	0.31	-0.12	Bper
										0.93	0.79	0.93	0.79	0.64	0.86	0.86	0.64	0.00	-0.21	0.79	0.04	0.32	0.79	0.64	-0.21	0.43	0.89	0.26	0.31	0.07	-0.07	0.29	-0.00	InP
											1.00	0.95	1.00	0.88	0.98	0.95	0.68	-0.04	-0.31	0.98	0.04	0.46	0.98	0.83	-0.33	0.74	0.94	0.37	0.14	0.05	-0.19	0.26	-0.00	PAH16
												1.00	0.95	0.83	0.98	0.95	0.68	0.04	-0.41	0.93	0.04	0.32	0.93	0.79	-0.38	0.69	0.89	0.26	0.31	0.12	-0.17	0.41	0.07	PAHCar
													1.00	0.88	0.98	0.95	0.68	-0.04	-0.31	0.98	0.04	0.46	0.98	0.83	-0.33	0.74	0.94	0.37	0.14	0.05	-0.19	0.26	-0.00	PAHNon-car
														1.00	0.86	0.81	0.46	-0.18	0.05	0.83	0.04	0.25	0.83	0.79	-0.12	0.81	0.94	0.71	0.03	-0.33	-0.02	0.10	-0.32	PAHL
															1.00	0.98	0.61	0.04	-0.29	0.95	0.04	0.39	0.95	0.81	-0.26	0.76	0.94	0.37	0.14	0.10	-0.14	0.38	0.10	PAHM
																1.00	0.61	0.04	-0.33	0.98	0.04	0.46	0.98	0.88	-0.31	0.71	0.94	0.37	0.14	0.14	-0.19	0.43	0.12	PAHH
																	0.89	-0.04	-0.46	0.68	-0.04	0.21	0.68	0.46	-0.54	0.18	0.40	0.00	0.53	-0.04	-0.39	0.18	-0.11	OP
																		0.54	-0.39	-0.04	0.00	0.04	-0.04	-0.11	-0.18	-0.04	-0.20	-0.33	-0.47	0.46	0.04	0.25	0.54	NP
																			1.00	-0.36	0.04	-0.25	-0.36	-0.31	0.88	0.05	0.14	0.66	-0.09	-0.60	0.52	-0.52	-0.38	BPA
																				1.00	0.04	0.54	1.00	0.91	-0.38	0.69	0.94	0.37	0.14	0.10	-0.24	0.31	0.02	C_{10}-C_{40}
																					0.04	0.04	0.04	0.04	0.04	0.04	0.07	0.07	-0.07	-0.04	0.04	-0.04	-0.04	C_{10}-C_{12}
																						0.96	0.54	0.46	-0.25	0.25	0.13	0.00	-0.40	0.11	-0.46	0.04	0.18	C_{12}-C_{16}
																							1.00	0.91	-0.38	0.69	0.94	0.37	0.14	0.10	-0.24	0.31	0.02	C_{16}-C_{35}
																								1.00	-0.43	0.74	0.83	0.26	-0.09	0.00	-0.29	0.45	-0.02	C_{35}-C_{40}
																									1.00	0.19	0.33	0.78	-0.13	-0.52	0.66	-0.17	-0.28	TOC
																										1.00	0.90	0.42	-0.25	-0.02	0.20	0.46	0.12	TSS
																											1.00	0.53	0.13	-0.13	0.33	0.38	0.05	Turb
																												1.00	0.20	-0.87	0.20	-0.12	-0.73	Cond
																													1.00	-0.10	0.03	-0.15	-0.32	pH
																														1.00	0.01	0.45	0.93	Depth
																															1.00	-0.13	0.14	ADP
																																1.00	0.63	I_{mean}
																																	1.00	I_{peak}

* One of the EMC values of DahA (rain event C), which returned misleading correlation coefficients, was excluded from the data set as a suspicious outlier. No extra water was available to reanalyze the sample.

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Paper II

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Performance of a gross pollutant trap-biofilter and sand filter treatment train for the removal of organic micropollutants from highway stormwater (Field study)

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Performance of a gross pollutant trap-biofilter and sand filter treatment train for the removal of organic micropollutants from highway stormwater (Field study)

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Abstract

This field study assessed the occurrence, event mean concentrations (EMCs), and removal of selected organic micro-pollutants (OMPs), namely, polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbons (PHCs), nonylphenol (NP), 4-t-octylphenol (OP), and bisphenol A (BPA), in a gross pollutant trap (GPT)-biofilter/sand filter stormwater treatment train in Sundsvall, Sweden. The effects of design features of each treatment unit, including pre-sedimentation (GPT), sand filter medium, vegetation, and chalk amendment, were investigated by comparing the units' removal performances. Overall, the treatment train removed most OMPs from highway runoff effectively. The results showed that although the sand filter provided moderate (<50% for phenolic substances) to high (50–80% for PAHs and PHCs) removal of OMPs, adding a vegetated soil layer on top of the sand filter considerably improved the removal performance (by at least 30%), especially for BPA, OP, and suspended solids. Moreover, GTP did not contribute to the treatment significantly. Uncertainties in the removal efficiencies of PAHs and PHCs by the filter cells increased substantially when the ratio of the influent concentration to the limit of quantification decreased. Thus, accounting for such uncertainties due to the low OMP concentrations should be considered when evaluating the removal performance of biofilters.

Keywords: Road runoff; Bioretention; Retention soil filter; Vegetation; Censored data; Uncertainty analysis; Risk analysis

Highlights

- Overall, treatment train reliably removes OMPs and reduces their environmental risk
- Filter cells effectively improve water quality
- Vegetated biofilters are more effective than non-vegetated sand filters
- Concentrations and removal uncertainties of OMPs in field studies can be considerable

1. Introduction

Traffic-related activities are known to be one of the major sources of organic micropollutants (OMPs) in road runoff. Recent studies have shown that hazardous OMPs, such as phthalates, alkylphenols and polycyclic aromatic hydrocarbons (PAHs), have been frequently detected in road runoff at concentrations exceeding environmental quality standards (EQS) (Gasperi et al., 2022; Mutzner et al., 2022; Wicke et al., 2021). Many types of OMPs can resist biodegradation, bioaccumulate, and potentially cause ecological risk to receiving water bodies (Diblasi et al., 2009; Markiewicz et al., 2017). Although the dilution of runoff in receiving water bodies is expected to limit the risks, OMPs can still cause acute or chronic adverse effects (Rehrl, 2019; Spahr et al., 2019). Thus, stormwater biofilters (or bioretention) are one of the stormwater control measures (SCMs) developed to enhance the quality of runoff using infiltration processes through (often sand-based) filter media (Prince George's County, 2007).

Usually, a more effective stormwater treatment can be achieved by combining complementary treatment processes in stormwater treatment trains (TT). Biofilters can be equipped with a so-called forebay or gross pollutant trap (GPT) for coarse particle sedimentation and oil separation (Andersson et al., 2018). Although there have been successful examples of utilizing pre-sedimentation tanks to treat highway runoff (Andersson et al., 2018; Hunt et al., 2015; Purvis et al., 2019), some field observations (Greenway et al., 2012; Lange et al., 2021) have revealed

that GPT may not perform well enough for removal of suspended solids (TSS), N nutrients, and microplastics. This study tried to determine the effectiveness of a GPT within a TT for removing OMPs from highway runoff.

Often, biofilter media targeting water quality treatment are sand or sandy-loam based engineered soils with a relatively low content of organic matter (to avoid nutrient leaching) (DWA-M 187, 2005). To enhance their performance, various amendments have been proposed. For example, chalk ($CaCO_3$) may compensate for low organic matter content and increase the filter media's buffer capacity, enhancing solute adsorption on the solid phase (DWA-M 187, 2005; Søberg et al., 2019). Originally, adding chalk was considered to enhance metal adsorption for highway runoff (DWA-M 187, 2005; Grotehusmann et al., 2016). However, there have been very few studies of the effect of chalk-amended biofilters on OMP treatment performance.

Vegetation is another key feature of biofilters since vegetated biofilters can have several positive benefits in relation to quality compared to non-vegetated sand filters. Plant cover can mechanically filter particulate pollutants, prevent clogging, and may remove pollutants directly by uptake or indirectly by increasing microbial activity (Chu et al., 2021; Le Coustumer et al., 2012; Muerdter et al., 2016). While most previous biofilter studies on the effect of vegetation species have focused on TSS, metal, and nutrient removal (Dagenais et al., 2018), a few have investigated removal of OMPs by biofilters, but under controlled conditions using artificial runoff (Leroy et al., 2015; Randelovic et al., 2016; Zhang et al., 2014). However, there is still a need for further knowledge on vegetation as a factor for OMP removal under field conditions with real runoff.

Some laboratory or pilot-scale studies have shown that OMPs such as PAHs, plasticizers, and bisphenol-A (BPA) (Bester & Schäfer, 2009; Leroy et al., 2015; Lu & Chen, 2018) can be effectively removed by biofilter systems. However, the behavior of micropollutants in laboratory-scale columns or mesocosm experiments under controlled conditions may not always be representative of that for field systems where there are more complex and varying environmental conditions (Flanagan et al., 2019). A few recent field studies have shown that biofiltration can be effective for OMP removal, particularly for hydrophobic and highly particulate substances such as polychlorinated biphenyls (PCBs), PAHs, and total petroleum hydrocarbons (PHCs) (David et al., 2015; Diblasi et al., 2009; Flanagan et al., 2018), though with a more limited effect for more hydrophilic and soluble substances such as plasticizers (phthalates and benzoates), BPA, polyfluorinated alkyl substances (PFAS), and herbicides (Boehm et al., 2020; Spahr et al., 2019; Zhang et al., 2016). There are still limited data about the treatment performance evaluation and validation of biofilter systems (specially treatment trains) under field conditions in relation to OMPs, in particular less-studied OMPs such as BPA and alkylphenols (compared with solids, nutrients, and metals).

The main objective of this study was to assess the performance of a full-scale GPT-biofilter/sand filter stormwater treatment train (TT) for the removal of target OMPs (i.e. sixteen PAHs, four fractions of PHCs, eight alkylphenols (APs), and BPA) from a highway bridge catchment. First, we evaluated the role of the GPT pre-treatment and then the effects of vegetation and chalk factors on the OMP treatment by three different biofilter cells: vegetated without chalk, vegetated with chalk, and non-vegetated without chalk. Finally, we investigated the performance of the TT in reducing potential environmental risks of OMPs and identified the most relevant OMPs in the highway runoff and in the effluent of different units, based on comparative ranking of the risk levels, something which has been rarely carried out in prior studies.

2. Methodology

2.1. Study site

This field study was carried out using a gross pollutant trap (GPT)-biofilter/sand filter treatment train (TT) located in Sundsvall, Sweden (62°23'0.5"N 17°20'50.5"E), which has Continental Subarctic Climate (Dfc) and cool summers. The system receives stormwater from an impervious catchment area of 4.7 ha including the 1.9 ha E4 highway bridge with an average traffic load of 13,000 vehicles/day, a highway exit way, main roads associated with a roundabout and sidewalk paths (Figure S1).

The TT (Figure 1) was designed according to German stormwater biofilter guidelines for treatment of highway runoff (DWA-M 187, 2005) and was constructed in 2018 i.e. it was 3 years old at the time of sampling.

Downstream of the road catchment, the collected stormwater is first transported by a 100-m-long underground pipe (slope 0.5% and diameter 0.8 m) to the GPT section which includes a sedimentation chamber and an oil separator. The stormwater in the GPT is then discharged through a stepwise valve-controlled siphon system to three parallel filter cells divided by EPDM membranes where it infiltrates through the sand-based filter media. One of the filter cells is non-vegetated (*sand filter SF*), and the other two are vegetated (*biofilters BFC* and *BF*). The vegetation layer is made of salt-tolerant meadow sod (Veg Tech AB, Sweden) with 17 different plant species pre-cultivated in a 3–4 cm deep sandy or silty-sandy soil with 2.5–5% w/w mulch (see Figure S2). The filter media in one of the biofilters (*BFC*) is amended with 10% w/w crushed grey chalk ($CaCO_3$). Afterwards, the treated stormwater is drained from the cells through a gravel drain layer with embedded drainpipes, then led to three sampling wells, and finally collected and released to the downstream recipient. If the runoff inflow exceeds the GPT's active detention volume (~23.3 m^3) during each charging and discharge step, the stormwater is bypassed from the TT at the GPT entrance. See Table S1 and Figure S3 for more technical information on the TT compartments. In previous research, the same treatment train has been investigated for total, dissolved and truly dissolved metals by Lange et al. (2022), and microplastics by Lange et al. (2021).

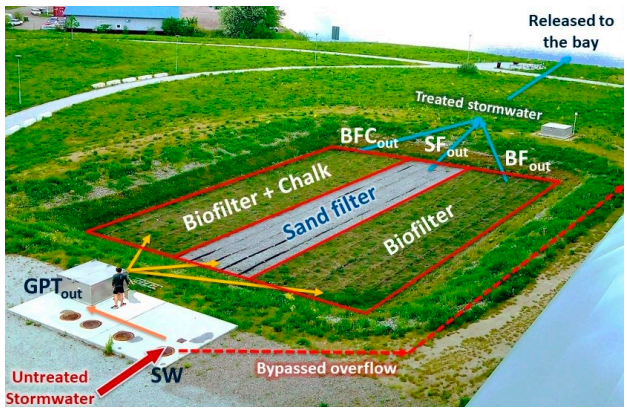


Figure 1. GPT-biofilter/sand filter treatment train (TT) studied in Sundsvall, Sweden (SW, GPT_{out}, BFC_{out}, SF_{out}, and BF_{out} are the abbreviations for the locations where the samples are taken from stormwater inflow, and the outflow of gross pollutant trap and the filter cells respectively)

2.2. Sampling procedure and strategies

The performance of the TT was investigated for 11 rain events between September 2020 and September 2021 (Rain A–K in Table S2). Samples were collected from five locations in the system:

- **SW**: stormwater received at GPT inlet from the catchment
- **GPT_{out}**: gross pollutant trap outflow (or filters inflow)
- **BFC_{out}**: chalk-amended vegetated biofilter outflow
- **SF_{out}**: non-vegetated sand filter outflow
- **BF_{out}**: vegetated biofilter outflow

Rainfall data were collected using a tipping bucket rain gauge (ISCO 674) next to the highway catchment (Figure S1). Volume-proportional samples were taken during the rain events using ISCO-6712 automatic samplers. The samplers were programmed to collect a maximum of 8 volume-proportional subsamples estimated at each location. Flow was also measured at each sampling location: the GPT's influent and effluent by counting the number of discharge valve signals (supported by data from an ultrasound flowmeter at the inlet (PCM 4, NIVUS GmbH, Eppingen)), and the effluent of each filter cell by using pipe-insertion electromagnetic flowmeters (MAG 5100 Siemens AG). The discharge valves are triggered by a floating water level meter installed in the GPT. When the valves are open, the GPT discharges 23.3 m^3 stormwater to the filter cells and simultaneously, a signal is sent to the samplers dedicated to the SW and GPT_{out} locations to take one subsample. The samplers at BFC_{out}, SF_{out}, and BF_{out} were triggered by the insertion flowmeter signals. Therefore, the total number of signals needed for

programming the samplers at a certain rain event was estimated according to the maximum possible outflow volume of the filter cells to cover the entire outflow. Rain characteristics, including depth, peak/mean intensity (I_{peak} and I_{mean}), and antecedent dry period (ADP), number of subsamples taken, and the total and sampled volumes at each sampling location for all events are summarized in Table S2. Due to practical limitations such as uncertainties of rain depth and duration forecasts, as well as the time taken to deliver samples to the laboratory, it was not possible to cover the entire runoff volume in some events (see Table S2).

Each sampler was equipped with 24 lay flat Teflon™ PFA bags (Welch Fluorocarbon) (i.e. three bags per subsample), except for the sampler at BF_{out} where the subsamples were collected in a 10-liter glass container (i.e. one composite sample). The Teflon bags and the container were washed with tap water before each sampling event. The samples collected were delivered to the laboratory within one day after sampling. In case of time delay in delivery (e.g. weekends), all OMPs samples were stored in a refrigerator (1−4˚C), and TOC samples in a freezer (< -15˚C).

2.3. Water quality analysis

All samples were analyzed for a number of selected OMPs and global parameters, including phenolic substances (bisphenol A, 4-t-octylphenol (OP), nonylphenol (NP), octylphenol ethoxylates (OPnEO; n=1, 2, 3), nonylphenol ethoxylates (NPnEO; n=1, 2, 3)), 16 PAHs, 4 fractions of PHCs, total organic carbons (TOC), total suspended solids (TSS), turbidity, conductivity, pH, and temperature. A full list of the OMPs with their abbreviations and limits of quantification is given in Table 1. OMPs and TOC were analyzed by the accredited laboratory ALS Czech Republic, and TSS by accredited ALS Scandinavia AB. It should be noted that reporting limits (RL) for phenolic substances (except BPA) were sometimes affected by matrix interference during chemical analysis, meaning that the RLs varied over the experiments (see Table 1). Global parameters were all measured during sampling events on site. Table S3 summarizes the analytical methods and equipment used in this study.

In order to assess any potential leaching of OMPs from the sampling bags and tubes, batch blank tests were carried out onsite and in the laboratory. The procedure for blank testing is described in our previous study in detail (Beryani et al., Submitted). The results showed that the OMPs of concern were not found in the water in contact with sampling equipment. Nevertheless, after the first 6–7 events, we changed the Teflon bags of all samplers for a new series of bags. Moreover, to avoid cross-contamination throughout the experiments, we allocated each sampling bag to the same position in the identical sampler.

Table 1. List of selected organic micropollutants (OMPs) analyzed in the stormwater and treatment train (TT)

Category	Parameter	Abbreviation	Reporting limit (µg/L)
Phenolic substances	Bisphenol-A	**BPA**	0.05
	4-tert-octylphenol	**OP**	0.01–0.25*
	Octylphenol monoethoxylate	**OP1EO**	0.01–0.03*
	Octylphenol diethoxylate	**OP2EO**	0.01–0.02*
	Octylphenol triethoxylate	**OP3EO**	0.01–0.033*
	Nonylphenol_mixture of isomers	**NP**	0.1–1.35*
	Nonylphenol monoethoxylate	**NP1EO**	0.1–0.3*
	Nonylphenol diethoxylate	**NP2EO**	0.1–2.54*
	Nonylphenol triethoxylate	**NP3EO**	0.1–3.12*
Polycyclic aromatic hydrocarbons (PAHs)	Naphthalene	**Nap**	0.03
	Acenaphthylene	**Acyl**	0.01
	Acenaphthene	**Acen**	0.01
	Fluorene	**Flu**	0.01
	Phenanthrene	**Phen**	0.02
	Anthracene	**Anth**	0.01
	Fluoranthene	**Flth**	0.01
	Pyrene	**Pyr**	0.01
	Benz(a)anthracene	**BaA**	0.01
	Chrysene	**Chry**	0.01

	Benzo(b)fluoranthene	**BbF**	0.01
	Benzo(k)fluoranthene	**BkF**	0.01
	Benzo(a)pyrene	**BaP**	0.01
	Dibenz(a.h)anthracene	**DahA**	0.01
	Benzo(ghi)perylene	**Bper**	0.01
	Indeno(1.2.3-cd)pyrene	**InP**	0.01
	Sum of all PAHs	**Σ16PAHs**	–
	Carcinogenic PAHs	**ΣCar.PAHs**[#]	–
	Non-carcinogenic PAHs	**Σnon-Car.PAHs**[$]	–
	Light-weight PAH molecules	**ΣLMW-PAHs**[¥]	–
	Medium-weight PAH molecules	**ΣMMW-PAHs**[€]	–
	High-weight PAH molecules	**ΣHMW-PAHs**[₹]	–
Petroleum hydrocarbons (PHCs)	Total PHCs PHC fractions	**C_{10} - C_{40}**	50
		C_{10} - C_{12}	5
		C_{12} - C_{16}	5
		C_{16} - C_{35}	30
		C_{35} - C_{40}	10
Global parameters	Total organic carbons	**TOC**	500
	Total suspended solids	**TSS**	2200
	Turbidity	**Turb**	–
	Electric conductivity	**EC**	–
	pH	**pH**	–
	Temperature	**Temp.**	–

[*] The lower limit represents the min RL analytically expected and the upper limit represents the max RL reported by the laboratory for a certain substance (RL varies between the range due to matrix interference during chemical analysis.)
[#] Nap, BaA, Chry, BbF, BkF, BaP, BahA, Bper
[$] Acyl, Acen, Flu, Phen, Anth, Flth, Pyr, IP
[¥] Nap, Acyl, Acen, Flu, Phen, Anth
[€] Flth, Pyr
[₹] BaA, Chry, BbF, BkF, BaP, DahA, Bper, IP

2.4. Data analysis

2.4.1. Event mean concentration (EMC)

To evaluate treatment performance, the event mean concentration (EMC) of OMPs at each sampling location was estimated using the subsamples' concentrations and flow records. The EMC is an expression of the total mass (M_T) conveyed by the total stormwater volume (V_T) at a specific location during the entire event period (Equation 1). In Equation 1, n is the number of subsamples, m_i is the pollutant mass conveyed during the collection of the i^{th} subsample, c_i is the i^{th} subsample concentration, and v_i is the corresponding stormwater volume passed.

$$\mathrm{EMC} = \frac{\mathrm{M_T}}{\mathrm{V_T}} = \frac{\sum \mathrm{m_i}}{\sum \mathrm{v_i}} = \frac{\sum_{i=1}^{n} \mathrm{c_i v_i}}{\sum_{i=1}^{n} \mathrm{v_i}} \qquad \textit{Equation 1}$$

For some events, no water was collected from a given sampling location due to practical reasons (see Table S2). In that scenario, to estimate a more accurate EMC following a suggestion made by Furuta et al. (2022), EMC calculations were adjusted by weighting the final subsample concentration with the missing volume in addition to the original volume sampled. In this adjustment, rain event G at SW and GPT_{out} was an exception where the first 17% of stormwater was not covered. Thus, using the same analogy, the missing part of the rain event was assigned to the first subsample for EMC calculations.

2.4.2. Estimation of best EMCs and their associated uncertainties

To spread the uncertainty in the EMC due to analytical issues and missing data in individual analyses, a Monte-Carlo (MC) simulation was used in R software. In the MC method, Equation 1 was used to find the EMC distribution at a given sampling point for a certain rain event. Details of the MC simulation are given in the supporting information. The median of the final EMC distribution was considered to be the best-estimate event mean concentration (EMC_{best}), and the range between 2.5% and 97.5% quantiles as the EMC's lower and upper limits of uncertainty ($-\Delta_l$, $+\Delta_u$).

The EMCs for PAH fractions (Σ16-, ΣCar-, Σnon-Car-, ΣLMW-, ΣMMW-, and ΣHMW- PAHs) and their uncertainties were estimated by running the MC method twice. In the first step, a concentration distribution for a certain PAH fraction was generated for each subsample using PAH substance group data under that fraction. In the next step, those distributions were used as input distributions to estimate the PAH fraction's EMC_{best} and its uncertainty at each sampling location (as explained before).

To visualize, assess, and compare the EMCs of OMPs at different sampling points, EMC non-exceedance probability (NEP) plots for all rain events were generated. To create these NEP plots, the Kaplan-Meier method, which is commonly applied to left-censored data analysis (Helsel, 2010), was used from the "EnvStats" V2.3.0 package for environmental statistics in R. Furthermore, to assess the stormwater quality at different treatment stages, the EMCs of OMPs shown in the NEP plots were compared with the existing lowest Predicted No-Effect Concentrations (PNECs) in freshwater (NORMAN, 2012). PNECs are considered as a basis for the environmental quality standards (EQSs) prioritized by European Union Water Framework Directive (2013/39/EU; WFD).

2.4.3. Removal efficiencies and uncertainties

Removal efficiencies (RE%) of different treatment sections were calculated using Equation 2, where EMC_{in} and EMC_{out} stand for EMC_{best} at the section's inlet and outlet. Since the uncertainties in EMCs cause an error in the removal efficiencies, the absolute removal error (Err_{Re}%) was also calculated using Equation 3 according to Taylor (1997), assuming that the EMC's uncertainties for the inlet and outlet (Δ_{in} and Δ_{out}) are independent. It should be noted that in the MC method used, the EMC_{best} for a censored EMC (i.e. if the concentrations of all subsamples were censored) was almost equal to half the LoQ. However, in cases where both inlet and outlet EMCs were censored for a given event, the calculated Re% and Err_{Re}% were excluded from our statistical analysis. Therefore, the number of data points for analyzing Re% and Err_{Re}% ranged from five to nine.

$$\mathrm{Re}\ (\%) = 100 \times \frac{\mathrm{EMC_{in}} - \mathrm{EMC_{out}}}{\mathrm{EMC_{in}}} \qquad \textit{Equation 2}$$

$$\mathrm{Err_{Re}}(\%) = 100 \times \sqrt{\left(\Delta_{\mathrm{in}} \cdot \frac{\mathrm{EMC_{out}}}{\mathrm{EMC_{in}}^2}\right)^2 + \left(\Delta_{\mathrm{out}} \cdot \frac{1}{\mathrm{EMC_{in}}}\right)^2} \qquad \textit{Equation 3}$$

2.4.4. Statistical analysis

The significance of differences between the concentrations of a certain parameter (*N= 8−11* rain events, except for ethoxylate alkylphenols) at the inlet and outlet of each treatment section were evaluated to gauge treatability. The differences between the EMCs of filter cells' outlets were also tested to compare statistically the filter cells' treatment efficiencies. Here, we used the Peto & Peto generalized Wilcoxon test, which is the most suitable way for assessing the significance of differences in left-censored log-normal data (our case) (Helsel, 2005). The Chi-square (X^2) calculated for the relative deviation of datasets was assumed statistically significant when the p-value (p) ≤ 0.05 (Null hypothesis, H_0: there is no difference between the concentrations of sampling points). For some points, correlation tests were carried out between TSS, turbidity, and other OMPs (refer to supporting information for details about the methods). All the statistical tests for censored data analysis were carried out using "NADA" (Nondetects and Data Analysis for Environmental Data) package in R (V4.1.3).

2.4.5. Risk analysis

According to Skivington (1997), risk refers to the combination of the occurrence likelihood of a defined hazard (presence of OMP) and the magnitude of the occurrence consequences. Equation 4 was used to estimate the total environmental risk (R_T) associated with an OMP at a particular sampling point during the entire experiment. An OMP's environmental hazard, or potential criticality, was assessed using the risk quotient (RQ_i), which is

calculated by dividing the observed concentration of the OMP by the chronic environmental quality standard (EQS) for freshwater (Mutzner et al., 2022). Here, the EQS was derived from the PNEC value (if available) for an OMP in an ecotoxicological database. For OMPs without a PNEC, no RQ was calculated; they were excluded from our risk ranking. Occurrence probability (P_j) of EMCs was quantified by dividing one by the number of events studied at a given sampling location. The calculated R_Ts were then used to compare the risk posed by OMPs at different stages in stormwater. Additionally, OMPs with an R_T>1 were deemed to be potentially risky pollutants for the receiving water body, although the dilution effect in that recipient may mitigate the risks in reality.

$$R_T = \sum_j P_j . RQ_j = \sum_j P_j . (EMC_j \pm \Delta_j)/PNEC \qquad (j\text{: rain event}) \qquad \text{Equation 4}$$

3. Results

3.1. EMC and occurrence analysis of OMPs

The EMC and occurrence analysis of OMPs in treated and untreated stormwater is presented below. A summary of the statistical analysis for the calculated EMCs of all OMPs is given in Table 2.

Table 2. Statistical summary of the calculated EMCs over events (N= $n_{quantified}$ + $n_{censored}$) at different sampling spots

Parameter	Conc. unit	SW			GPT			BFC			SF			BF			Water quality objective*
		n (quantified)	n (censored)	(min; mean; max; SD)	n (quantified)	n (censored)	(min; mean; max; SD)	n (quantified)	n (censored)	(min; mean; max; SD)	n (quantified)	n (censored)	(min; mean; max; SD)	n (quantified)	n (censored)	(min; mean; max; SD)	
Nap	µg/L	0	8	(-;-;<0.03;-)	0	8	(-;-;100%<0.03;-)	0	8	(-;-;100%<0.03;-)	0	9	(-;-;100%<0.03;-)	0	9	(-;-;100%<0.03;-)	2
Acyl	µg/L	0	8	(-;-;<0.01;-)	0	8	(-;-;100%<0.01;-)	0	8	(-;-;100%<0.01;-)	0	9	(-;-;100%<0.01;-)	0	9	(-;-;100%<0.01;-)	1.3
Acen	µg/L	0	8	(-;-;<0.01;-)	0	8	(-;-;100%<0.01;-)	0	8	(-;-;100%<0.01;-)	0	9	(-;-;100%<0.01;-)	0	9	(-;-;100%<0.01;-)	3.7
Flu	µg/L	0	8	(-;-;<0.01;-)	1	7	(87.5% <0.006;-;0.01;-)	0	8	(-;-;100%<0.01;-)	0	9	(-;-;100%<0.01;-)	0	9	(-;-;100%<0.01;-)	0.25
Phen	µg/L	5	3	(<0.015;0.026;0.065;0.017)	4	4	(<0.02;0.027;0.058;0.012)	0	8	(-;-;100%<0.02;-)	0	9	(-;-;100%<0.02;-)	0	9	(-;-;100%<0.02;-)	0.5
Anth	µg/L	0	8	(-;-;<0.01;-)	1	7	(87.5% <0.009;-;0.01;-)	0	8	(-;-;100%<0.01;-)	0	9	(-;-;100%<0.01;-)	0	9	(-;-;100%<0.01;-)	0.1
Flth	µg/L	8	0	(0.008;0.069;0.163;0.059)	7	1	(<0.007;0.062;0.142;0.053)	0	8	(-;-;100%<0.01;-)	5	4	(<0.005;0.01;0.033;0.008)	1	8	(88.9% <0.01;-;0.027;-)	0.0063
Pyr	µg/L	8	0	(0.038;0.12;0.262;0.088)	8	0	(0.03;0.102;0.235;0.08)	0	8	(-;-;100%<0.01;-)	9	0	(0.017;0.026;0.065;0.015)	1	8	(88.9% <0.01;-;0.042;-)	0.0046
BaA	µg/L	6	2	(<0.008;0.021;0.044;0.014)	6	2	(<0.006;0.02;0.038;0.012)	0	8	(-;-;100%<0.01;-)	2	7	(0.006;0.008;0.01;0.002)	1	8	(88.9% <0.01;-;0.016;-)	0.012
Chry	µg/L	7	1	(<0.009;0.029;0.069;0.023)	6	2	(<0.008;0.028;0.057;0.019)	0	8	(-;-;100%<0.01;-)	6	3	(0.005;0.008;0.017;0.003)	1	8	(88.9% <0.01;-;0.024;-)	0.0029
BbF	µg/L	8	0	(0.013;0.061;0.14;0.049)	8	0	(0.006;0.055;0.131;0.048)	0	8	(-;-;100%<0.01;-)	9	0	(0.008;0.013;0.037;0.009)	1	8	(88.9% <0.01;-;0.045;-)	0.017
BkF	µg/L	6	2	(<0.006;0.016;0.031;0.01)	6	2	(<0.006;0.015;0.031;0.01)	0	8	(-;-;100%<0.01;-)	1	8	(88.9% <0.008;-;0.01;-)	1	8	(88.9% <0.01;-;0.011;-)	0.017
BaP	µg/L	8	0	(0.006;0.028;0.064;0.024)	6	2	(<0.007;0.025;0.054;0.019)	0	8	(-;-;100%<0.01;-)	2	7	(0.007;0.007;0.015;0.003)	1	8	(88.9% <0.01;-;0.025;-)	0.00017
DahA	µg/L	5	3	(<0.006;0.011;0.027;0.006)	4	4	(<0.01;0.013;0.026;0.006)	0	8	(-;-;100%<0.01;-)	1	8	(88.9% <0.008;-;0.01;-)	1	8	(88.9% <0.01;-;0.011;-)	0.0014
BP	µg/L	8	0	(0.013;0.066;0.145;0.054)	8	0	(0.007;0.054;0.158;0.05)	1	7	(87.5% <0.007;-;0.01;-)	9	0	(0.008;0.014;0.042;0.011)	1	8	(88.9% <0.01;-;0.043;-)	0.0082
IP	µg/L	7	1	(<0.006;0.029;0.072;0.023)	6	2	(<0.008;0.029;0.075;0.023)	0	8	(-;-;100%<0.01;-)	3	6	(<0.005;0.008;0.022;0.005)	1	8	(88.9% <0.01;-;0.028;-)	0.27
Σ16PAHs	µg/L	8	0	(0.165;0.507;1.052;0.372)	8	0	(0.127;0.455;0.997;0.34)	1	7	(87.5% <0.04;-;0.095;-)	9	0	(0.114;0.143;0.301;0.062)	1	8	(88.9% <0.095;-;0.317;-)	-
ΣCarPAHs	µg/L	8	0	(0.061;0.208;0.438;0.155)	8	0	(0.051;0.195;0.409;0.145)	0	8	(-;-;100%<0.035;-)	9	0	(0.052;0.065;0.131;0.025)	1	8	(88.9% <0.035;-;0.175;-)	-
Σnon-Car.PAHs	µg/L	8	0	(0.104;0.3;0.631;0.218)	8	0	(0.074;0.26;0.588;0.197)	1	7	(87.5% <0.026;-;0.06;-)	9	0	(0.061;0.078;0.17;0.035)	1	8	(88.9% <0.06;-;0.142;-)	-
ΣLWM-PAHs	µg/L	8	0	(0.045;0.059;0.1;0.019)	8	0	(0.045;0.058;0.097;0.018)	0	8	(-;-;100%<0.025;-)	0	9	(-;-;100%<0.025;-)	0	9	(-;-;100%<0.025;-)	-
ΣMWM-PAHs	µg/L	8	0	(0.047;0.19;0.41;0.147)	8	0	(0.037;0.163;0.377;0.135)	0	8	(-;-;100%<0.01;-)	9	0	(0.023;0.034;0.098;0.024)	1	8	(88.9% <0.03;-;0.069;-)	-
ΣHWM-PAHs	µg/L	8	0	(0.066;0.258;0.566;0.208)	8	0	(0.045;0.234;0.552;0.193)	1	7	(87.5% <0.019;-;0.04;-)	9	0	(0.045;0.063;0.158;0.036)	1	8	(88.9% <0.04;-;0.203;-)	-
C_{10} - C_{40}	µg/L	8	0	(172.2;613.2;1545.6;506.1)	8	0	(144.6;514.9;1213.9;385.6)	1	7	(87.5% <50;-;65.7;-)	9	0	(118.0;173.0;373.2;78.5)	1	9	(90% <50;-;426;-)	1000[£]
C_{10} - C_{12}	µg/L	2	6	(<2.772;3.283;5;0.512)	1	7	(87.5% <3.663;-;5;-)	0	8	(-;-;100%<5;-)	0	9	(-;-;100%<5;-)	0	10	(100%<7.5;-;-)	90[§]; 300[€]

C_{12} - C_{16}	µg/L	7	1	(<4.551;9.375;13.392;3.445)	7	1	(<3.913;7.707;13.343;3.328)	0	8	(-;-;100%<5;-)	5	4	(<2.819;3.223;5;0.565)	0	10	(100%<7.5;-;-)	90[$]; 300[€]
C_{16} - C_{35}	µg/L	8	0	(138.6;471.0;1167.7;380.8)	8	0	(119.3;399.8;941.3;293.9)	1	7	(87.5% <30;-;49.53;-)	9	0	(93.3;140.11;298.04;62.5)	2	8	(<30;59.5;319;86.5)	90[$] (Arom.)
C_{35} - C_{40}	µg/L	8	0	(29.7;131;361.5;123.5)	8	0	(21.8;105.8;259.7;90.1)	1	7	(87.5% <10;-;14.16;-)	9	0	(20.2;30.6;71.2;15.6)	2	8	(<10;19.2;102;27.6)	-
OP	µg/L	6	2	(<0.041;0.131;0.338;0.104)	6	2	(<0.061;0.139;0.303;0.085)	0	8	(-;-;100%<0.02;-)	5	4	(<0.026;0.049;0.124;0.032)	0	8	(-;-;100%<0.02;-)	0.1
OP1EO	µg/L	0	6	(-;-;<0.024;-)	0	6	(-;-;100%<0.01;-)	0	6	(-;-;100%<0.02;-)	0	6	(-;-;100%<0.01;-)	0	5	(-;-;100%<0.01;-)	0.9
OP2EO	µg/L	0	6	(-;-;<0.45;-)	0	6	(-;-;100%<0.01;-)	0	6	(-;-;100%<0.02;-)	0	6	(-;-;100%<0.01;-)	0	5	(-;-;100%<0.01;-)	0.91
OP3EO	µg/L	0	6	(-;-;<0.033;-)	0	6	(-;-;100%<0.028;-)	0	6	(-;-;100%<0.02;-)	0	6	(-;-;100%<0.04;-)	0	5	(-;-;100%<0.011;-)	0.91
NP	µg/L	5	3	(<0.166;0.374;1.19;0.181)	5	3	(<0.2;0.397;1.11;0.201)	5	3	(<0.22;0.428;0.673;0.167)	6	3	(<0.17;0.416;1.18;0.207)	2	6	(<0.089;0.127;0.392;0.1)	0.3
NP1EO	µg/L	0	6	(-;-;<0.18;-)	0	6	(-;-;100%<0.22;-)	0	6	(-;-;100%<0.2;-)	0	6	(-;-;100%<0.18;-)	0	5	(-;-;100%<0.15;-)	0.64
NP2EO	µg/L	0	6	(-;-;<2.54;-)	0	6	(-;-;100%<1.49;-)	0	6	(-;-;100%<0.36;-)	1	5	(83.3% <0.067;-;1.66;-)	0	5	(-;-;100%<0.38;-)	0.37
NP3EO	µg/L	0	6	(-;-;<1.27;-)	0	6	(-;-;100%<1.49;-)	0	6	(-;-;100%<0.42;-)	0	6	(-;-;100%<3.54;-)	0	5	(-;-;100%<0.74;-)	0.3
BPA	µg/L	8	0	(0.247;0.542;1.179;0.314)	8	0	(0.169;0.48;0.933;0.249)	3	5	(<0.042;0.051;0.097;0.018)	9	0	(0.158;0.365;0.58;0.164)	3	7	(<0.05;0.054;0.074;0.008)	0.24
TOC	mg/L	11	0	(2.34;10.06;23.03;7.08)	11	0	(2.06;10.56;24.96;7.5)	8	0	(2.95;8.9;19.303;6.618)	9	0	(2.963;11.19;22.4;7.096)	10	0	(1.51;8.978;19.1;6.652)	12[¥]
TSS	mg/L	11	0	(22.4;74.3;205.8;56.9)	11	0	(18.9;69.0;200.8;55.1)	6	2	(<1.93;5.5;23.9;7.1)	9	0	(11.5;19.7;33.5;6.7)	5	3	(<2.5;5.6;15;4.1)	25[©]
Turb.	NTU	9	0	(40.39;107.17;201.11;54.79)	9	0	(43.06;112.93;236.77;62.51)	8	0	(1.405;19.9;78.24;25.4)	9	0	(28.3;44.87;87.49;18.82)	8	0	(6.47;29.78;73.7;25.38)	-
EC	µS/cm	9	0	(32.77;138.39;299.49;82.08)	9	0	(38.54;141.83;318.53;87.16)	8	0	(114.52;305.58;495.57;140.1)	9	0	(52.34;157.51;327;89.8)	8	0	(50.3;205.37;398;141.66)	-
pH	-	9	0	(6.799;7.148;7.308;0.156)	9	0	(7.026;7.148;7.409;0.11)	8	0	(7.543;7.867;8.135;0.181)	9	0	(6.965;7.109;7.22;0.098)	8	0	(5.62;7.083;7.797;0.646)	-
Temp.	°C	9	0	(11.62;16.52;22.35;3.38)	9	0	(12.1;16.71;22.91;3.4)	8	0	(13.45;18.15;23.62;3.27)	9	0	(14.13;18.04;24.22;2.92)	8	0	(7.23;16.28;23.7;4.7)	-

* The water quality objectives refer to the lowest Predicted No-Effect Concentrations (PNEC) for freshwater from NORMAN Ecotoxicology Database, unless another guideline is mentioned.
[£] City of Gothenburg's guideline value for aliphatic and aromatic hydrocarbons (Miljöförvaltningen, 2013)
[$] WHO's recommendation for aromatic PHCs in drinking water (WHO, 2008)
[€] WHO's recommendation for aliphatic PHCs in drinking water (WHO, 2008)
[¥] Gothenburg's stormwater annual average benchmark concentration at the point of discharge to receiving water bodies (Miljöförvaltningen, 2013)
[©] Protective threshold concentration against chronic effects on fish in freshwater (EC, 2006)

3.1.1. *Phenolic substances*

BPA was quantified in all samples at SW, GPT_{out}, and SF_{out}, but only in three of eight rain events at BFC_{out} and three of ten at BF_{out}, respectively (Table 2). The occurrence of alkylphenols (APs: OP and NP) was, however, lower in the stormwater (six and five of eight events for OP and NP, respectively) and the outlet of treatment sections, in general. At SF_{out}, the occurrences of OP and NP were identical to those at SW and GPT_{out} (5−6 of nine events), while OP was never found but NP was quantified in two and five events (out of eight) at BF_{out} and BFC_{out}, respectively, with relatively comparable concentration levels measured at SW (see section 4.5).

As shown in Figure 2 (a)−(c), the median EMCs of phenolic substances (except alkylphenol ethoxylates) at both SW and GPT_{out} were often similar and exceeded PNECs for freshwater (BPA: 0.40±0.10 µg/L, NP: 0.36±0.15 µg/L, and OP: 0.08±0.02 µg/). Downstream, at the outlet of the vegetated biofilters (BF_{out} and BFC_{out}), the EMCs of BPA (median <0.05 µg/L) and OP (all non-detects) significantly decreased to below corresponding PNECs (always <PNEC), but this was not the case for NP in 4−6 (the range takes uncertainty into account) of nine events (median: 0.41±0.12 µg/L). The EMCs after the non-vegetated filter (SF), however, revealed that BPA and NP concentrations remained almost at the same levels as at the SF's inlet (i.e. no statistically significant difference in EMCs between GPT_{out} and SF_{out}: $X^2<0.6$, $p>0.05$) so that the PNECs (0.24 and 0.3 µg/L, respectively) were still exceeded in seven of nine rain events for BPA and, accounting for uncertainties, 3−7 of nine events for NP. EMCs of OP at the SF_{out}, on the other hand, considerably decreased to low risk levels with a median of 0.035±0.013 µg/L (EMCs < PNEC=0.1 µg/L in eight of nine events).

The event-based results showed that OPnEO and NPnEO (n=1,2,3) were not quantified at SW or in any effluent section, except NP2EO which was found at SF_{out} for one event (possibly due to leaching: see section 4.5) Thus, the performance of the TT remained unclear for those substances.

3.1.2. *Polycyclic aromatic hydrocarbons (PAHs)*

Most PAHs (except Nap, Acyl, Acen, Anth, and Flu from LMW-PAH fractions) were frequently quantified in the untreated stormwater (SW) where EMCs exceeded PNECs. The occurrence assessment also showed that the occurrence and EMC levels of PAHs in the GPT_{out} followed similar patterns as observed in SW (NEP plots in Figure 2d−h and Figure S4a–l). No significant difference of EMCs was identified when comparing SW and GPT_{out}: $X^2<0.53$ and $p>0.05$ for all PAHs except for Anth and Flu which were occasionally found in the GPT_{out}, but not in SW for the same event (discussed in section 4.1).

Phen was the only LMW-PAH quantified in five and four of eight events at SW and GPT_{out}, respectively, (median EMC: 0.017±0.05 µg/L) but never exceeded the PNEC (0.3 µg/L). Phen was never quantified in the filter outlets. MMW-PAH fractions including Flth and Pyr were almost always quantified in SW and GPT_{out} (seven or eight of eight events), while HMW-PAH occurrence at these two sampling points varied between four and eight of eight events in this order: BbF = Bper > BaP > Chry = InP > BaA > DahA. At SW and GPT_{out}, the EMCs of Flth and Pyr with estimated medians of 0.050±0.008 µg/L and 0.079±0.022 µg/L, respectively, were also frequently above the corresponding PNEC levels (7−8 of eight events). Six of eight HMW-PAHs exhibited risky concentration levels (EMC > PNEC) at SW and GPT_{out}. Of these, BaP, BaA, Chry, BbF, and DahA are classified as extremely or possibly carcinogenic (see Figure 2d−e and Figure S4 a, b, e). In general, 41−43% of Σ16PAH concentrations in the range 0.110−1.131 µg/L at SW and GPT_{out} could be attributed to carcinogenic substances.

PAHs were rarely observed at BFC_{out} and BF_{out}, except for one event (rain C) during which all MMW-PAHs and HMW-PAHs were found at BF_{out}, as well as Benzo(ghi)perylene in BFC_{out}. In this rain event, PAH EMCs were also observed at their maximum levels in SW and GPT_{out}. The non-vegetated biofilter SF results, however, varied for the different quantified PAHs in terms of occurrence and EMC. Both MMW-PAHs and HMW-PAHs (but none of the LMW-PAHs) were quantified during at least one up to nine of nine events at the SF_{out}: Pyr, BbF, and Bper with the highest occurrence, Chry and Flth with a moderate occurrence, and IP, BaA, BaP, BkF, and DahA with the lowest occurrence. Some of the hazardous PAHs (having relatively low PNECs (<0.01 µg/L)) found in SF_{out}, such as Pyr and Chry, were measured with considerably higher concentrations than their quality objectives in freshwater. Although more dangerous substances including BaP and DahA (with very low PNECs) occurred only a few times in SF_{out}, the actual risk levels after the treatment still remained unclear for such PAHs since their

RLs (0.01 µg/L) were higher than the corresponding PNEC levels (this is also the case for all non-detects of BaP, DahA, Chry, Flth, and Bper at all other sampling points). Further detailed information about the occurrence and EMC of PAHs for all sampling points is provided in Table 2.

3.1.3. Petroleum hydrocarbons (PHCs)

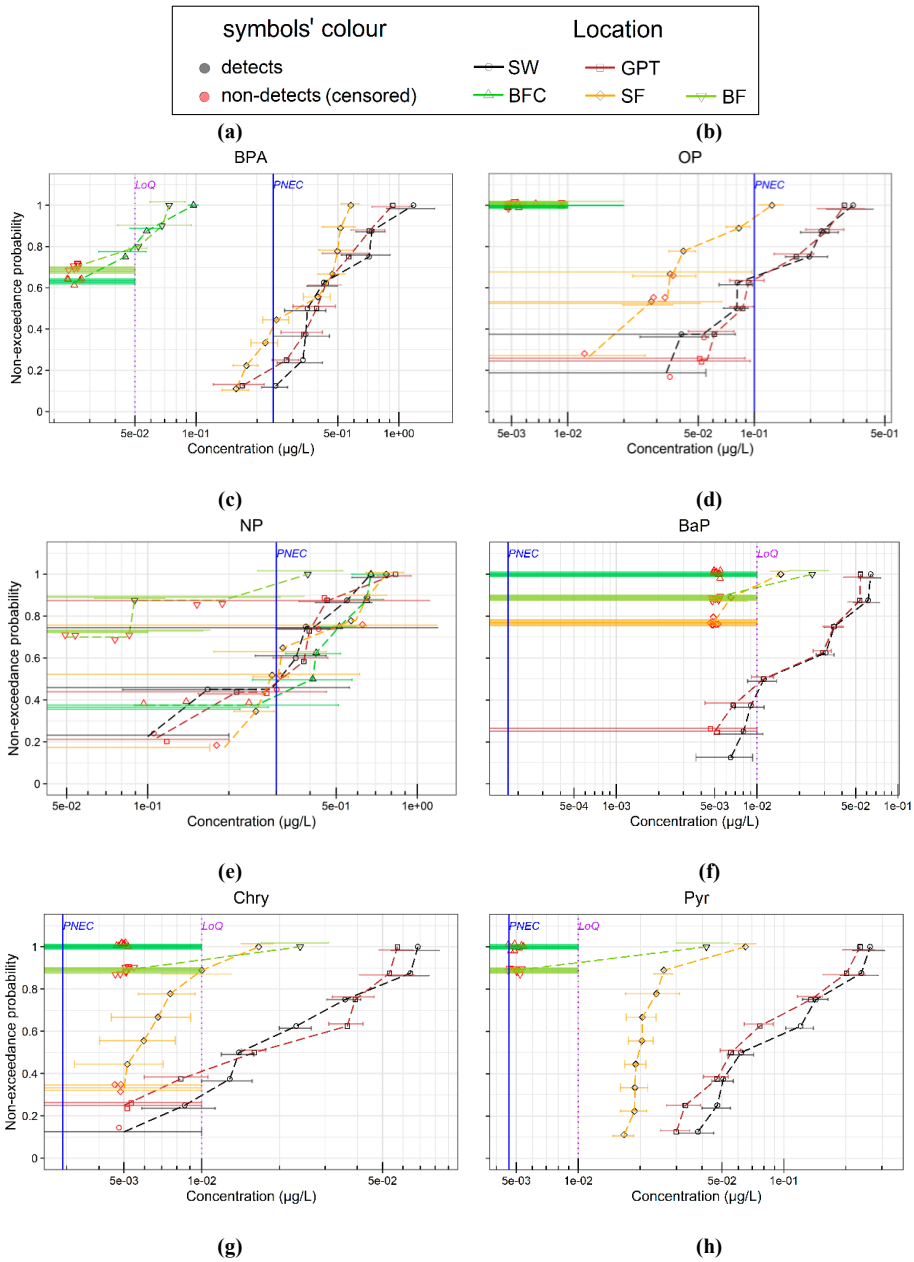
Total PHCs (C_{10}-C_{40}) were quantified in all events at SW and GPT_{out}. Again, data analysis showed similar range/trend for the EMCs of all PHC fractions at both SW and GPT_{out} (Figure 2i). EMCs of C_{10}-C_{40} (associated with the uncertainties) varied in the range of 145−1886 µg/L for SW, and 122−1431 µg/L for GPT_{out}, but both had a similar median of approximately 380±70 µg/L (X^2=0.39 and p>0.05: no significant difference in PHCs between SW and GPT_{out}). Considering Gothenburg's local guideline for aquatic receiving water bodies (Miljöförvaltningen, 2013), the observed C_{10}-C_{40} EMCs exceeded the maximum stormwater PHC concentration threshold of 1000 µg/L during two of eight and one of eight events at SW and GPT_{out}, respectively. After the TT, PHCs were repeatedly quantified at the SF_{out} (C_{10}-C_{40} median EMC: 148±19 µg/L and always below the guideline value 1000 µg/L), while seldom at BFC_{out} and BF_{out} (only found in rain events C and D). C_{16}-C_{35} and C_{35}-C_{40} (i.e. heavier PHC molecules) were identified as the predominant PHC fractions in all samples, and C_{10}-C_{12} and C_{12}-C_{16} (lighter fractions) only accounted for a maximum of 1−4% of total PHCs concentrations in different sampling locations. The EMCs of C_{16}-C_{35} were always higher than C_{35}-C_{40} with mean ratios of 3.6, 3.8, 3.5, 4.6, and 3.1 at SW, GPT_{out}, BFC_{out}, SF_{out}, and BF_{out}, respectively. See Table 2 for further details about PHC occurrence and EMCs.

3.1.4. Conventional water quality parameters

EMCs of TSS were in a similar range at SW and GPT_{out} (18.9–231.4 mg/L; median: 54.5±6.6 mg/L and X^2=0.08, p>0.05, i.e. no significant difference between SW and GPT_{out}) so that 9–11 of eleven events exceeded the European quality objective of 25 mg/L for TSS (the protective threshold against chronic effects in freshwater (EC, 2006)). The event mean turbidity at those two locations similarly varied between 40.4 and 236.8 NTU for all rain events (Figure 2k). As shown in Figure 2j, TSS levels considerably dropped into the range of 10.4–35.0 mg/L (median=18.9±2.3) after the non-vegetated SF, and even more significantly after the vegetated BF and BFC, within <2.5–26.7 mg/L (median=3.0±0.9). In general, the TSS measured at the outlet of filter cells rarely exceeded the threshold concentration of 25 mg/L recommended for freshwater (EC, 2006). Turbidity followed a similar pattern to TSS with mean values decreasing moving downstream from SW and GPT to the subsequent filter cells.

TOC was always quantified at all sampling points. The EMCs of TOC in untreated stormwater (SW) ranged between 2.3 and 26.2 mg/L with a median of 7.0±0.6 mg/L for all rain events. The results (Figure 2l) showed that TOC levels in SW did not significantly change after the GPT and SF treatment sections (X^2<0.24, p>0.05). Therefore, a similar EMC variation over the events was observed at those sampling points as at SW (Table 2). Considering Gothenburg's guidelines for stormwater, TOC levels exceeded the threshold of 12 mg/L during (4–5) of eleven events at SW and GPT_{out}. TOC concentrations, however, slightly decreased after the vegetated biofilters (though not statistically significantly: X^2<1.4, p>0.05) so that the EMCs varied in the range of 1.5–22.9 mg/L with medians of 7.4±0.8 at BFC_{out} and 6.7±1.0 mg/L at BF_{out}. Nevertheless, it exceeded the 12 mg/L recommended level in four of eight, five of nine, and five of ten events at BF_{out}, SF_{out}, and BFC_{out}, respectively.

The stormwater pH value at SW, GPT_{out}, BF_{out}, and SF_{out} remained unchanged in the neutral range of 5.6 and 7.4 (median: 7.15±0.05), while noticeably increasing after BFC to 7.5–8.1 with a median of 7.9. All event mean pH values were within the recommended range (6.5–9) for stormwater discharged to freshwater (Miljöförvaltningen, 2013), except in rain event J at BF_{out} with the minimum pH measured 5.6.


symbols' colour
detects
non-detects (censored)
Location
SW
BFC
GPT
SF
BF
(a)
BPA
LoQ
PNEC
Non-exceedance probability
Concentration (µg/L)
(b)
OP
PNEC
Concentration (µg/L)
(c)
NP
PNEC
Non-exceedance probability
Concentration (µg/L)
(d)
BaP
PNEC
LoQ
Concentration (µg/L)
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Concentration (µg/L)
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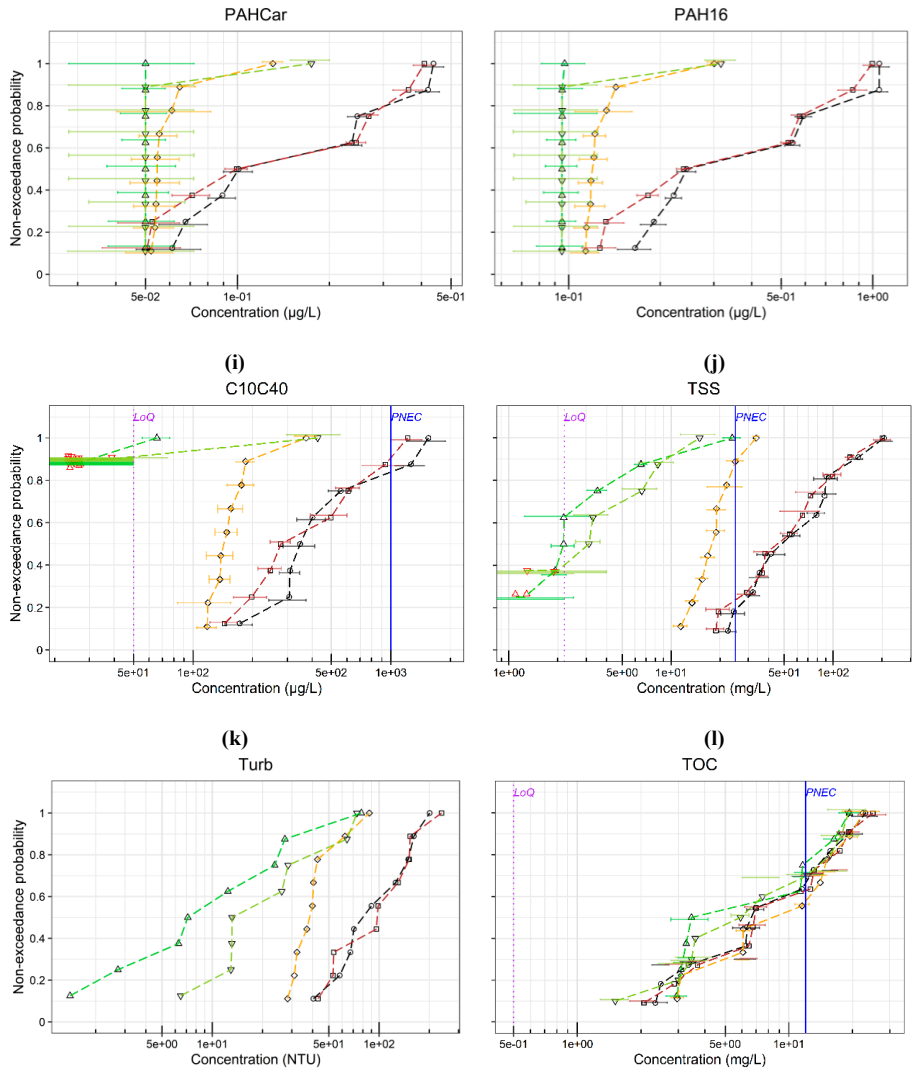

Figure 2. Non-exceedance probability distribution (cumulative probability of the occurrence) of the calculated event mean concentrations (EMCs) at different sampling locations (SW, GPT_{out}, BFC_{out}, SF_{out}, and BF_{out}) for selected OMPs. Symbols represent the best EMC estimates connected by a dashed line for each sampling location, error bars represent the propagated uncertainties of EMCs, and the dotted blue lines represent the water quality objectives (dots and error bars have been moved a little (jittered) to avoid overlapping) (no single LoQ line could be applied for alkylphenols due to matrix interference)

3.2. Treatment train performance for OMP removal

3.2.1. Gross pollutant trap (GPT) removal efficiency

The results revealed that the GPT did not contribute to the stormwater treatment significantly, with median OMP removals less than 20%. Figure 3 shows a statistical summary of mean removal efficiencies and errors of the OMPs and global parameters for different treatment units. The overall median removal efficiencies (Re% associated with its Err_{Re}%) for the GPT section were 11.6±14.2% for Σ16PAHs, 13.2±30.3% for PHCs, 3.2±42.6% for BPA, 11.4±26.4% for TSS, and -7.0% for Turbidity. REs for OP, NP, and TOC were all near or

below zero (see Figure 3). For C_{12}-C_{16} (one of the lighter and more volatile PHC fractions), GPT showed slightly better performance with a median removal of 32.1±30.8%, which might be related to the effect of the oil separator compartment in GPT designed to trap oils and volatile pollutants at the water's surface. Thus, GPT effluent quality followed almost the same level and pattern as observed at SW (thus, no significant difference in the EMCs of any OMPs between SW and GPT_{out}, as shown in Table S7) and did not considerably improve the stormwater quality (see NEPs in Figure 2). Furthermore, OMP removal efficiencies by the GPT were often accompanied with large errors (most often median Err_{Re} between 30–50%, Figure 3).

3.2.2. Non-vegetated sand filter (SF) removal efficiency

In contrast to the GPT section, the SF moderately to substantially removed most of the OMPs from stormwater, although the removal efficiencies and errors for each OMP varied a great deal between events (Figure 3). The observed variation in Re% was directly related to the ratio between the inflow EMC and LoQ of a given OMP. The closer the EMCs to the LoQ, the wider the range of Re% became (discussed in section 4.6). The median Re%s were as follows: BPA: 43±22%, OP: 51±24%, Σ16PAHs: 61±5%, BaP: 73±18%, C_{10}-C_{40}: 60±14%, TSS: 70±8%, and turbidity: 57%. Meanwhile, a negative and nearly zero median removal percentage was observed for NP (-5±46%) and TOC (9±21%). The difference in EMCs between GPT_{out} and SF_{out} were significant with relatively high Chi-squares (X^2>4.9 and $p<0.05$) for OP, PAHs, C_{12}-C_{40}, TSS, and turbidity. However, the difference for BPA, BkF, and BbF (as well as NP and TOC) was insignificant (see Table S7) i.e. the SF performance was inadequate for these substances. Uncertainty analysis revealed that the absolute removal errors in SF_{out} were often higher for phenolic substances (median: 23–45%), followed by TOC (21%), PAHs (8–30%, excluding Phen and DahA) and PHCs (13–20%), and TSS (8%).

In contrast to phenolic substances with lower treatment efficiencies, PAH and PHC removal by SF ranged between 55–90% when their influent concentration (i.e. GPT_{out}) was at least four times bigger than the corresponding LoQ. Of the quantified PAH substances, the medium and high weight molecules Flth, BbF, Bper, and InP had the highest removal efficiencies (median >70%) with lowest errors (~10%). On the other hand, Phen, and DahA had, relatively, the lowest efficiencies (median< 60%) and highest Err_{Re} (≥30%) (Figure 3). Further, SF treated non-carcinogenic PAHs better than carcinogenic ones: ΣNon-car.PAHs ranged within 17–80% (median 63±7%), whereas ΣCar.PAHs ranged within 0–78% (median 57±9%). Among PHC fractions, a similar distribution of Re% among the events was observed for C_{12}-C_{16}, C_{16}-C_{35}, and C_{35}-C_{40} (like total PHCs) in SF, but the C_{12}-C_{16} removal errors were slightly (~6%) higher than the other fractions (Figure 3).

3.2.3. Vegetated biofilters (BFC and BF) removal efficiencies

Both vegetated filters (BFC and BF) performed better than the non-vegetated filter (SF) in improving stormwater quality. In general, both vegetated biofilters behaved similarly and were able to remove a majority of OMPs to a greater and better degree than SF. As shown in Figure 3, the median Re%s for the BFC section were for BPA: 94±6%, OP: 95±6%, Σ16PAHs: 60±6%, BaP: 69±33%, C_{10}-C_{40}: 91±9%, TSS: 95±3%, and turbidity: 88%. The corresponding treatment performances by the BF cell were for BPA: 91±7%, OP: 96±4%, Σ16PAHs: 75±6%, BaP: 69±19%, C_{10}-C_{40}: 91±9%, TSS: 95±3%, and turbidity: 79%. The removal result showed that the differences between the performance of the vegetated and non-vegetated filters were significant for BPA, OP, NP (in BF only), Pyr, C_{16}-C_{40}, and TSS removals (Re% in BFC and BF > 90%, which were at least 30% higher than those in SF), but not as great for the rest of PAH substances and PHC fractions. As with SF, the BFC cell showed a negative or low removal efficiency for NP: -10±66% and TOC: 20±18%. Further, a lower TOC removal percentage (10±27%) was achieved by the BF cell. In contrast, BF treated NP efficiently but this was associated with a high uncertainty (median: 74±19%). NP was the only OMP for which BFC and BF significantly differed regarding treatment performance (X^2>6 and $p<0.05$) (discussed in section 4.5). There were statistically significant differences between the EMCs at GPT_{out} and BFC/BF_{out} for phenolic substances, PAHs, PHC fractions, TSS, and turbidity, except for DahA (due to large analytical uncertainties leading to median Err_{Re} >38%) and TOC in the outflow of both vegetated cells, and for NP in BFC_{out} (see X^2 and p-values in Table S7). Although the maximum Re% for most OMPs reached between >70% and 98% (except for NP), the removal percentage for most OMPs varied in a wide range and was greatly affected by the influent EMC level with respect to LoQ (discussed in section 4.6).

Furthermore, the uncertainty analysis revealed that, unlike the SF cell, BFC and BF exhibited low absolute removal errors (<15%) for phenolic substances, except for NP in BFC which varied within a wide range of 20–67%. As with the SF cell, the removal errors of PAHs varied greatly among the substances and events so that the medians oscillated between 8% and 58% but their maximum error could occasionally reach as high as 80% (Figure 3). Comparing both vegetated biofilters, PAHs' Err_{Re}% in BF was always moderately lower than that in BFC, although the errors calculated for PAH fractions (with medians <11%) did not show a significant difference between the two cells. Likewise, BF and BFC had a similar error range of <20% for total and heavier PHC fractions and TSS, while the errors for C_{12}-C_{16} reached 56% in BFC and 83% in BF (see discussion in section 4.5).

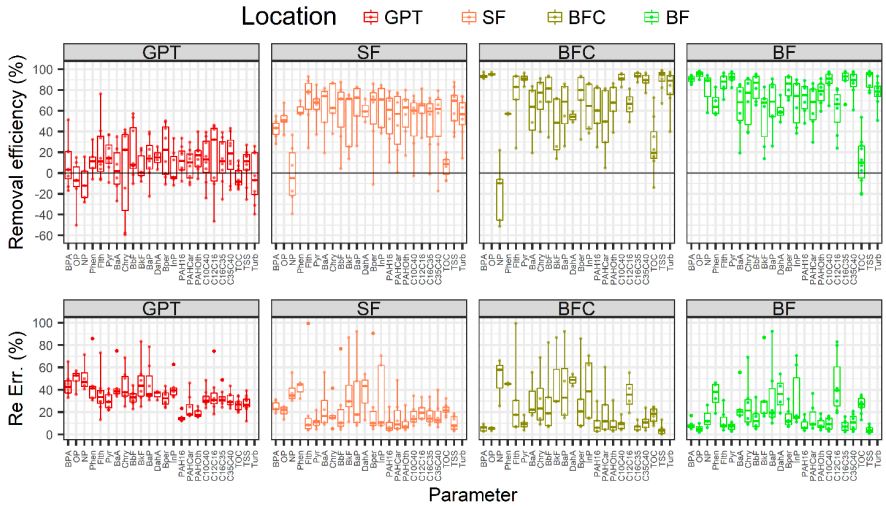

Figure 3. Mean removal efficiencies (Re%) and errors (Err_{Re}%) of the parameters for various treatment sections

3.3. OMP environmental risk analysis

The environmental risk of selected OMPs in untreated stormwater was determined and compared with that in the outflow of each treatment unit. Out of 32 parameters measured, 15 OMPs were not considered in our risk analysis due to: 1) no available PNEC (4 TPH fractions), or 2) all concentration values or a majority of them at any sampling location were below LoQ and LoQ<PNEC (i.e. no potential risk existed for Nap, Acel, Acen, Flu, Anth, and OPnEO and NPnEO; n=1, 2, 3). Figure 4 illustrates the total risk (R_T) for the other 17 parameters at different sampling locations.

The results revealed that, in the untreated stormwater, the R_T of TSS and 11 OMPs (BPA, OP, NP, and eight PAHs: Flth, Pyr, BaA, Chry, BbF, BaP, DahA, Bper) exceeded one, which may potentially pose a risk to the environment, while that was not the case for C_{10}-C_{40}, TOC, and other PAHs (i.e. Phen, BkF, and InP). Meanwhile, the associated errors for the total risk render our findings uncertain for OP and NP in SW since the error bars cross the critical risk threshold in those cases.

As shown in Figure 4, GPT exhibited slightly a lower but almost equal R_T as observed in SW, meaning that GPT did not reliably reduce the environmental risk of OMPs. The SF section, however, did reduce the risk of OMPs and TSS compared to SW and GPT_{out} to some extent, except NP (discussed in section 4.5). In the cases of TSS, OP, BaA, BbF, BkF, and probably Flth and DahA (considering the associated uncertainties), the SF section performed so efficiently that the risks with $R_T \geq 1$ dropped below one, to the safe level zone. On the other hand, SF did not reduce the risk levels of BPA, Pyr, Chry, BaP, DahA, and Bper sufficiently. For the vegetated biofilters, BFC and BF generally reduced the OMP risk levels to a greater extent than SF. In terms of environmental risk reduction, BFC and BF both performed equally efficiently for BPA, OP, Flth, BaA, BbF, Bper, and TSS, (R_T dropped down to safe levels below one), which previously had high risks at the SW and GPT_{out}. However, it cannot be concluded whether extremely hazardous OMPs (Pyr, Chry, BaP, and DahA) reached a safe level after

BFC and BF treatment, as the very low PNEC concentration was below LoQ in the present study. As with the removal efficiency results, we did not see a significant difference between the R_T in BFC and BF outlets to identify the effect of chalk amendment on risk reduction.

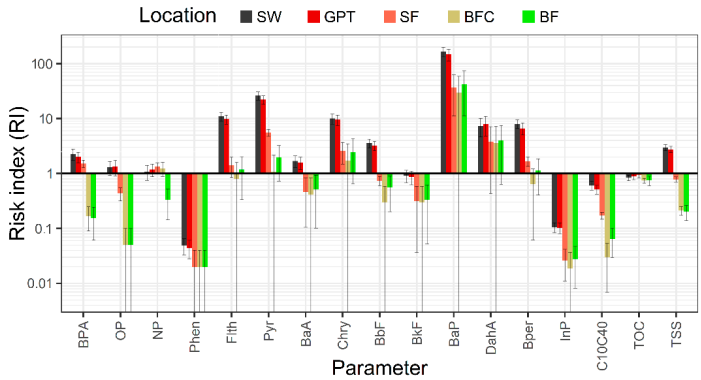

Figure 4. Total risk (R_T) (with error bar) for selected parameters at different sampling locations

4. Discussion

A comprehensive discussion of the concentrations, occurrence, and possible sources of OMPs in the untreated stormwater, as well as the comparison of our results with other major road runoff studies, can be found in (Beryani et al., Submitted). The effect of each treatment unit in OMPs removal will now be discussed and compared with other studies**.**

4.1. Impact of Gross pollutant trap (GPT)

The results revealed that the GPT section had, in general, a low removal efficiency which is in line with previous studies of sedimentation facilities, with a maximum 10–25% removal for various substances such as TSS, metals, PAHs, NP, NP1EO, and NP2EO (Björklund et al., 2009; Lange et al., 2021, 2022; Pettersson et al., 2005). In some cases, the GPT effluent contained even higher concentrations for many OMPs than those in the stormwater (i.e. negative RE%) which showed that the GPT may sometimes release previously accumulated OMPs in the chamber. It is likely that the high turbulent inflow in the GPT might re-suspend the previously deposited sediments at the bottom of the chamber. In addition, the GPT's discharge system (i.e. pulse valve opening) could be a reason for sediment resuspension by causing a fluctuating and relatively high discharge flow from the facility when the valves were open.

Further, the GPT's low treatment efficiencies could be connected to the size of particles in relation to the GPT dimensions. Stormwater normally contains many fine particles which are not efficiently removed by such small sedimentation facilities (Li et al., 2005; Lieske et al., 2021; Pamuru et al., 2022). For this site, the GPT size was only about 15% of Massachusetts's EPA minimum recommended capacity of ~6.3 mm runoff per ha impervious catchment for forebays (MDEP, 2022).

4.2. Impact of Sand filter media

In general, the SF cell improved the GPT's outflow quality (see section 3.2.2), but it behaved differently in response to different OMPs depending on their physiochemical properties, as discussed below.

In this study, SF treatment performance was relatively less efficient for TSS (35–90%; median: ~70%) than previously reported for sand-based biofilters (>90%) (e.g. Davis, 2007; Zarezadeh et al., 2018). The EMCs of TSS during five (out of nine) events were also higher than the SCM predevelopment target level of 20 mg/L suggested by Davis (2007). Turbidity removal by SF was even lower than TSS for most rain events (except E and J), which may suggest that a sand filter is less able to retain highly suspended, smaller colloids than larger/denser particles, as previously concluded by other studies (Davis, 2007; Lange et al., 2021). So, a high TSS removal may not be achieved by SF, especially for high flow intensities and high TSS loads. Conversely, there have been also

non-vegetated facilities containing sand layers that had low TSS removal, due to fine material release from unestablished filter beds or long ADP adverse effects (Blecken et al., 2009; Davis, 2007), neither of which were the case in our study.

Regarding OMP removal, apart from the negative Re% for NP (separately discussed in section 4.5), SF was mostly less efficient (and associated with slightly higher removal errors) for treating phenolic substances (i.e. BPA and OP), compared with quantified PAHs, PHCs and TSS. MWH-PAHs, HWH-PAHs and C_{16}-C_{40} fractions typically have a much higher particle-bound fraction compared to BPA, OP, and NP, because they have less solubility, higher hydrophobicity (larger K_{OW}), and more absorbability of organic content of sediments and Fe particles (larger K_{OC}) (see Table S4, Table S5, Table S6) (Andersson et al., 2018; Diblasi et al., 2009; Leroy et al., 2016). Therefore, the quantified PAHs and PHCs were more likely to be retained in the SF medium by a particle (TSS) filtering process (David et al., 2015; Furén et al., 2022) than the phenolic substances for which a higher dissolved/colloidal phase breakthrough may occur (Gasperi et al., 2022; Ruppelt et al., 2020; Shehab et al., 2020). Flanagan et al. (2018) also reported that alkylphenols are less efficiently removed by a bioswale facility than PAHs and PHCs, having higher partitioning to suspended solids. Consequently, the Re% of most PAHs (except Phen, Chry, BkF, DahA), and heavier PHC fractions (i.e. C_{16}-C_{40}) were strongly correlated with Re% of TSS and turbidity for the SF cell, whereas none of the phenolic substance removals were statistically associated with them. Our finding is consistent with the few available previous studies concluding that sand filters may not function adequately for treating more soluble OMPs such as triazine herbicides, biocides, and triclosan-methyl (Spahr et al., 2019).

We were not able to investigate the treatability of lighter PAH and PHC fractions by the SF (as well as the other filters) properly because they were not often quantified in the influent stormwater, probably due to partial loss through volatilization, and more limited use of gasoline with lighter fractions than diesel (Leroy et al., 2016). In addition, the ratio of C_{16}-C_{35} over C_{35}-C_{40} in SF_{out} increased for about 20% of that in the inflow, which may again support our hypothesis that sand filtration basically performs better for retaining heavier hydrocarbon molecules due to their greater hydrophobicity and higher affinity to the solid phase.

Considering the results for different groups of OMPs, the predominant mechanisms responsible for the removal in a sand-based filter are most likely physical particle straining, colloidal attachment to the filter medium and, to a lesser extent, solute adsorption to the organic matter retained on the filter material surface. Therefore, a supplementary treatment unit with more reliable filtration and/or adsorption abilities will be required for treating more soluble OMPs such as phenolic substances as well as the dissolved fraction of all OMPs when a SF is the only existing filter cell in a biofilter facility. Although further detailed studies are needed to determine the exact size ranges of OMP particles that can be filtered using sand-based filtration, a vegetated biofilter may address the issue of more reliable treatment (see section 4.3).

4.3. Impact of Vegetation layer

To evaluate the effect of the vegetation layer, the OMP removal efficiencies of the vegetated sand filter (BF) were compared with the non-vegetated sand filter (SF). The presence of vegetation on the sand filter media substantially improved the removal of BPA, OP, NP, Pyr, Bper, Σ16PAHs, all PAH fractions except ΣLMW-PAHs, C_{10}-C_{40} (predominantly C_{16}-C_{40}), and, to a lesser extent, turbidity (Table S7). Two possible factors were suggested as the reason for the positive effect of vegetation during wet periods: plant-related processes (uptake, retention in root, preferential flow paths, and microbial degradation in the rhizosphere) and filtration processes by the (finer) topsoil layer on the vegetated filters.

Some laboratory biofilter column studies have already shown that certain plants can directly take up some hydrocarbons, such as naphthalene (up to 23% for grass), and phenanthrene and pyrene to a certain extent (Kacálková & Tlustoš, 2011; Lefevre et al., 2012). However, the plant uptake is probably negligible here because most of the quantified OMPs were classified as organic substances with very low solubility and very high hydrophobicity (log K_{OW} >4; see Table S4, Table S5, Table S6) which makes them unavailable for plant uptake through cell membranes (and therefore no subsequent processes such as phyto-accumulation/volatilization and metabolic transformation). However, they can still be retained and stabilized in the root epidermis (Leroy et al., 2015; Ruppelt et al., 2020). It is also believed that uptake, accumulation, and metabolic transformation of organic compounds by vegetation potentially occur when there is major contamination with contaminants more resistant to biodegradation (Imfeld et al., 2009), while generally low concentrations of OMPs were found in the highway

stormwater and the GPT outflow. The plant-related effect is probably more relevant for the fate and treatment of OMPs during dry periods between the events (which was not specifically investigated in this study) where the surrounding area of plant root (rhizosphere) provides conditions that promote microbial decomposition (mineralization) of hydrocarbons retained in the soil (Dagenais et al., 2018; Muerdter et al., 2018). Nevertheless, further studies are needed to determine the direct effect of plant uptake by examining the plant tissues, especially for BPA and OP (and lower molecular weight PAHs if quantified also) with higher water solubility and less hydrophobicity (log K_{OW} around or less than four).

It is likely that filtration processes in the 3–4 cm vegetation topsoil are more relevant than direct vegetation uptake to better performance of the BF. As evidence, the presence of vegetation topsoil (sand to silty-sand) in BF and BFC noticeably decreased the infiltration rate and prolonged the filtration effect at the beginning of the runoff event (but not for most of the infiltration duration, following saturation towards the end of the event) compared to the SF. The OMP results agreed with Lange et al. (2021) and Fahlbeck Carlsson (2021) who observed slightly (but not statistically significantly) better removal efficiencies for microplastics (specially for the smaller particle size range 100–300 μm) and metals (both total and even more pronounced dissolved) by the vegetated filters (BF and BFC) compared to the SF, due to further particulate filtration capacity of the vegetation soil layer. During the filtration processes on particle-bound pollutants, a vegetation layer can greatly contribute to the removal of OMPs by trapping particles in the topsoil (especially larger ones, while smaller particles are further transported and removed in the underlying filter media (Chu et al., 2021)).

The vegetation soil layer was amended with 2.5–5% organic mulch (supporting plant growth) which can contribute to the absorption of BPA, OP, NP, and colloidal/dissolved fractions of MMW-PAHs, HMW-PAHs and C_{16}-C_{40} that have higher log K_{OC} (see Table S4, Table S5, Table S6) (Duan et al., 2015; Furén et al., 2022; Hong et al., 2006). Beyond that, the organic matter from decaying vegetation (dead plant tissues) may enhance the removal by absorbing OMPs in the biofilters. The root surfaces may also play a role in OMP adsorption (Hutchinson et al., 2003).

Thus, the predominant processes responsible for the positive effect of vegetation in OMP removal can be linked to absorption by the vegetation soil and organic matter, as well as straining and sedimentation during filtration into the layer.

4.4. Impact of chalk amendment

Chalk ($CaCO_3$) is used to increase buffer capacity (to avoid acidification caused by microbial activities and consequent leaching) and compensate for low organic matter content of the filter media, both of which may improve solute adsorption on the solid phase (Søberg et al., 2019; Tondera et al., 2019). No comparable studies have been carried out so far to investigate the impact of $CaCO_3$ on bioretention. Studies of groundwater in geological chalk formations have suggested that the organic content of chalk grains can contribute to organic pollutant absorption (Graber & Borisover, 2003; Wefer-Roehl et al., 2001). Further, chalk can positively affect the physical deposition of particle-bound OMPs by changing water chemistry. Increasing pH and ionic strength (salt content) of stormwater greatly influences the precipitation of suspended solids (Behbahani et al., 2021; Diblasi et al., 2009; Randelovic et al., 2016).

Although the chalk amendment (10% w/w crashed limestone in BFC) caused an increase in the event mean values of median pH (for about 0.8 with a significant difference between BF_{out} and BFC_{out}, Table S7) and median EC (for about 100 μS/cm, but not statistically significant), the results did not show any statistically significant difference between the performance of BF and BFC in OMP removal (except NP which was linked to a potential leaching; see section 4.5). Thus, it is likely that chalk has no or only small practical importance in sand-based biofilter media. However, a general conclusion that chalk amendment is not useful for OMP treatment cannot be drawn based on this single study.

4.5. Potential leaching of alkylphenols

Comparing the results for the three different filter cells, inconsistent behavior was observed among phenolic substances exhibiting almost equivalent characteristics. While the removal of both BPA and OP were improved by the sand filtration and vegetation factors, NP exhibited negative removal efficiencies in BFC and SF, as well as a significant difference between BFC and BF. In general, negative removal, which suggests undetermined,

additional sources of NP other than the inflow stormwater, can be either due to remobilization from the filter material or leaching from the facility's construction material and sampling equipment (Flanagan et al., 2019; Tondera et al., 2013). However, blank tests already showed no alkylphenols leaching from the sampling equipment. Remobilization was not probable from the filter media because a similar result to BF would be expected for SF and BFC if so. Therefore, it could be likely that there is NP leaching from the facility's construction material although this cannot be further identified at the site.

It was not possible to determine a specific source for potential OMP leaching from the facility's construction materials, including stormwater pipeline, filters' drainage pipes, cell separator membranes, and geotextiles. However, the three filter cells were separated by ethylene propylene diene monomer (EPDM) rubber membranes. EPDM could specifically be a potential source of alkylphenols, phthalates, and other specified aromatics such as benzothiazole (highest potential), and perhaps PAHs, aliphatic C_{24}–C_{35} hydrocarbons, and volatile organic carbons (VOCs) (Magnusson & Mácsik, 2017; Nilsson et al., 2008) even though the leaching from newer, underground EPDM rubber membranes is expected to be much lower. Other studies have also demonstrated that phenols and their derivatives were found in the water in contact with new and recycled EPDM (Magnusson & Mácsik, 2017; Nilsson et al., 2008). Furthermore, in this site, the geotextile used for covering the EPDM membrane is made of polypropylene which could be another potential source of NP leaching. Although polymers of low polarity such as polypropylene are less sensitive to chemical degradation, trace leaching of their additives into the surrounding soil water may occur mainly when microparticles have been formed from the geotextile (Wiewel & Lamoree, 2016). Previous field studies have shown potential emissions of BPA, NPs, and OPs (in the order of 10 ng/L) from the polypropylene geotextile and plastic drain pipe used in a biofilter swale and a green roof system (Flanagan et al., 2019; Gromaire et al., 2014).

As a general observation, it should also be noted that the conclusion regarding NP leaching might be influenced by the high uncertainties in NP removal efficiencies (due to matrix interference and LoQ fluctuation).

4.6. Uncertainty analysis

There were several sources of uncertainties in EMCs and removal calculations, which are discussed below.

4.6.1. EMC calculation

Analytical and sampling constraints linked the EMCs with uncertainties which may influence the accuracy and interpretation of EMCs. Our investigations clearly illustrated that the analytical measurement uncertainties (δ_i) and the number of censored data among subsamples of a certain OMP are critical in the estimated EMC error for a given event. Figure S5 shows EMC errors associated with each OMP at different sampling locations. This reveals that EMC errors for all non-censored OMPs mostly varied between 10% and 40% (medians: 15–31%). The median EMC errors of phenolic substances at SW and GPT_{out} were slightly higher than PAHs and PHCs due to higher δ_i (about 10%) in subsamples. In SF, however, contrasting behavior was often observed because the number of censored EMCs for phenolic substances was lower than for most PAHs, which dominated the effect of the δ_i difference. It was not possible to analyze and compare the EMC errors of the different OMPs at BFC_{out} and BF_{out} due to the many censored mean concentrations (0<EMC<LoQ). Furthermore, in the cases of NP and OP, matrix interference during the analysis of given subsamples adversely affected their LoQs and increased the EMC error range spread as a result of using the MC method. The EMCs of NP were affected by this, particularly at GPT_{out}, SF_{out}, and BFC_{out}.

A minor source of uncertainty in EMC calculations was the MC method itself. The EMC uncertainty level estimated by the MC simulation is always lower than the original δ_i in subsamples. Therefore, as shown in Figure S5, the EMC errors for PAH fractions were about 10% lower than those for PAH substances at SW, GPT_{out}, and SF_{out}, since the MC method was applied twice for PAH fraction EMC estimation.

Uncertainty in the volume calculation for the first subsample taken from SW and GPT (v_1) was another minor source of EMC errors. The uncertainty in v_1 was due to unknown, pre-existing stormwater in the GPT chamber (max. 21 m^3) before the start of the rain. Considering the number of subsamples, v_1 errors did not significantly contribute to the overall uncertainty of EMCs at those points (for more information refer to (Beryani et al., Submitted).

4.6.2. *Removal efficiencies*

Censored and low concentrations of OMPs in stormwater samples may not only increase the EMC uncertainties but also influence the calculation of the removal efficiencies in the facility. The results showed that, since most EMCs at BFC_{out} and BF_{out} and almost half of those in SF_{out} were censored ($EMC_{out}/LoQ \approx 0.5$=const.), then Re% and Err_{Re}% were considerably influenced by the ratio of influent concentration (EMC_{in}) to LoQ. As illustrated in Figure 5, the closer EMC_{in} is to the LoQ, the lower the Re% and higher the corresponding Err_{Re}%. This trend was clearly observed for the filter cells when reaching a EMC_{in}/LoQ ratio below a certain threshold which was different for each filter cell i.e. 4 in SF, 12 in BFC, and >15 in BF. This implies that the calculated Re% at the EMC_{in}/LoQ ratios below the threshold were underestimated in the filter cells, otherwise they can be assumed to be real percentages. As the removal performances of BF and BFC were higher than those of SF, a higher threshold was observed for BF and BFC. So, a higher EMC_{in} should have been recorded in order to calculate the real Re% in the vegetated filters (to be able to quantify OMPs in the effluent).

BPA influent concentrations were often above the ratio threshold defined for each cell. However, PAH substances and PHC fractions often fell below the threshold. This is the main reason why, for the BFC and BF cells, the removal efficiencies for most PAHs and PHCs (particularly lighter weight fractions due to lower EMC_{in}/LoQ ratios) were estimated at lower levels than expected with a wider range of errors. A few other studies have also stated that the removal efficiencies are lower and the errors higher when the OMP concentrations are closer to LoQ because of higher analytical uncertainties (Choubert et al., 2011; Diblasi et al., 2009; Flanagan et al., 2018; Ruppelt et al., 2020). Ruppelt et al. (2020) reported removal uncertainties of 30−100% for low inflow concentrations of OMPs (<2.5×LoQ), but <30% for high concentration levels (>10×LoQ) in pilot-scale sand columns, which are comparable with our results.

Another finding shown in Figure 5 is that those points without censored effluent concentration data for a given filter cell ($EMC_{out}/LoQ>1$) did not conform to the trend curve, meaning that the Re% represents a real removal percentage and has not been underestimated (or overestimated), so the corresponding removal error is less affected by the EMC_{in}/LoQ ratio. It is worth noting that due to the poor performance of GPT, no clear association between Re% and EMC_{in}/LoQ was observed.

The uncertainty analysis showed that the removal percentages/errors calculated for SF were less affected by EMC errors so that the efficiency values are more reliable for SF, while not for BFC and BF, since a greater number of data points were below the defined threshold in the two vegetated filters.

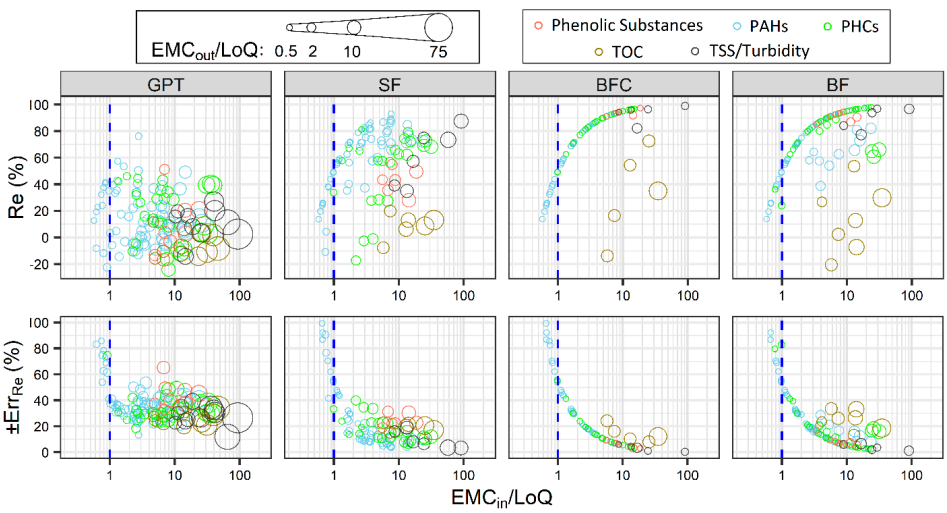

Figure 5. Removal efficiencies (Re%) and their associated errors (Err_{Re}%) with respect to the ratio of influent/effluent mean concentration to the limit of quantification for different OMPs and rain events

4.7. Risk analysis vs. removal efficiency

A study of runoff quality has already shown that BPA, OP, NP, and eight PAHs including Flth, Pyr, BaA, Chry, BbF, BaP, DahA, Bper (as well as TSS) frequently exceeded their PNECs, suggesting that they may potentially pose a risk to the receiving water body (Beryani et al., Submitted). Previous road runoff quality studies have also reported that these OMPs are among the most frequently detected micropollutants in stormwater with concentrations typically exceeding their EQSs (Mutzner et al., 2022). Thus, in this study, two methods were used to examine the performance of the TT in removing/mitigating the effects of OMPs: 1) removal efficiencies in the separate TT units, and 2) total risk assessment and risk reductions by the TT units. Although calculating removal efficiency is the conventional way to evaluate the treatment capacity of a facility, it may not be enough to see the entire picture of SCM functionality in relation to environmental impacts of the actual concentration levels in the outlet. Just as with the removal performance results, the TT reduced the risks of OMPs differently − slightly to substantially − depending on OMP and treatment unit type. A few other data-driven or hypothetical studies on the risk assessment of biofilter outflows have shown that such systems can reduce health risks associated with heavy metals and pathogens (if combined with UV treatment) to a level such that the effluent water quality meets different reuse purposes (e.g. irrigation and toilet flushing) (Fang et al., 2021; Murphy et al., 2017).

Regarding the effectiveness of the evaluated factors (i.e. pretreatment, sand filtration, vegetation, and chalk amendment), the same results were achieved in terms of risk reduction, in general. However, for some OMPs, there were differences between removal efficiency results and what their risk ranking suggested. Sometimes, the EMCs in the outflows might pose a potential risk (R_T>1), while a high Re% was often observed for them by a given treatment unit. This was the case for Flth and BaP in all filter cells and Pyr in BFC and BF. Conversely, Re% can be low, and thus assumed inadequate, while the outflow concentrations may not be a concern from an ecotoxicological perspective. This was the case for Phen, BaA, and TOC in all cells, NP in BF, as well as OP, BbF, C_{10}-C_{40}, and maybe TSS in SF. Other than these two situations, a similar conclusion was reached for OMPs in both methods, meaning that a low Re% agreed with a high risk ranking and vice versa.

The proposed risk-based approach can be a useful management tool that complements removal studies (Fang et al., 2021) and assists with decision-making and setting pollutant priorities on a comparative basis (Figuière et al., 2022). Meanwhile, to improve the level of confidence in the results of risk analysis, sampling more rain events would have been beneficial to obtain more accurate occurrence probabilities and to cover a wider range of rain depths and intensities, especially when the TT cannot cope with the excess amount of water and bypasses it during heavy rainfall.

5. Conclusion

This study contributed to the understanding of OMP removal performance of stormwater treatment trains by evaluating three biofilter cells combined with a pretreatment unit under field conditions. The findings are important for future design modifications of such systems as well as strategies in choosing BMP for road catchments.

First, GPT removal pretreatment was not reliably efficient for any of the OMPs, TSS, and turbidity (Q75 percentile always below 40%, sometimes negative removal, and relatively high removal errors), mainly due to design shortcomings. Second, the non-vegetated sand filter (SF) performed moderately to sufficiently (median removal of 50–80%) for PAH and PHC treatment, but weakly to moderately (<50%) for the more hydrophilic phenolic substances. Nevertheless, Pyr, BbF, BaP, Chry, and Flth were among the dangerous PAHs (as well as BPA and NP) which were often estimated at SF_{out} to have EMCs above PNECs. So, in general, the SF's removal performance was not adequate enough for the studied OMPs. Third, a vegetation layer in biofilter cells (BFC and BF) improved the sand filtration removal substantially so that the EMCs of OMPs were most often below the LoQs, and TSS below 10 mg/L. However, environmental risks might still be high for some PAHs (i.e. BaP, Chry, Pyr, Flth, and DahA) as their LoQs >>PNECs. The additional filtration and absorption capacity of the topsoil was assumed to be the main reason for the positive effect of the vegetation layer. Fourth, we could not quantify the effect of chalk amendment on OMP removal because the many non-detects in samples from the BFC and BF outlets made them impossible to compare, due to either a significant impact of the vegetation on removal, or low

inflow concentrations. Furthermore, NP leaching from the biofilters' construction material most likely occurred, as it was sometimes measured at higher levels in the filter cell outlets.

This study clearly demonstrated that uncertainties can be high for OMPs in field investigations under real conditions and low concentration levels; it is therefore important to consider them when analyzing the removal performance of biofilter treatment systems. Since many outlet concentrations of filter cells were below LoQs, then the inflow EMC with respect to LoQ became decisive in determining removal efficiencies and their removal errors. The approach used here provides a method for obtaining reliable conclusions even when working with this high-uncertainty data influenced by a substantial number of non-detects. As a general finding, by decreasing EMC_{in}/LoQ, the efficiency decreases and the error correspondingly rises. It was found that SF was less affected by the inflow concentration, therefore, showed lower removal errors compared with BFC and BF.

Finally, the pollutant risk analysis provided a more comprehensive tool for stormwater quality assessment which accounted for not only concentration analysis but also other influential factors in ecological impact assessments (occurrence frequency and hazard threshold). According to the risk rankings, the overall treatment performance of the TT was reliable/adequate (R_T<<1) and robust (>90% risk reduction) for InP and C_{10}-C_{40}, moderate (R_T<1 but probably not adequate enough risk reduction) for OP (only in SF_{out}), BaA, BbF, BkF, and TSS (only in SF_{out}), but insufficient (R_T>1) or unreliable (low risk reduction) for BPA (only in SF_{out}), NP, Flth, Pyr, Chry, BaP, DahA, Bper, and TOC. Including such risk analyses in future stormwater treatment research is highly recommended.

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Declaration of competing interest

Not applicable.

CRediT author statement

Ali Beryani: Conceptualization, Methodology, Field investigation, Validation, Formal analysis, Visualization, Writing – original draft & review & editing. **Kelsey Flanagan**: Conceptualization, Methodology, Validation, Formal analysis, Writing – review & editing. **Maria Viklander**: Supervision, Writing – review & editing, Project administration, Funding acquisition. **Godecke-Tobias Blecken**: Conceptualization, Methodology, Validation, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Data Availability

All the data generated/analysed in this study are included in the manuscript, supplementary information. The dataset is available at https://doi.org/10.5878/nny1-2045.

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Supporting information

Performance of a gross pollutant trap-biofilter and sand filter treatment train for the removal of organic micropollutants from highway stormwater (Field study)

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Table of Contents

1. Field study site

Table S1. Technical characteristics of GPT-biofilter treatment train (TT)

Gross pollutant trap (GPT)			
Max water volume (m^3)	Max water depth (m)	Discharge volume (m^3)	Discharge depth (m)
~40	~1.86	~23.3	~0.8

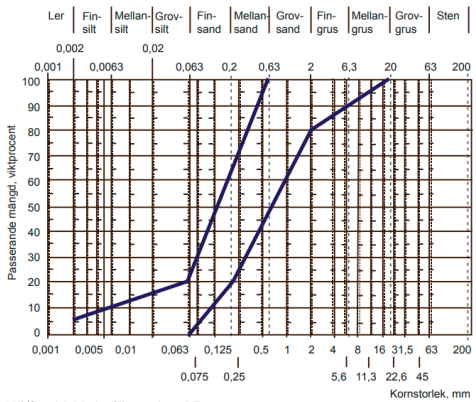
Filter Cells			
	BFC	**SF**	**BF**
Filter media	Sand filter according to DWA-M 187 (2005); (BFC also has chalk)		
Mean grain size: D_{50} (mm)	0.77	0.77	0.77
Uniformity coefficient: C_u (-)	0.27	0.27	0.27
Vegetation layer (soil depth)[*]	Yes (3–4 cm)	No	Yes (3–4 cm)
Chalk amendment	Yes (10% w/w)	No	No
Filter media depth (m)	0.5	0.5	0.5
Bed surface area (m^2)	165	165	165
Max unsaturated infiltration rate (m/s)	10^{-4}	10^{-4}	10^{-4}
Max outflow (l/s)	8.25	8.25	8.25
Detention time of 20 mm rain (hr)	~24	~24	~24
Ponding volume capacity (m^3)	693 (common space on top of the three cells)		

[*] Details of vegetation layer in Figure S2

Figure S1. Site plan in Sundsvall, Sweden, and the catchment area coloured in green

Sikt mm	0,002	0,063	0,2	0,63	2	20
Max %	5	20	60	100	2	20
Min %	-	0	20	50	80	100

Tabellvärden illustreras i nedanstående diagram



Källa: AMA Anläggning 13

Figure S2. Vegetation layer soil composition (soil depth: 3–4 cm; soil type according to USCS: "sand" or "silty sand" with 2.5–5% w/w mulch; basic fertilization with NPK ratio 11-5-18)

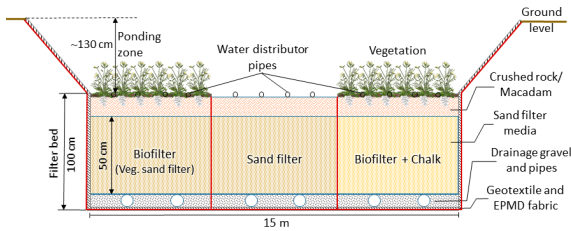


Figure S3. Structure of the filter cells

2. Sampling, analytical methods, and pollutant characteristics

Table S2. Rain events characteristics, and sampling and flow volume information

Rain event characteristics							Total and sampled volumes at sampling locations									
							SW		GPT_{out}		BFC_{out}		SF_{out}		BF_{out} €	
Rain event	Sampling date (2020-21)	Rain (mm)	Rain duration (hr)	ADP¥ (day)	Mean intensity: I_{mean} (mm/hr)	Peak intensity: I_{peak} (mm/hr)	Tot. vol. passed* (m3)	Vol. sampled (%)	Tot. vol. passed* (m3)	Vol. sampled (%)	Tot. vol. passed (m3)	Vol. sampled ** (%)	Tot. vol. passed (m3)	Vol. sampled ** (%)	Tot. vol. passed (m3)	Vol. sampled ** (%)
A	15 Sep	7.3	14.3	3	0.6	0.9	257	100	257	100	129.4	-	40.4	-	102.3	95
B	21 Oct	4.6	13.8	0.8	0.3	0.4	195	100	195	100	53.8	-	90	-	25.5	55
C	17 May	7.8§	3.25§	1.7§	1.3§	1.7§	373	100	373	100	72.6	-	202.9	98	53.1	80
D	12 Jun	4.1	6.5	25.3	0.7	1.0	-	-	-	-	71.2	78	28	68	44	98
E	15 Jun	3.2	6.25	2.4	0.6	0.8	-	-	-	-	23.1	99	35.3	99	9.2	99
F	20 Jun	7.5	10	4.5	2.2	5.4	-	-	-	-	100.3	92	119	99	65	95
G	30 Jun	3.8	18.6	6.7	0.4	1.6	128	83 $	128	83$	10.2	51	92.7	89	<0.1	-
H	11 Jul	8.3	13.7	10.5	2.7	5.0	280	100	280	100	141.5	99	80.6	99	106	99
I	20 Aug	32.4	40.9	1	0.6	0.9	2353	79#	1921##	79#	680.6	98	628.2	99	611.4	91
J	25 Aug	7.9	46.7	6.3	0.9	1.5	303	96	303	96	57.6	63	196.8	84	17.7	68
K	24 Sep	17.8	24.4	10.4	0.9	1.3	932	59	932	59	324.6	97	349.2	99	268.3	90

¥ Antecedent dry period (precipitations less than 1 mm were ignored)

€ One composite sample was taken from BF_{out} outflow except for rain events A and B which had separate subsamples.

* Estimated using the number and volume of pulses (~23.3 m^3/pulse) received from the GPT discharge valve.

** The percentage of non-sampled outflow in BFC_{out}, SF_{out}, and BF_{out} is after sampling.

$ The first portion of inflow was not sampled.

§ Due to missing data, the rain characteristics were reported from another weather station close to the catchment (1500 m away from our rain gauge).

21% of inflow was not sampled during the last quarter because of at least one of these reasons: bypassed overflow (16%), GPT's discharge valve stayed open due to a very high inflow (sending no new signal to the SW and GPT_{out} samplers in this mode), or the sampling program ended (final 5%).

16% of inflow bypassed during the last quarter. The bypassed volume was estimated using the total volume summation of BFC_{out}, SF_{out}, and BF_{out}.

31 *Table S3. Analytical standard methods for the organic substances and other parameters*

Parameter	Analytical method
TPH	Determination of extractable compounds in the range of hydrocarbons C_{10}–C_{40}, their fractions calculated from the measured values using gas chromatography method with FID detection according to methods: CSN EN ISO 9377-2, US EPA 8015, US EPA 3510, TNRCC Method 1006.
PAHs	Determination of semi-volatile organic compounds using gas chromatography with MS or MS/MS detection according to methods: US EPA 8270D, US EPA 8082A, CSN EN ISO 6468, US EPA 8000D, samples preparation as per CZ_SOP_D06_03_P01 chap. 9.1, 9.4.1. Calculation of semi-volatile organic compounds sums from measured values.
BPA and APs	Determination of alkylphenols and alkylphenol ethoxylates using gas chromatography with MS or MS/MS detection according to CSN EN ISO 18857-2 method. Calculation of alkylphenols and alkylphenol ethoxylates sums from measured values.
TOC	Determination of total organic carbon (TOC) using IR detection according to CSN EN 1484, SM 5310 method.
TSS	Gravimetrical determination of suspended solids using SS-EN 872-2:2005 method.
Turbidity	2100Q IS Portable Turbidimeter, HACH, calibrated with Formazin primary StablCal Standards.
Conductivity and temperature	pHenomenal® Conductivity/TDS/°C Meter, Handheld, CO 3100 H, VWR, calibrated using the control standard KCl solution.
pH	pH 330i meter, Handheld, WTW GmbH, Weilheim, calibrated using buffer solutions.
DO	Dissolved Oxygen Meter - YSI Model 58, classic handheld, Xylem Inc.

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33 *Table S4. Characteristics of phenolic substances (Ahel & Giger, 1993a, 1993b; Staples et al., 2008; Xu et al., 2008)*

Phenolic substances	Molecular mass (g/mol)	Water solubility[¥] (mg/L at 0.5 ˚C)	Vapor pressure[$] (Pa at 25 ˚C)	Boiling point (˚C)	Log K_{OW}[$]	Log K_{OC}[£] (L/kg)
Bisphenol-A (BPA)	228.3	120[$]	5e-6	251	3.41	2.5–3.3[$]
4-tert-Octylphenol (OP)	206.3	12.6	0.07	280	4.12	3.5–4.2
Octylphenol ethoxylates						
OP1EO	250.4	8.0	NA	NA	4.1[*]	NA
OP2EO	300.4	13.2	NA	402	4.0[*]	NA
OP3EO	350.4	18.4	NA	441	3.9[*]	NA
Nonylphenol (NP)	220.3	5.4	0.07	304	4.48	4–4.7
Nonylphenol ethoxylates						
NP1EO	264	3.0	<1e-4	367	4.17[*]	NA
NP2EO	308.5	3.4	<1e-4	409	4.21[*]	NA
NP3EO	352.5	5.9	<1e-4	NA	4.20[*]	NA

[£] K_{OC}: Sediment organic carbon-water partition coefficient (estimated values)
[$] @ 25 ˚C
[*] The octanol-water partition coefficients (Kow) of the chemicals in this group are not considered to be a reliable indicator of the partitioning behavior of surface-active substances in the environment (McWilliams and Payne, 2001; Shorts, et al., 2010).

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35 *Table S5. Characteristics of polycyclic aromatic hydrocarbons (PAHs)*

PAH	Abbr.	Molecular mass (Daltons)	No. of rings	fraction	Carcino-genicity group*	Water solubility¥ (mg/L_25˚C)	Vapor pressure# (Pa_25˚C)	Log $K_{OW}$$	Log K_{OC}£ (L/kg)
Naphthalene	Nap	128	2	LMW	2B	31.6	10.4	3.37	2.95
Acephthylene	Acyl	152	3	LMW	-	16	9.0e-1	4.00	3.13
Acephthene	Acen	154	3	LMW	3	4.5	30e-1	3.92	3.46
Fluorene	Flu	166	3	LMW	3	1.8	9.0e-2	4.18	3.71
Phenthrene	Phen	178	3	LMW	3	1.3	2.0e-2	4.57	3.79
Anthracene	Anth	178	3	LMW	3	0.07	1.0e-3	4.54	4.57
Fluoranthene	Flth	202	4	MMW	3	0.24	1.2e-3	5.22	4.24
Pyrene	Pyr	202	4	MMW	3	0.14	6.0e-4	5.18	4.39
Benz(a) anthracene	BaA	228	4	HMW	2B	0.01	2.8e-5	5.91	5.09
Chrysene	Chry	228	4	HMW	2B	0.003	5.7e-7	5.65	5.41
Benzo(b) fluoranthene	BbF	252	5	HMW	2B	<0.001	-	5.80	5.70 <
Benzo(k) fluoranthene	BkF	252	5	HMW	2B	<0.001	5.2e-8	6.00	5.70 <
Benzo(a)pyrene	BaP	252	5	HMW	1	<0.001	7.0e-7	6.04	5.70 <
Dibenz(a.h) anthracene	BahA	278	5	HMW	2A	<0.001	3.7e-10	6.75	5.70 <
Benzo(g.h.i) perylene	IP	276	6	HMW	3	<0.001	-	6.50	5.70 <
Indeno(1.2.3.cd) pyrene	Bper	276	6	HMW	2B	<0.001	6e-8	6.58	5.70 <

¥ (Monaco et al., 2017)
(Joa et al., 2009)
$ K_{OW}: Octanol-water partition coefficient (Joa et al., 2009)
£ K_{OC}: Sediment organic carbon-water partition coefficient (Khodadoust et al., 2005)
* (1): carcinogenic to humans; (2A): probably carcinogenic to humans; (2B): possibly carcinogenic to humans; (3): not classifiable as carcinogenic to humans (IARC Working Group, 2010).

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37 *Table S6. Characteristics of petroleum hydrocarbons (PHCs) (Reed & Stemer, 2002)*

Petroleum Hydrocarbons (only C_{10}< fractions)	Molecular Weight	Water solubility¥ (mg/L at 25˚C)	Vapor pressure$ (Pa at 25˚C)	Boiling point (˚C)	Log K_{OC}£ (L/kg)
Aliphatic					
C_{10}-C_{12}	160	0.026	7.9e+1	200	5.4
C_{12}-C_{16}	200	5.9e-4	3.5	260	6.7
C_{16}-C_{21}	270	1.0e-6	1.7e-1	320	8.8
Aromatic					
C_{10}-C_{12}	130	25	7.8e+1	200	3.4
C_{12}-C_{16}	150	5.8	3.5	260	3.7
C_{16}-C_{21}	190	0.51	1.7e-1	320	4.2
C_{21}-C_{35}	240	0.0066	7.9e-4	340	5.1

Note: Values are based on pure compounds; behaviour may differ in complex mixtures.
£ K_{OC}: Sediment organic carbon-water partition coefficient (estimated values)

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3. Data analysis

3.1. Monte-Carlo simulation

To obtain the best estimation for EMCs at each sampling location and propagate their uncertainty distributions, Monte-Carlo (MC) simulation was used in R software. In the MC method, Equation S1 was used to find the EMC distribution at a given sampling point and for a certain rain event. In doing so, concentrations (c_i) of all subsamples and the volume passed during the first subsample (v_1) at SW and GPT_{out} were associated with uncertainties. The source of uncertainties in c_i and v_i were analytical measurement uncertainty ($\pm\delta_i$) and the pre-existing stormwater in the GPT chamber (max. 21 m^3), respectively. It should be noted that since we knew the discharge volume of the GPT chamber for each pulse (23.3 m^3), we could assume a negligible uncertainty in v_i values for the subsequent subsamples at SW and GPT_{out}. Furthermore, uncertainties in measuring the filter cell's outflow volumes were insignificant (+0.2%), according to the flowmeter datasheets. Normal distribution was assumed for the quantified concentrations ($c_i \geq$ RL) with $\delta_i/2$ as the standard deviation (according to the laboratory reports), and uniform distributions for censored values or non-detects ($c_i <$ RL) and the first subsample's volume (v_1) taken at SW and GPT_{out} (see Equation S2). Further details about the MC simulation are given in (Beryani et al., Submitted).

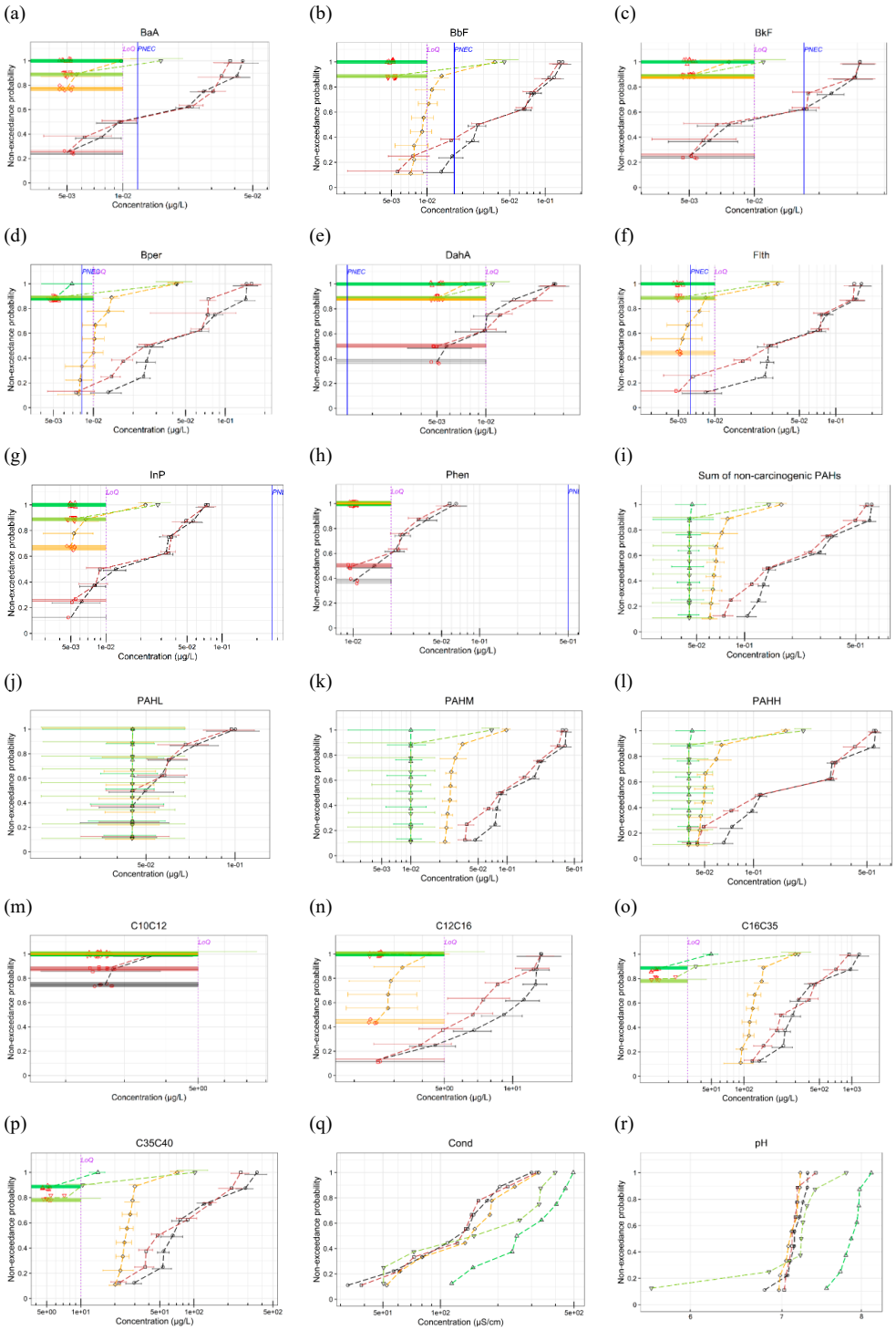
$$EMC = \frac{M_T}{V_T} = \frac{\sum m_i}{\sum v_i} = \frac{\sum_{i=1}^{n} c_i v_i}{\sum_{i=1}^{n} v_i} \qquad \text{Equation S1}$$

$$\begin{cases} C_i \sim N(\mu = c_i, \sigma = \delta_i/2) & \text{if } C_i \text{ quantified} \\ C_i \sim U(\min = 0, \max = RL) & \text{if } C_i \text{ censored} \\ V_1 \sim U\left(\min = v_1 - 21^{(m^3)}, \max = v_1\right) & \end{cases} \qquad \textit{Equation S2}$$

The EMC distribution was generated using the MC method through an iterative process (10^5 times in this study) of random sampling from the specified uncertainty distributions of the parameters in Equation S2. The median of the final EMC distribution was considered to be the best-estimate event mean concentration (EMC_{best}), and the range between 2.5% and 97.5% quantiles as the EMC's lower and upper limits of uncertainty ($-\Delta_l$, $+\Delta_u$).

3.2. Methods for statistical correlation tests:

We evaluated the correlations between some parameters (OMP EMCs, global parameters, and rain characteristics (depth, I_{mean}, I_{peak}, and ADP)) at some sampling locations over $N=8-11$ rain events. Most parameters did not follow a normal distribution, according to a Shapiro-Wilk normality check. Therefore, non-parametric pairwise Spearman or Kendall's tau correlation tests were respectively applied for all quantified concentrations or, in either case, for two datasets at least one of which included left-censored value(s). The correlation coefficients were finally classified as very weak, weak, moderate, strong, and very strong. In doing so, the ranking levels of 0.9, 0.7, 0.3, and 0.1 were set for Spearman's rho and 0.7, 0.5, 0.2, and 0.1 for Kendall's Tau classifications (for both positive and negative associations). In both tests, the correlation was considered statistically significant for a p-value (p) $\leq$0.05 (H_0: the two parameters are not truly correlated).



68 *Figure S4. Non-exceedance probability plots for OMPs and parameters at SW (○), GPT_{out} (□), SF_{out} (◇), BFC_{out} (△), BF_{out} (▽)*

Table S7. Summary of significance of difference tests for event mean concentrations (EMCs) of OMPs between two target sampling points (SW: influent of treatment train; and GPT_{out}, SF_{out}, BFC_{out}, and BF_{out}: effluent of treatment sections)

Parameter	Sampling locations to compare	N_obs	Chisq (X^2)	p-val
Nap	SW_GPT	8	0	NA
Nap	GPT_BFC	8	0	NA
Nap	GPT_SF	8	0	NA
Nap	GPT_BF	8	0	NA
Nap	SF_BF	9	0	NA
Nap	BFC_BF	8	0	NA
Acy	SW_GPT	8	0	NA
Acy	GPT_BFC	8	0	NA
Acy	GPT_SF	8	0	NA
Acy	GPT_BF	8	0	NA
Acy	SF_BF	9	0	NA
Acy	BFC_BF	8	0	NA
Ace	SW_GPT	8	0	NA
Ace	GPT_BFC	8	0	NA
Ace	GPT_SF	8	0	NA
Ace	GPT_BF	8	0	NA
Ace	SF_BF	9	0	NA
Ace	BFC_BF	8	0	NA
Flu	SW_GPT	8	0	1
Flu	GPT_BFC	8	0	1
Flu	GPT_SF	8	0	1
Flu	GPT_BF	8	0	1
Flu	SF_BF	9	0	NA
Flu	BFC_BF	8	0	NA
Phen	SW_GPT	8	0.012	0.9
Phen	GPT_BFC	8	4.923	0.03
Phen	GPT_SF	8	5.538	0.02
Phen	GPT_BF	8	5.538	0.02
Phen	SF_BF	9	0	NA
Phen	BFC_BF	8	0	NA
Anth	SW_GPT	8	0	1
Anth	GPT_BFC	8	0	1
Anth	GPT_SF	8	0	1
Anth	GPT_BF	8	0	1
Anth	SF_BF	9	0	NA
Anth	BFC_BF	8	0	NA
Flth	SW_GPT	8	0.244	0.6
Flth	GPT_BFC	8	8.727	0.003
Flth	GPT_SF	8	6.365	0.01
Flth	GPT_BF	8	7.788	0.005
Flth	SF_BF	9	0.007	0.9
Flth	BFC_BF	8	0.889	0.3
Pyr	SW_GPT	8	0.531	0.5
Pyr	GPT_BFC	8	14.222	0.0002
Pyr	GPT_SF	8	11.703	0.0006
Pyr	GPT_BF	8	13.64	0.0002
Pyr	SF_BF	9	9.58	0.002
Pyr	BFC_BF	8	0.889	0.3
BaA	SW_GPT	8	0.011	0.9
BaA	GPT_BFC	8	4.923	0.03
BaA	GPT_SF	8	4.209	0.04
BaA	GPT_BF	8	3.793	0.05
BaA	SF_BF	9	1	0.3
BaA	BFC_BF	8	0.889	0.3
Chry	SW_GPT	8	0.056	0.8
Chry	GPT_BFC	8	6.667	0.01
Chry	GPT_SF	8	5.921	0.01
Chry	GPT_BF	8	5.298	0.02
Chry	SF_BF	9	0.226	0.6
Chry	BFC_BF	8	0.889	0.3
BbF	SW_GPT	8	0.173	0.7
BbF	GPT_BFC	8	8.727	0.003
BbF	GPT_SF	8	2.897	0.09
BbF	GPT_BF	8	7.067	0.008
BbF	SF_BF	9	1.648	0.2
BbF	BFC_BF	8	0.889	0.3

BkF	SW_GPT	8	0.046	0.8
BkF	GPT_BFC	8	4.923	0.03
BkF	GPT_SF	8	2.751	0.1
BkF	GPT_BF	8	3.793	0.05
BkF	SF_BF	9	1	0.3
BkF	BFC_BF	8	0.889	0.3
BaP	SW_GPT	8	0.199	0.7
BaP	GPT_BFC	8	6.667	0.01
BaP	GPT_SF	8	6.231	0.01
BaP	GPT_BF	8	5.298	0.02
BaP	SF_BF	9	0.007	0.9
BaP	BFC_BF	8	0.889	0.3
DahA	SW_GPT	8	0.003	1
DahA	GPT_BFC	8	3.429	0.06
DahA	GPT_SF	8	4.857	0.03
DahA	GPT_BF	8	2.068	0.2
DahA	SF_BF	9	1	0.3
DahA	BFC_BF	8	0.889	0.3
Bper	SW_GPT	8	0.271	0.6
Bper	GPT_BFC	8	12.191	0.0005
Bper	GPT_SF	8	5.51	0.02
Bper	GPT_BF	8	9.17	0.002
Bper	SF_BF	9	3.87	0.05
Bper	BFC_BF	8	0.889	0.3
InP	SW_GPT	8	0.07	0.8
InP	GPT_BFC	8	4.923	0.03
InP	GPT_SF	8	5.975	0.01
InP	GPT_BF	8	3.793	0.05
InP	SF_BF	9	0.007	0.9
InP	BFC_BF	8	0.889	0.3
PAH16	SW_GPT	8	0.531	0.5
PAH16	GPT_BFC	8	14.222	0.0002
PAH16	GPT_SF	8	8.385	0.004
PAH16	GPT_BF	8	11.703	0.0006
PAH16	SF_BF	9	9	0.003
PAH16	BFC_BF	8	0.036	0.8
PAHCar	SW_GPT	8	0.173	0.7
PAHCar	GPT_BFC	8	14.222	0.0002
PAHCar	GPT_SF	8	2.897	0.09
PAHCar	GPT_BF	8	11.703	0.0006
PAHCar	SF_BF	9	9	0.003
PAHCar	BFC_BF	8	0.33	0.6
PAHOth	SW_GPT	8	0.531	0.5
PAHOth	GPT_BFC	8	14.222	0.0002
PAHOth	GPT_SF	8	10.768	0.001
PAHOth	GPT_BF	8	11.703	0.0006
PAHOth	SF_BF	9	9.58	0.002
PAHOth	BFC_BF	8	0.227	0.6
PAHL	SW_GPT	8	0	1
PAHL	GPT_BFC	8	3.713	0.05
PAHL	GPT_SF	8	3.169	0.08
PAHL	GPT_BF	8	4.388	0.04
PAHL	SF_BF	9	0.017	0.9
PAHL	BFC_BF	8	0.083	0.8
PAHM	SW_GPT	8	0.531	0.5
PAHM	GPT_BFC	8	14.222	0.0002
PAHM	GPT_SF	8	11.703	0.0006
PAHM	GPT_BF	8	12.626	0.0004
PAHM	SF_BF	9	9.58	0.002
PAHM	BFC_BF	8	0.735	0.4
PAHH	SW_GPT	8	0.173	0.7
PAHH	GPT_BFC	8	14.222	0.0002
PAHH	GPT_SF	8	4.04	0.04
PAHH	GPT_BF	8	11.703	0.0006
PAHH	SF_BF	9	9	0.003
PAHH	BFC_BF	8	0.227	0.6
OP	SW_GPT	8	0.408	0.5
OP	GPT_BFC	8	11.168	0.0008
OP	GPT_SF	8	6.537	0.01

OP	GPT_BF	8	11.168	0.0008
OP	SF_BF	8	8.709	0.003
OP	BFC_BF	8	0	NA
OP1EO	SW_GPT	6	0	NA
OP1EO	GPT_BFC	6	0	NA
OP1EO	GPT_SF	6	0	NA
OP1EO	GPT_BF	5	0	NA
OP1EO	SF_BF	5	0	NA
OP1EO	BFC_BF	5	0	NA
OP2EO	SW_GPT	6	0	NA
OP2EO	GPT_BFC	6	0	NA
OP2EO	GPT_SF	6	0	NA
OP2EO	GPT_BF	5	0	NA
OP2EO	SF_BF	5	0	NA
OP2EO	BFC_BF	5	0	NA
OP3EO	SW_GPT	6	0	NA
OP3EO	GPT_BFC	6	0	NA
OP3EO	GPT_SF	6	0	NA
OP3EO	GPT_BF	5	0	NA
OP3EO	SF_BF	5	0	NA
OP3EO	BFC_BF	5	0	NA
NP	SW_GPT	8	0.061	0.8
NP	GPT_BFC	8	0.404	0.5
NP	GPT_SF	8	0.022	0.9
NP	GPT_BF	8	5.875	0.02
NP	SF_BF	8	5.895	0.02
NP	BFC_BF	8	6.075	0.01
NP1EO	SW_GPT	6	0	NA
NP1EO	GPT_BFC	6	0	NA
NP1EO	GPT_SF	6	0	NA
NP1EO	GPT_BF	5	0	NA
NP1EO	SF_BF	5	0	NA
NP1EO	BFC_BF	5	0	NA
NP2EO	SW_GPT	6	0	NA
NP2EO	GPT_BFC	6	0	NA
NP2EO	GPT_SF	6	0	1
NP2EO	GPT_BF	5	0	NA
NP2EO	SF_BF	5	0	1
NP2EO	BFC_BF	5	0	NA
NP3EO	SW_GPT	6	0	NA
NP3EO	GPT_BFC	6	0	NA
NP3EO	GPT_SF	6	0	NA
NP3EO	GPT_BF	5	0	NA
NP3EO	SF_BF	5	0	NA
NP3EO	BFC_BF	5	0	NA
C10C40	SW_GPT	8	0.392	0.5
C10C40	GPT_BFC	8	14.222	0.0002
C10C40	GPT_SF	8	8.43	0.004
C10C40	GPT_BF	8	13.292	0.0003
C10C40	SF_BF	9	10.473	0.001
C10C40	BFC_BF	8	0.002	1
C10C12	SW_GPT	8	0	1
C10C12	GPT_BFC	8	0	1
C10C12	GPT_SF	8	0	1
C10C12	GPT_BF	8	0	1
C10C12	SF_BF	9	0	NA
C10C12	BFC_BF	8	0	NA
C12C16	SW_GPT	8	0.897	0.3
C12C16	GPT_BFC	8	6.667	0.01
C12C16	GPT_SF	8	10.58	0.001
C12C16	GPT_BF	8	8.017	0.005
C12C16	SF_BF	9	0	1
C12C16	BFC_BF	8	0	NA
C16C35	SW_GPT	8	0.392	0.5
C16C35	GPT_BFC	8	14.222	0.0002
C16C35	GPT_SF	8	8.43	0.004
C16C35	GPT_BF	8	13.292	0.0003
C16C35	SF_BF	9	10.473	0.001
C16C35	BFC_BF	8	0.194	0.7

C35C40	SW_GPT	8	0.392	0.5
C35C40	GPT_BFC	8	14.222	0.0002
C35C40	GPT_SF	8	6.614	0.01
C35C40	GPT_BF	8	12.405	0.0004
C35C40	SF_BF	9	10.473	0.001
C35C40	BFC_BF	8	0.223	0.6
BPA	SW_GPT	8	0.043	0.8
BPA	GPT_BFC	8	14.222	0.0002
BPA	GPT_SF	8	0.591	0.4
BPA	GPT_BF	8	17.778	0.00002
BPA	SF_BF	9	18	0.00002
BPA	BFC_BF	8	0.013	0.9
TOC	SW_GPT	11	0.086	0.8
TOC	GPT_BFC	8	1.292	0.3
TOC	GPT_SF	9	0.238	0.6
TOC	GPT_BF	10	1.417	0.2
TOC	SF_BF	9	0.423	0.5
TOC	BFC_BF	8	0.048	0.8
TSS	SW_GPT	11	0.086	0.8
TSS	GPT_BFC	8	9.117	0.003
TSS	GPT_SF	9	5.488	0.02
TSS	GPT_BF	8	9.916	0.002
TSS	SF_BF	8	12.397	0.0004
TSS	BFC_BF	8	0.883	0.3
Turb	SW_GPT	9	0.017	0.9
Turb	GPT_BFC	8	11.524	0.0007
Turb	GPT_SF	9	10.723	0.001
Turb	GPT_BF	8	9.16	0.002
Turb	SF_BF	8	3.496	0.06
Turb	BFC_BF	8	1.894	0.2
Cond	SW_GPT	9	0.002	1
Cond	GPT_BFC	8	6.477	0.01
Cond	GPT_SF	9	0.323	0.6
Cond	GPT_BF	8	0.762	0.4
Cond	SF_BF	8	0.234	0.6
Cond	BFC_BF	8	1.878	0.2
pH	SW_GPT	9	0.325	0.6
pH	GPT_BFC	8	16	0.00006
pH	GPT_SF	9	0.094	0.8
pH	GPT_BF	8	1.661	0.2
pH	SF_BF	8	3.349	0.07
pH	BFC_BF	8	10.993	0.0009
DO	SW_GPT	8	0.097	0.8
DO	GPT_BFC	7	0.052	0.8
DO	GPT_SF	8	0.272	0.6
DO	GPT_BF	7	0	1
DO	SF_BF	7	0.212	0.6
DO	BFC_BF	7	0.196	0.7
Temp	SW_GPT	9	0.094	0.8
Temp	GPT_BFC	8	0.589	0.4
Temp	GPT_SF	9	1.025	0.3
Temp	GPT_BF	8	0.009	0.9
Temp	SF_BF	8	1.315	0.3
Temp	BFC_BF	8	1.108	0.3

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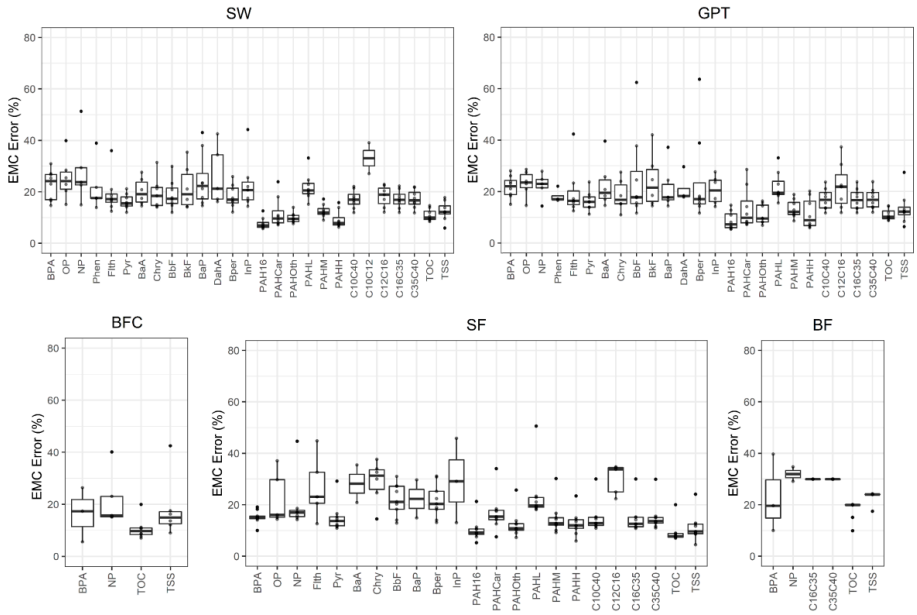

Figure S5. Errors in event mean concentrations calculated for OMPs at each sampling point (OMPs having only less than two quantified EMCs over all the events have been excluded from the boxplots)

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Paper III

Beryani A.; Viklander M.; Blecken G.T.

The intra-event dynamics of the removal of organic micro-pollutants (OMP) in stormwater treatment trains: gross pollutant trap and biofilter

Presented at the 15th International Conference on Urban Drainage, 2021

The intra-event dynamics of the removal of organic micro-pollutants (OMP) in stormwater treatment trains: gross pollutant trap and biofilter

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Highlights

- GPT-biofilter system can remove some OMPs from road stormwater efficiently.
- Vegetation can improve the removal efficiency only for some OMPs.
- OMPs intra-event concentration has an decreasing trend after infiltration.

Introduction

Biofilter (also called bioretention) is one of the low-impact, sustainable stormwater urban drainage systems (SUDS) (Blecken et al., 2017; Søberg et al., 2019). Some field observations (DiBlasi et al., 2009; Zhang et al., 2014; Flanagan et al., 2019) and lab studies (Hong et al., 2006; LeFevre et al., 2012) have shown that biofilters can have promising results for the removal of organic micro-pollutants (OMPs) from urban stormwater. However, compared to e.g. metals and nutrients, bioretention research is limited when it comes to removal of OMPs. Further, while most stormwater treatment studies have focused on overall removal efficiency by measuring event mean concentrations (EMC), the literature is very limited on intra-event concentration measurements, especially for field studies (DiBlasi et al., 2009; Zhang et al., 2014; Flanagan et al., 2019). Fewer full-scale bioretention facilities have been investigated under the real environmental conditions so far, especially in Scandinavian climate/ambient conditions. Biofilters are often combined with a pre-sedimentation facility to remove sediment before the water is discharged to the filter. Limited knowledge is available on the exact contribution of such pre-treatment on the overall OMP-removal performance.
This field study has been done on a gross pollutants trap (GPT)-biofilter treatment train located in Sundsvall, Sweden. The objective of the study is to evaluate the performance of a vegetated and a non-vegetated biofilter cell in removing prioritized OMPs in road runoff water during a number of rainfall events. Beside the overall removal efficiency, the other main aim is to analyse the concentration variations during the active treatment cycles (obtaining the intra-event pollutographs).

Methodology

System set up, sampling, and analytical methods:

The GPT-biofilter system receives stormwater runoff from a road bridge close to the facility (Fig. 1). The treatment system consists of a GPT (pre-sedimentation and oil trap chambers) and three parallel downstream biofilter cells of a sand-based filter material with/without vegetation on top, and a drainage layer at the bottom. The stormwater percolates through the system by gravity. To log the rainfall data, there is a rain gauge installed on the site. To measure the hydraulic data, a continuous flow meter was used at the outlet and a signal counting method at the inflow.
Stormwater samples were taken volume proportionally by ISCO automatic samplers. Programming was done according to the features of each forecasted rain event (e.g. duration, intensity distribution). Maximum eight samples were taken over the rain duration at four sampling points: one from incoming stormwater, one after GPT, and one at the outlet of each biofilter (F3: vegetated and F2: non-vegetated). Five to six rain events are supposed to be covered in this study. All the samples were analysed in ALS Scandinavia AB labs.

Contaminants of concern and experimental parameters:

The OMPs studied were Poly-Aromatic Hydrocarbons (PAHs), Total Petroleum Hydrocarbons (TPHs), Nonyl- and 4-t-Octyl-phenols (NP and OP), and Bisphenol A (BPA). These stormwater contaminants were prioritized among a list of relevant organic substances already detected in various studies on urban stormwater quality. Other aspects such as their environmental risks and standard limits, detectability in solely roads runoff, feasibility of sampling, and financial reasons were important in our prioritizing. Other analysed parameters include total organic carbon (TOC) and total suspended solids (TSS). Turbidity, DO, conductivity, pH, and

temperature were continuously monitored by the online sensors. These parameters are important in analysing the physio-chemical processes of treatment.

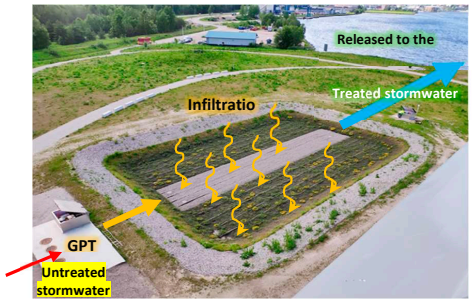

Figure 1. GPT-biofilter treatment system used in the study (in Sundsvall, Sweden)

Results and discussion

Overall performance:

The sampling campaign is currently ongoing. So far, only preliminary results are available. We assume that we will have sampled 5-6 rain events until the ICUD conference in October.

Preliminary results of EMC in figure 2 show that the GPT-biofilter system can considerably reduce the levels of OMPs of concern in the road runoff water. GPT- F2 biofilter without vegetation had an overall efficiency of 75%, 75.1%, 46.0%, 25.8%, 37.2%, and 69.7% in removing TSS, PAHs, OP, NP, BPA, and TPHs (C10-C40 fractions), respectively. The corresponding values for GPT-F3 biofilter with vegetation were >85%, 72.8%, >80%, ~40%, >85%, and 66.2%. The vegetation factor significantly improves the removal of TSS, BPA and OP, although it reduced the infiltration rate and so the total mass deposition. Another finding was that biofilter cells do not impact TOC levels either in vegetated or non-vegetated conditions. It was also found out that the biofilter cells may cause an increase in TOC and conductivity average levels. The observed effect was more pronounced in the cells with vegetation.

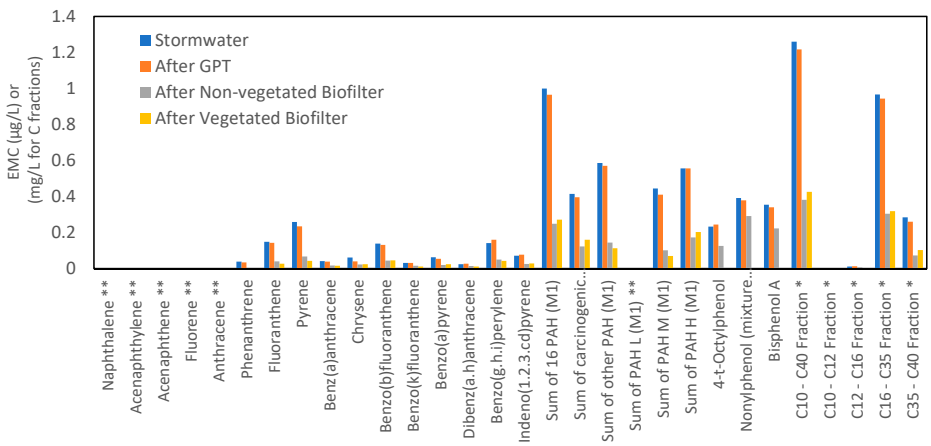

Figure 2. Event mean concentrations of the organic micro-pollutants at different sampling point
(*) the concentration unit for C fractions is mg/L; (**) Not detected in stormwater.

Comparison of the TSS levels and OMPs concentrations before and after GPT revealed that, contrary to our hypothesis, GPT did not improve the stormwater quality. This observation could be due to a undersized GPT and/or the high flow velocity and turbulence during stormwater discharge from the GPT chamber to the biofilter cells. The discharge is not continuous but step-wise through valves which are triggered and open for a short period of time. Thus, 23 m^3 water are discharged within about 4 minutes. The probably turbulent flow is likely to resuspend the sediments that are already deposited. A solution with continuous flow to the biofilter may have performed better.

Intra-event analysis:

Fig. 3 presents the pollutographs (concentration variations) of the OMPs at the three sampling points (inlet, after GPT, biofilter outlet) for one rain event. The preliminary results of pollutographs show that in spite of disordered variations of the concentrations at the inflow (Fig. 1a), most of the OMP concentrations at the outlet of biofilter F2 have a decreasing trend during the infiltration period (Fig 1c). We observed a high correlation (R^2>95) between the pollutographs of TSS (or turbidity) and some of the OMPs including PAHs and TPHs. This is likely due to the fact that some OMPs tend to be associated with suspended particles and be transported and/or deposited by them, but more data are needed for verifying it. In addition, the same results was observed about the ineffectiveness of GPT on the removals during the rain event (Fig 1b).

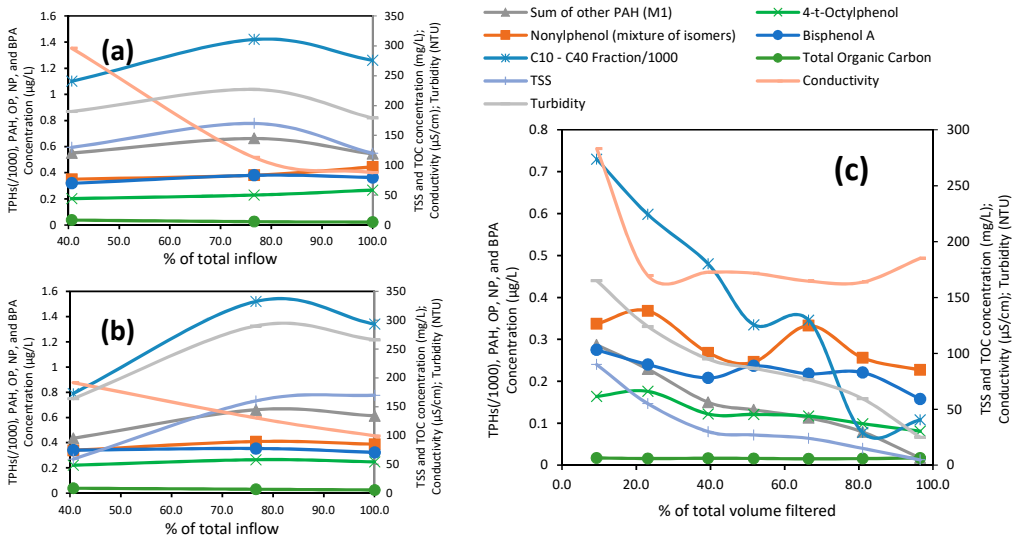

Figure 3. Pollutographs for some of the selected organic micro-pollutants at (a) inlet or untreated stormwater, (b) after GPT, (c) outlet of non-vegetated biofilter F2.

Conclusions and future work

This field study gives us a deeper understanding of the dynamics of removal processes in biofilters within single rain events and how they response to the inlet concentration variations. The samplings and analyses are still ongoing and the more complete results will be available until October.

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