CRITICAL REVIEW

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Hydrophilic trace organic contaminants in urban stormwater: occurrence, toxicological relevance, and the need to enhance green stormwater infrastructure

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Hydrophilic trace organic contaminants (hyphil-TrOCs) are polar, often ionizable organic compounds of anthropogenic origin that have various applications in the urban environment *e.g.*, as pesticides, plasticizers, and flame retardants. Hyphil-TrOCs can be washed off in storm events and enter surface waters *via* untreated urban stormwater discharges or combined sewer overflows. Though trace concentrations of these chemicals may pose a risk to ecosystem and human health, information on their presence in urban stormwater remains elusive. Monitoring and source apportionment of hyphil-TrOCs in urban stormwater is complicated by the vast number and sources of organic contaminants and the high variability in aqueous concentration over time and space. Here, we present the current state of knowledge on the occurrence and toxicological relevance of hyphil-TrOCs in urban stormwater. To mitigate negative impacts of contaminated surface runoff to receiving water bodies and to prevent sanitary or combined sewer overflows, many cities implement sustainable green stormwater infrastructure, also called best management practices (BMPs). Current knowledge suggests that conventional stormwater BMPs such as detention basins, constructed wetlands, and biofilters often fail to remove hyphil-TrOCs. We identify future research needs to enhance green stormwater infrastructure with respect to water quality and safe use of urban stormwater for non-potable applications or groundwater recharge and present potential benefits of geomedia amendments in BMPs (*e.g.*, activated carbon or biochar-amended biofilters). We highlight the need to improve stormwater monitoring strategies by combining chemical and bioanalytical tools to better assess effects of complex chemical mixtures and the treatment performance of BMPs and assure safe stormwater use for water supply.

1 Introduction

Hydrophilic trace organic contaminants (hyphil-TrOCs) are polar and often ionizable compounds of anthropogenic origin used *e.g.*, as pesticides, plasticizers, flame retardants, corrosion inhibitors, personal care products, and pharmaceuticals.[1,2] Hyphil-TrOCs are mobile in the aquatic environment and possess low sorption tendency due to their polarity and water solubility.[1–3] Moreover, many hyphil-TrOCs are recalcitrant and poorly removed in traditional water treatment systems.[1–3] Therefore, hyphil-TrOCs are ubiquitous in surface waters and groundwater and have been also detected in finished drinking water.[1,3–8] Numerous hyphil-TrOCs cause biological effects such as endocrine

Water impact

Urban stormwater contains diverse mixtures of hydrophilic trace organic contaminants (hyphil-TrOCs) that contribute to water quality impairments. To protect aquatic ecosystems and enable safe stormwater harvesting, we need cost-effective and reliable hyphil-TrOC removal strategies. This review discusses the occurrence of hyphil-TrOCs in urban stormwater and highlights future research needs for enhanced monitoring and abatement of hyphil-TrOCs in green stormwater infrastructure.

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disruption at trace concentrations, which pose risks to ecosystem and human health.[9,10] One major point source of hyphil-TrOCs are effluents from conventional wastewater treatment plants.[2,11] Also, hyphil-TrOCs can be washed off from urban areas during storm events and enter the aquatic environment through urban surface runoff or combined sewer overflow (CSO).[12,13]

It has been known for decades that urban stormwater is a contributor to the impairment of water quality.[14] Thus, monitoring and management programs have focused on conventional stormwater pollutants such as total suspended solids (TSS),[15–17] nutrients,[15,18] pathogens,[19–21] metals,[15–18,22,23] polycyclic aromatic hydrocarbons (PAHs),[17,24–26] polychlorinated biphenyls,[27] and certain

pesticides.[28,29] While stormwater research has long concentrated on particle-associated pollutants, a review article by LeFevre et al.[18] highlighted the importance of dissolved stormwater pollutants (mainly nutrients, toxic metals, and hydrocarbons) and identified a major lack of knowledge about hyphil-TrOCs. Recently, urban stormwater runoff has received increased attention as an important but often overlooked input pathway of hyphil-TrOCs to receiving water bodies.[12,30–32]

In the face of global water scarcity, urban stormwater is increasingly valued as a currently underused freshwater resource.[33–35] The capture, treatment, and recharge of stormwater runoff can augment urban water supplies and diversify urban water supply portfolios.[34–36] However, safe

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Stephanie Spahr is a junior research group leader in the Center for Applied Geoscience at the University of Tübingen, Germany. Stephanie was a postdoctoral research scholar at the Department of Civil and Environmental Engineering at Stanford University, California prior to starting in Tübingen. Stephanie holds a PhD in Environmental Chemistry from the Swiss Federal In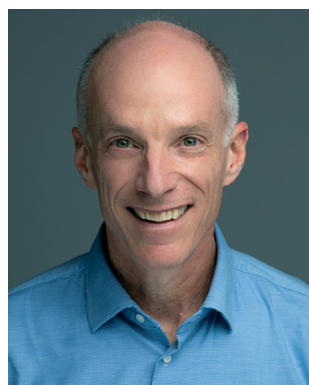stitute of Technology in Lausanne (EPFL) and worked at the Swiss Federal Institute of Aquatic Science and Technology (Eawag). Her research focuses on the fate and removal of anthropogenic trace organic contaminants in natural aquatic systems and engineered water treatment schemes.

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non-potable and potable use of urban runoff requires water quality monitoring with respect to pathogens and potentially harmful chemical contaminants.[35] In fact, infiltration of urban stormwater runoff may increase the concentrations of hyphil-TrOCs, such as bisphenol A (BPA), in groundwater.[37] Data on the occurrence of hyphil-TrOCs in stormwater are necessary for the development of a regulatory framework for stormwater harvesting and its public acceptance, cost-effective stormwater treatment technologies, and risk-based water quality guidance.

This review article is the first to present the state-of-the-art knowledge on hyphil-TrOCs in urban stormwater. We use the octanol–water partition coefficient (K_{OW} for neutral compounds) and the octanol–water distribution coefficient (D_{OW} for ionizable compounds) as approximate indicator of aquatic mobility[3] and focus predominantly on compounds with $\log K_{OW}$ or $\log D_{OW}$ values in the range of −1 to 4. This polarity range is well covered by reversed-phase liquid chromatography coupled to (high-resolution) mass spectrometry (LC-(HR)MS) which is the main analytical technique for the identification and quantification of hyphil-TrOCs in wastewater and stormwater.[3,12,38] We highlight challenges associated with sampling and monitoring strategies of hyphil-TrOCs and discuss sources of these chemicals in the urban environment. We compile concentrations of hyphil-TrOCs reported in urban stormwater runoff, storm sewer discharge, and combined sewer overflow (CSO), and present current findings on stormwater toxicity. Moreover, we point out that conventional stormwater best management practices (BMPs) such as detention basins, constructed wetlands, and biofilters often fail to remove hyphil-TrOCs. Next generation green infrastructure elements such as biofilters amended with reactive geomedia (e.g., metal oxides) or adsorbents (e.g., activated carbon or biochar) are discussed that show promise to effectively remove hyphil-TrOCs from urban stormwater.

2 Stormwater sampling and monitoring of hydrophilic TrOCs

Monitoring of hyphil-TrOCs in stormwater is essential to identify the need for stormwater treatment and to assess the efficiency of treatment measures.[39] The types and concentrations of hyphil-TrOCs present in urban stormwater can be highly variable over time and space and depend on various factors including intensity of the storm event, catchment characteristics, and application patterns of chemicals.

2.1 Metadata collection

The intensity of the storm event and the resulting volume of urban runoff impacts both the mobilization of hyphil-TrOCs from surfaces as well as their transport and spatio-temporal concentration patterns. In order to better understand the dynamics of hyphil-TrOC occurrence in samples collected during a storm event, the latter needs to be well characterized in terms of precipitation depth, duration, mean intensity over the rain event, and maximum intensity.[26] When reporting hyphil-TrOCs in CSO, the overflow volume, duration, average overflow rate and maximum flow rate should be reported in addition to storm-related information.[13]

Land use is a key driver affecting stormwater composition.[25,40] Therefore, the catchment of interest needs to be well characterized in terms of geography, total catchment area, impervious area, runoff coefficient, land-use type, land slope, and traffic (e.g., vehicles per day).[26,41,42] We identified 18 key peer-reviewed publications that report the occurrence of hyphil-TrOCs in urban surface runoff, separate storm sewers, and combined sewer overflows. Table 1 compiles metadata for the selected studies including country, catchment type and area, sampling site and period, number of storm events sampled, sampling method, as well as the number of analyzed and detected compounds. The catchments were characterized as urban, residential, commercial, or industrial (Table 1). The catchment areas varied significantly ranging from 1.3–100 000 ha. Data on hyphil-TrOC occurrence are mainly reported in stormwater conveyance pipes, storm sewer outlets, and CSO (Table 1). Samples collected at these locations contain hyphil-TrOCs washed off from the entire catchment, with the concentrations being diluted by the precipitation volume. A higher spatial resolution is warranted including sampling locations near sources of contamination in order to link the presence of hyphil-TrOCs in urban stormwater to land-use patterns or specific applications of chemicals. To date, studies investigating hyphil-TrOCs in stormwater collected close to the source (e.g., next to highways or recreational sites[43]) are scarce.

To assess seasonal trends of hyphil-TrOCs in urban stormwater and to better understand concentration dynamics within one storm event as well as in-between events, many studies sample multiple storm events at the same site over a period of several months to years (Table 1). The site-specific number of rain events sampled in the 18 peer-reviewed publications range from 1 to 24 (Table 1). Dry weather periods in between consecutive rain events require reporting[13,26] as chemicals may be predominantly applied during dry weather (e.g., urban-use pesticides) and accumulate on surfaces. Dry weather runoff, caused by e.g., extensive irrigation or car-washing, may reflect the seasonal use and application volume of chemicals that can be mobilized in the next storm event. However, few studies investigated hyphil-TrOCs in dry weather runoff[30,44,45] and their mobilization patterns in first flush and peak flows.

2.2 Stormwater sampling methods

Stormwater quantity and quality is highly variable over time and space and the concentration of hyphil-TrOCs and other pollutants varies within one single storm event as well as

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Table 1 Important peer-reviewed publications reporting the occurrence of hyphil-TrOCs in irrigation and surface runoff, separate storm sewers, and combined sewer overflow (CSO). Key metadata describe the catchment, sampling site and period, number of events sampled, sampling method, and total number of compounds analyzed and detected. Values in parentheses refer to the number of hyphil-TrOCs detected. Data are reported as measured concentrations (conc), event mean concentrations (EMC), annual loads (AL), or mass load per event (m_{event})

Source	Country	Catchment type	Catchment area (ha)	Sampling site	Sampling period	Number of storm events sampled	Sampling method	Number of compounds analyzed	Number of compounds detected	Data reporting
Irrigation runoff										
Gan et al.[44]	CA, USA	Residential	—	Storm drain outfall	July 2006–Dec 2008	DW[a] runoff	Grab	4	4	Conc
Surface runoff										
Wilkinson et al.[43]	England	Motorway	—	Street runoff	—	Various	Grab	13	7	Conc
Wilkinson et al.[43]	England	Recreational	—	Grass field drainage	—	Various	Grab	13	7	Conc
Regnery and Püttmann[56]	Germany	Urban	—	SW[b] holding tank	May 2008–Apr 2009	—	Grab	6	6	Conc
Separate sewer system										
Becouze-Lareure et al.[42]	France	Industrial	185	Storm sewer outlet	Mar 2008–Sept 2009	14	FW-AS[c]	34[d]	23[d] (6[e])	EMC
Gasperi et al.[26]	France	Residential	228	Catchment outlet	July 2011–May 2013	24	FW-AS[c]	77[d]	42–48[d] (9[e])	EMC
Gasperi et al.[26]	France	Residential	30	Catchment outlet	July 2011–May 2013	18	FW-AS[c]	77[d]	42–48[d] (8[e])	EMC
Gasperi et al.[26]	France	Industrial	185	Catchment outlet	July 2011–May 2013	7	FW-AS[c]	77[d]	42–48[d] (9[e])	EMC
Burant et al.[40]	WI, USA	Residential	8.5	Storm sewer	Apr–Aug 2016	13	FW-AS[c]	81[d]	34[d] (~27[e])	EMC
Burant et al.[40]	WI, USA	Commercial	18.4	Storm sewer	June–Sept 2016	11	FW-AS[c]	81[d]	30[d] (~27[e])	EMC
Ensminger et al.[57]	CA, USA	Residential	Various	Storm drain outfalls	Apr 2008–June 2011	15 (DS[f]), 13 (RE[g])	Grab & AS	64[d]	32[d] (~18[e])	Conc
Rippy et al.[58]	Australia	(Peri-)urban	Various	Storm drain outlets	2011–2014	Various	Grab & FW-AS[c]	27	19	Conc
Deffontis et al.[45]	France	Downtown	439	Storm sewer outlet	Jan 2010–Feb 2011	12 (DW[e]), 8 (RE[g])	TB-AS[h]	24[d]	~10[d] (~4[e])	Conc & AL
Deffontis et al.[45]	France	Residential	1428	Storm sewer outlet	Jan 2010–Feb 2011	12 (DW[e]), 8 (RE[g])	TB-AS[h]	24[d]	~9[d] (~2[e])	Conc & AL
Fairbairn et al.[12]	MN, USA	Industrial, residential, university	1380	SW[b] conveyance pipe	Feb–Sept 2016	4[i]	Grab	384[d]	123[d]	Conc
Fairbairn et al.[12]	MN, USA	Residential, industrial, commercial	789	SW[b] conveyance pipe	Feb–Sept 2016	4[i]	Grab	384[d]	123[d]	Conc
Fairbairn et al.[12]	MN, USA	Residential	187	SW[b] conveyance pipe	Feb–Sept 2016	4[i]	Grab	384[d]	123[d]	Conc
Masoner et al.[31]	USA[j]	Various[j]	10–100 000	Culverts, canals, channels	Aug 2016–Dec 2017	1–4 (50[j])	FW-AS[c] & TWC[k]	438[d]	215[d]	Conc, loads
Zgheib et al.[59]	France	Residential	261	Storm sewer outlet	Feb 2008–Mar 2009	10	AS	88[d]	55[d] (~10[e])	Conc
Zgheib et al.[59]	France	Urban	230	Storm sewer outlet	Feb 2008–Mar 2009	6	AS	88[d]	55[d] (~10[e])	Conc
Zgheib et al.[59]	France	Residential, commercial	130	Storm sewer outlet	Feb 2008–Mar 2009	4	AS	88[d]	55[d] (~10[e])	Conc
Beckers et al.[30]	Germany	Residential	—	Storm sewer	Apr 2015–Apr 2016	12 (DW[e]), 6 (RE[g])	AS[l]	149	67	Loads
Bollmann et al.[60]	Denmark	Residential	21.5	Storm sewer outlet	Oct 2011–June 2012	12	FW-AS[c]	11	11	m_{event}
Birch et al.[46]	Denmark	Various	1.3–60	Storm sewer	Oct 2008–Sept 2009	Various	Grab	>50[d]	~31[d] (~6[e])	Conc
Boyd et al.[61]	LA, USA	Urban	24 300	Stormwater canals	Feb–July 2003	8	Grab	9	3	Conc
Combined sewer system										
Becouze-Lareure et al.[42]	France	Residential	245	CSO	Mar 2008–June 2009	12	FW-AS[c]	34[d]	23[d] (6[e])	EMC
Birch et al.[46]	Denmark	Residential	1100	CSO	Sept 2008	1	Vol. prop.[m]	>50[d]	~27[d] (~5[e])	Conc
Phillips et al.[62]	VT, USA	Urban	—	CSO bypass flow	Nov 2007–Dec 2008	10	FWC[n]	89	18	Conc, loads
Launay et al.[13]	Germany	Urban	3500	CSO outfall	July–Oct 2014	7	AS	69[d]	60[d] (38[e])	EMC

[a] Dry weather. [b] Stormwater. [c] Flow-weighted automated sampling (AS). [d] Includes hyphil-TrOCs and other pollutants (e.g., metals, PAHs, other hydrophobic organic compounds). [e] Hyphil-TrOCs ($\log D_{OW} < 4$). [f] Dry season. [g] Rain event. [h] Time-based automated sampling. [i] Rain events. [j] 50 storm events sampled across 21 sites (each 1–4 events) in 17 US states. [k] Manually collected time-weighted composite. [l] Volume proportional under dry conditions; discharge proportional if discharge rate >30 L s^{-1}. [m] Volume proportional. [n] Flow-weighted composite.

between different storm events and different sampling locations.[46,47] Owing to rapid fluctuations in pollutant concentrations and loads, stormwater sampling is often associated with many sources of uncertainty and bias.[39] In principle, three different types of stormwater sampling methods are employed: (i) grab sampling, (ii) installation of automated samplers, and (iii) installation of passive samplers. Grab sampling is the most easy, cost-effective, and widely applied stormwater sampling strategy.[41,46] Eight out of the 18 peer-reviewed publications summarized in Table 1 are based on grab samples taken at a specific location and time. However, grab samples are often not representative of the spatial and temporal variability of hyphil-TrOC concentrations in water streams such as stormwater runoff, CSOs, or receiving water bodies.[12,46,48] Automated samplers provide time-weighted or flow-weighted sampling of stormwater at a specific location where samples are repeatedly collected at a pre-defined constant time interval or a constant incremental volume of discharge, respectively.[14] Autosamplers can be used to collect discrete stormwater samples or composite samples that consist of multiple discrete samples collected in a common container.[14] The sampling strategy depends on the objective of the sampling campaign, the regulatory requirements as well as logistic considerations and costs.[47] The collection of numerous discrete samples during a storm event can enable a higher temporal resolution of variabilities in stormwater quality but is often associated with significant costs for sample analyses.[14] Therefore, flow-weighted composite samples, that represent specific compositing periods, are often the method of choice.[14] Flow-proportional and volume-proportional sampling are the most representative stormwater sampling methods that allow the calculation of event mean concentrations (EMC) as discussed below.[46] A less accurate method is precipitation dependent sampling where a rain gauge determines when samples are taken.[46] Flow-weighted stormwater samples are commonly collected using autosamplers (Table 1).[14] However, automated stormwater sampling entails higher costs than grab sampling and is often associated with practical challenges (e.g., equipment installation and maintenance).[14,39,41]

In order to avoid high costs of automated samplers and transport of large sample volumes, passive samplers might be a promising and cost-effective technique for the monitoring of hyphil-TrOCs in stormwater.[39,49,50] Passive samplers have been developed for the monitoring of water quality in surface waters and sediments.[51–54] The basic principle is passive diffusion of organic chemicals from water into a sorbing material placed in the sampler device.[50] The mass sorbed is assumed to be in equilibrium with the time-averaged concentration in the water over the period of passive sampler deployment.[50] Page et al.[50] successfully deployed five different types of passive samplers for monitoring of hyphil-TrOCs in urban stormwater recycling systems that enabled the qualitative detection of a large number of individual chemicals. Moschet et al.[52] found that

styrenedivinylbenzene reverse phase sulfonate (SDB-RPS) disks covered by a polyether sulfone (PES) membrane are suited to qualitatively screen surface water for the presence of more than 300 hyphil-TrOCs. While compounds with relatively constant aqueous concentrations could be quantified accurately in the field, compounds with highly fluctuating aqueous concentrations were difficult to quantify with passive samplers.[52] Concentrations of hyphil-TrOCs in stormwater are highly variable and may complicate uptake kinetics as well as potential desorption. Mutzner et al.[49] confirmed that the quantification of hyphil-TrOCs with passive samplers is associated with uncertainty that needs to be assessed especially when sampling storm events or CSOs over a long duration. Still, SDB-RPS passive samplers provided a useful estimate of hyphil-TrOC concentrations in sewers and CSOs that can help to identify locations at which concentrations of hyphil-TrOCs comply with or exceed the environmental quality standards.[49,55] Birch et al.[39] discussed the limitation of conventional time-integrated passive samplers for highly dynamic stormwater discharges and proposed the use of velocity-dependent flow-through passive sampling that provides higher weighting of actual runoff events than no-flow periods. Thus, field evaluation of both time-integrated and velocity-dependent passive sampling for the assessment of hyphil-TrOCs in stormwater is warranted. To date, passive samplers cannot replace traditional stormwater sampling techniques that provide a more accurate quantification of TrOCs as well as higher temporal resolution.[55]

2.3 Hyphil-TrOC analyses and data reporting

Hyphil-TrOCs are predominantly analyzed using liquid-chromatography (high-resolution) mass spectrometry (LC-(HR)MS).[12,13,31,40,55] The majority of peer-reviewed publications screened stormwater for the occurrence of various compound classes with the number of analyzed individual contaminants ranging from four to 438 (Table 1). However, these numbers often entail more hydrophobic organic contaminants such as PAHs.[12,26,31,59] To date, Fairbairn et al.[12] and Masoner et al.[31] have screened urban stormwater for the broadest suite of organic contaminants including pesticides, pharmaceuticals, and wastewater indicator compounds. Fairbairn et al.[12] detected 123 out of 384 analytes in stormwater with the median and maximum number of organic contaminants in individual samples being 35 and 54, respectively. Masoner et al.[31] conducted a study across the United States and screened 50 stormwater samples collected at 21 sites in 17 states for the occurrence of 438 organic chemicals of which 215 were detected at least once. The median and maximum number of analytes detected in individual samples was 73 and 103, respectively.[31]

The occurrence of hyphil-TrOCs and other stormwater contaminants is often reported as median or mean concentration derived from the analysis of samples collected during single or multiple rain events at one location (see

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Table 1). The measured hyphil-TrOC concentration in a sample can be used to calculate the mass load per storm event (m_{event}) as shown in eqn (1).

$$m_{\mathrm{event}} = \sum_{i=1}^{n} c_i \times V_i \qquad (1)$$

where n is the total number of samples collected during one particular storm event, i is the sample number, c_i is the measured concentration in sample i, and V_i is the measured discharge volume of stormwater corresponding to sample i.[14,41] Dividing the total mass of pollutant per storm event (m_{event}) by the total volume of stormwater (V_i) during that event provides the event mean concentration (EMC) as shown in eqn (2).[14,41]

$$\mathrm{EMC} = \frac{\sum_{i=1}^{n} c_i \times V_i}{\sum_{i=1}^{n} V_i} \qquad (2)$$

Site mean concentrations (SMCs) for a specific sampling site can be calculated using the EMCs and event volumes as shown in eqn (3).[41]

$$\mathrm{SMC} = \frac{\sum_{j=1}^{p} \mathrm{EMC}_j \times V_j}{\sum_{j=1}^{p} V_j} \qquad (3)$$

where p is the number of measured storm events, EMC_j is the event mean concentration of storm event j, and V_j is the measured discharge volume during event j.[41] McCarthy et al.[41] evaluated various random and fixed sampling strategies (i.e., randomly collecting few samples within one event to represent this event versus taking samples at prescribed periods during the event) for the estimation of SMCs of TSS, total nitrogen, and Escherichia coli through monitoring of multiple storm events. They found that random sampling strategies can reproduce SMCs for TSS and total nitrogen and that collection of only one random sample per event is sufficient, although a large number of storm events needs to be sampled (on average 27 events for characterizing SMCs of TSS).[41] Similar studies investigating sampling strategies for the assessment of SMCs of hyphil-TrOCs are needed to determine the most effective and cost-efficient sampling strategy that can inform stormwater management decisions.

3 Sources and occurrence of hydrophilic TrOCs in urban stormwater

Hyphil-TrOCs are ubiquitous in urban stormwater but their sources are often difficult to elucidate. In the following section, we reflect on our current understanding of the occurrence of hyphil-TrOCs in urban stormwater runoff and discuss storm-related input pathways into surface waters and groundwater. As depicted in Fig. 1, hyphil-TrOCs have been detected in precipitation, they can leach from building materials, or are washed off from green spaces or motorways. Hyphil-TrOCs can then enter receiving water bodies through
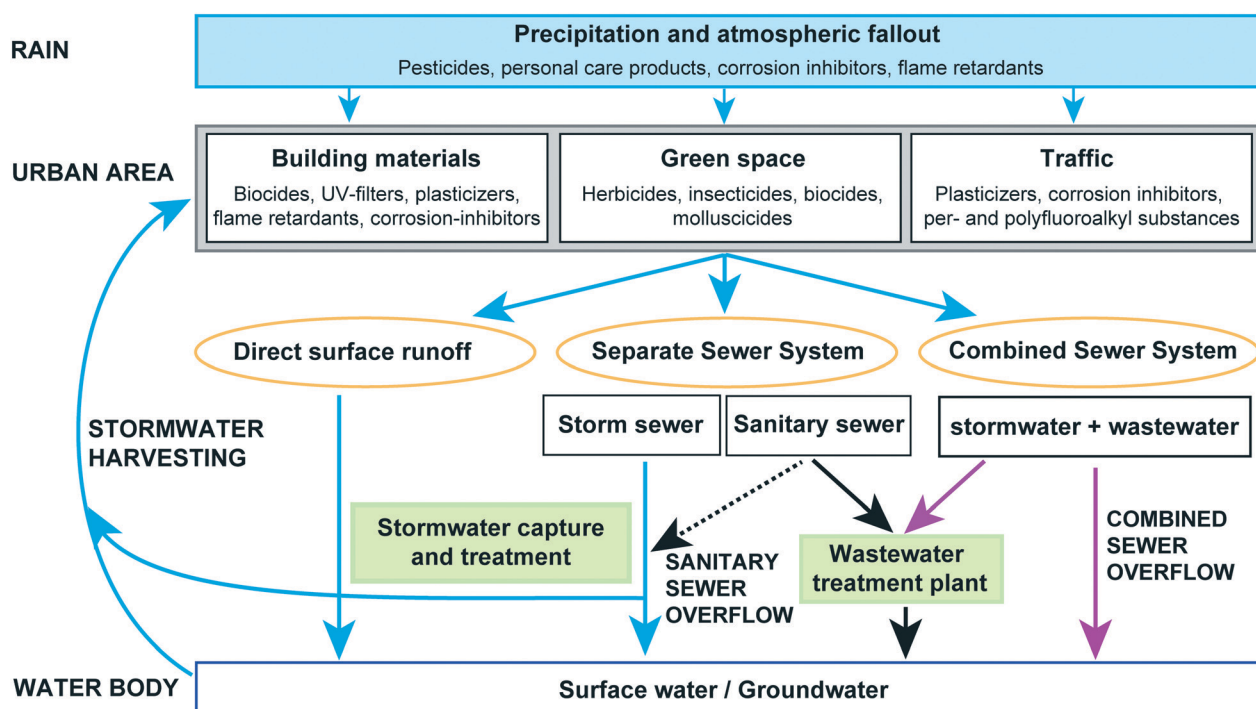

Fig. 1 Sources of hydrophilic trace organic contaminants (hyphil-TrOCs) in urban stormwater and input paths of stormwater- and wastewater-derived hyphil-TrOCs into receiving waters. Stormwater harvesting for the urban water supply requires stormwater capture and treatment technologies.

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(i) direct surface runoff, (ii) separate storm sewer discharge, or (iii) CSO.

3.1 Precipitation and atmospheric fallout

Knowledge on the occurrence of hyphil-TrOCs in precipitation and atmospheric fallout is scarce. Few studies report the presence of hyphil-TrOCs in rain water,[63–65] snow,[64,65] and atmospheric fallout.[26,64] Asman et al.[63] collected rain water in Denmark and found various pesticides including atrazine and isoproturon with maximum concentrations of 15 ng L^{-1} and 71 ng L^{-1}, respectively. Certain pesticides (e.g., atrazine and 2,4-D) were detected in rain even though they were not sold in Denmark.[63] Atmospheric transport distances for atrazine and 2,4-D were estimated as >280 km and >60 km, respectively.[63] Atmospheric transport and deposition of agricultural-use pesticides such as atrazine in urban areas has been reported elsewhere.[40] Ferrey et al.[64] analyzed atmospheric aerosol, rain, and snow for the presence of 126 pharmaceuticals, personal care products, and other hyphil-TrOCs. Only a few compounds were detected (seven in air, eight in rain, and ten in snow) and the concentration levels were low.[64] N,N-Diethyl-m-toluamide (DEET) and benzothiazole were detected in rain with concentrations up to 14.5 ng L^{-1} and 70 ng L^{-1}, respectively.[64] BPA, 4- and 5-methyl-1H-benzotriazole, caffeine, ciprofloxacin, sulfamethoxazole, perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) were found in trace concentrations.[64,65] In Germany and the US, organophosphorus flame retardants (OPs) have been detected in rain and snow samples with tris(2-chloro-1-methylethyl) phosphate (TCPP) being the most frequently detected species with concentrations up to 2659 ng L^{-1}.[56,66,67] Concentrations of OPs were significantly higher in urban than in rural precipitation indicating urban emissions to the atmosphere.[56] Gasperi et al.[26] determined organic contaminants in total atmospheric fallout that was collected on rooftops in three catchments in France. The contribution of total atmospheric fallout to the concentrations measured in stormwater from the catchment outlet was very low (<10% for BPA) indicating that atmospheric fallout is a minor contributor.[26] Sources of hyphil-TrOCs in air and precipitation are likely traffic, buildings, manufacturing facilities, wastewater treatment plants, and anthropogenic activities.[56,64,66] However, little is known about atmospheric transport, fate and wet deposition of hyphil-TrOCs.

3.2 Structural materials and pest control

Building materials have been identified as major contributors to the occurrence of hyphil-TrOCs in stormwater. Building paints and coatings, plastics, and concrete contain numerous chemicals including biocides, flame retardants, UV-filters, corrosion inhibitors, and plasticizers that can be released and washed off during storm events.[68] Biocides are the most frequently studied class of TrOCs leaching from construction materials.

Biocides in materials are used to prevent the growth of fungi, algae, and bacteria e.g., on building façades or roofs. Commonly used biocides are triazines and phenylurea compounds as algaecides, isothiazolinones as bactericides, and carbamates as fungicides.[60] To prevent growth of algae and fungi on façades, paints, coatings, and film preservatives often contain a mixture of three to eight different biocides with concentrations in the range of 0.1–2.0 g kg^{-1}.[69,68]

Terbutryn, diuron, carbendazim, and irgarol 1051 are among the most frequently found and most persistent biocides in paints and renders.[68,69] Other active ingredients are isothiazolinones and zinc pyrithione.[69] Mecoprop is commonly used as root protection agent in bitumen sheets for water proofing.[68–70]

Burkhardt et al.[68] investigated leaching of seven biocides from roofs, car parks, and façades of residential and commercial buildings in an urban catchment in Switzerland. Stormwater samples contained carbendazim and terbutryn at concentrations of up to a few hundred ng L^{-1}.[68] Much higher concentrations (in the range of 2 μg L^{-1}) were found for mecoprop that stemmed from root resistant sealing membranes in foundations and from green roofs of underground parking.[68] Bollmann et al.[60] analyzed 191 stormwater samples from 12 rain events in Denmark for 11 target biocides. Carbendazim and terbutryn were detected in all analyzed samples with high median concentrations of 45 ng L^{-1} and 52 ng L^{-1}, respectively (Table 2).[60] Diuron, isoproturon, propiconazole, mecoprop, and iodocarb were frequently detected with significantly lower median concentrations of 2–7 ng L^{-1}.[60]

Biocides in stormwater show complex concentration patterns that depend on multiple factors such as rainfall intensity and duration, façade orientation, wind direction and speed, age of the building materials, dilution of the biocide load along the water pathway, and persistence of the biocides.[68,71] Burkhardt et al.[68] found that biocide concentrations measured in runoff from new buildings were at least 1000-times higher than for aged buildings. Laboratory leaching experiments showed that biocides from render were mobilized at the very beginning of simulated rain events showing that even short rain events can lead to significant loads in runoff.[68] Biocides did not follow a typical first flush model, but were continuously released from the materials due to an underlying diffusion mechanism[68,72] or a solubility or partition controlled release mechanism.[71] This is in contrast to many conventional stormwater pollutants such as TSS that are transported according to the first-flush phenomenon i.e., 80% of the total pollutant mass is transported in the first 30% of volume discharge during storm events.[73]

Different pesticides are applied for structural pest control, i.e., the protection of buildings and other structures from pests of which some can carry and transmit diseases. Common active ingredients against ants and termites are the phenylpyrazole insecticide fipronil and the neonicotinoid insecticide imidacloprid, which were both detected with high

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Table 2 Concentrations and detection frequencies of biocides, insecticides, and herbicides in dry weather runoff (DWR), street runoff (SRO), stormwater from separate sewer systems (SW), and combined sewer overflow (CSO) in different countries. For reference, we show long-term environmental quality standards expressed as annual average concentration (AA-EQS) and short-term environmental quality standards expressed as maximum allowable concentration (MAC-EQS) for priority substances in inland surface waters as proposed by the EU Water Framework Directive.[107] For compounds not yet under EU regulation, we report chronic and acute quality standards proposed by the Swiss Ecotox Center (*).[108]

Contaminant group	Compound	AA-/MAC-EQSs ($\mu g\ L^{-1}$)	Median conc ($\mu g\ L^{-1}$)	Concentration range ($\mu g\ L^{-1}$)	Country	Sample type	Detection frequency	Source
Biocides	Carbendazim	0.44*/0.7*	0.045	0.306[a]	Denmark	SW	—	Bollmann et al.[60]
			0.701	0.0098–9.58	USA	SW	94%	Masoner et al.[31]
	Terbutryn	0.065/0.34	0.052	1.84[a]	Denmark	SW	—	Bollmann et al.[60]
			0.059[b]	0.317[a,b]	Germany	SW	100%[b]	Beckers et al.[30]
			0.083	0.055–0.122	Germany	CSO	—	Launay et al.[13]
Insecticides	Dimethoate	0.07*/0.98*	0.0056[b]	5.16[a,b]	Germany	SW	94%[b]	Beckers et al.[30]
	Diazinon	0.012*/0.02*	0.80	1.1[a]	CA, USA	SW	100%	Kratzer[109]
	Fipronil	—	0.033[c]; 0.076[d]	—	CA, USA	SW	51%[c]; 83%[d]	Budd et al.[74]
			0.0031–0.131	2.05[a,c]; 10.0[a,d]	CA, USA	DWR	66–100%	Gan et al.[44]
	Imidacloprid	0.013*/0.1*	0.013	0.0054–0.428	WI, USA	SW	100%	Burant et al.[40]
			0.023	0.0049–0.331	USA	SW	86%	Masoner et al.[31]
			0.05 (DS[e])	0.16[a] (DS[e])	CA, USA	SW	50%	Ensminger et al.[57]
			<RL[f] (SE[g])	0.67[a] (SE[g])	CA, USA	SW	51%	Ensminger et al.[57]
Herbicides	2,4-D	0.6*/4*	0.008–2.0[h]	—	Australia	SW	100%[b]	Rippy et al.[58]
			0.39	11.6[a]	MN, USA	SW	100%	Fairbairn et al.[12]
			0.08 (DS[e])	11.5[a] (DS[e])	CA, USA	SW	84%	Ensminger et al.[57]
			0.28 (SE[g])	10.4[a] (SE[g])	CA, USA	SW	66%	Ensminger et al.[57]
			0.47	0.095–2.87	WI, USA	SW	100%	Burant et al.[40]
	Atrazine	0.6/2.0	0.006–0.624[h]	—	Australia	SW	70%[b]	Rippy et al.[58]
			0.040	0.787[a]	MN, USA	SW	100%	Fairbairn et al.[12]
	Dicamba	2.2*/52*	0.01–0.241[h]	—	Australia	SW	60%[b]	Rippy et al.[58]
			<RL[f] (DS[e])	3.1[a] (DS[e])	CA, USA	SW	69%	Ensminger et al.[57]
			0.06 (SE[g])	1.2[a] (SE[g])	CA, USA	SW	42%	Ensminger et al.[57]
	Diuron	0.2/1.8	1.34[h]	0.08–10.78	CA, USA	SRO	—	Huang et al.[110]
		0.07*/0.25*	0.37	0.03–1.75	France	SW	100%	Zgheib et al.[59]
			1.213[h]	0.025–0.795	France	SW	71–100%	Gasperi et al.[26]
			0.009–0.895[h]	—	Australia	SW	90%[b]	Rippy et al.[58]
			0.020[b]	0.107[a,b]	Germany	SW	100%[b]	Beckers et al.[30]
			0.0077	0.0045–0.014	WI, USA	SW	100%	Burant et al.[40]
			0.019[h]	—	France	SW	100%	Becouze-Lareure et al.[42]
			0.072[h]	—	France	CSO	100%	Becouze-Lareure et al.[42]
			0.26	0.068–0.68	Germany	CSO	—	Launay et al.[13]
	Glyphosate	120*/360*	2.69[h]	1.36–9.44	CA, USA	SRO	—	Huang et al.[110]
			—	0.043–1.2	Denmark	SW	100%	Birch et al.[46]
			1.11	<0.03–232	France	SW	93%	Zgheib et al.[59]
			0.337[h]	0.095–0.198	France	SW	40–75%	Gasperi et al.[26]
	Isoproturon	0.3/1.0	0.09	0.05–0.2	Germany	SRO	—	Stachel et al.[89]
			0.088[h]	0.003–0.053	France	SW	29–100%	Gasperi et al.[26]
	Mecoprop	3.6*/190*	0.041[b]	0.103[a,b]	Germany	SW	100%[b]	Beckers et al.[30]
			0.151	0.031–1.062	WI, USA	SW	100%	Burant et al.[40]
			0.140	0.100–0.378	Germany	CSO	—	Launay et al.[13]
	Metolachlor	0.69*/3.3*	0.0179	0.489[a]	MN, USA	SW	81%	Fairbairn et al.[12]
	Oryzalin	—	11.41[h]	9.40–43.13	CA, USA	SRO	—	Huang et al.[110]
			0.155	0.018–1.186	WI, USA	SW	100%	Burant et al.[40]
	Simazine	1/4	0.13	0.24[a]	CA, USA	SW	100%	Kratzer[109]
			0.0375[h]	—	France	SW	100%	Becouze-Lareure et al.[42]
			0.0017[h]	—	France	CSO	100%	Becouze-Lareure et al.[42]
	Triclopyr	—	0.010–0.31[h]	—	Australia	SW	80%[b]	Rippy et al.[58]
			0.06 (DS[e])	1.5[a] (DS[e])	CA, USA	SW	40%	Ensminger et al.[57]
			0.13 (SE[g])	6.8[a] (SE[g])	CA, USA	SW	64%	Ensminger et al.[57]

[a] Reported maximum concentration. [b] Calculated from data in the respective supporting information. [c] Northern CA. [d] Southern CA. [e] DS = dry season. [f] Reporting limit. [g] SE = storm event. [h] Mean value.

frequency in urban stormwater (Table 2).[40,57,74] Anticoagulant rodenticides such as bromadiolone, warfarin, and chlorophacinone are commonly applied to control mice and rats.[75] One of the main applications of rodenticides in the urban environment is rodent control in sewer systems.[75] Yet, anticoagulant rodenticides remain poorly studied in urban stormwater discharges and CSOs.[75] While professional applicators are trained to minimize the release of pesticides into the environment by controlling application type, volume, and period, diffuse release of active ingredients as well as

mishandling of chemicals (*e.g.*, application shortly before rain events) can lead to increased pesticide concentrations in stormwater.

3.3 Urban green space

Urban green spaces such as gardens, parks, lawns, sports grounds, graveyards, and right of ways can be a source of herbicides, insecticides, fungicides, algaecides, molluscicides, and rodenticides to stormwater. While pesticides in surface and groundwater are believed to predominantly stem from agriculture, urban pesticides have been shown to contribute to the impairment of water quality.[76,77] However, information on the types and volumes of pesticides applied in urban areas is often lacking.[76] While agricultural pesticide application and urban pesticide use by licensed applicators can be assessed (*e.g.*, in California), private use by households or owners of public or commercial properties is usually not reported. The California Department of Pesticide Regulation conducted a survey of pesticide products sold in retail stores in Northern California and found a total of 593 products with 168 active ingredients including 2,4-D, glyphosate, dicamba, and triclopyr.[78] Interestingly, diuron and fipronil, which are often found in stormwater runoff, were absent in outdoor use products for residents, indicating that certain pesticides may be predominantly used by licensed applicators.[78] While pesticide tracking through point-of-sale data is a first step to assess urban pesticide usage, it does not provide temporal and geographic resolution of actual application patterns and resulting pesticide concentrations in stormwater.[79]

Few studies investigate the occurrence of pesticides and other hyphil-TrOCs in runoff from urban green spaces both during rain events as well as during dry periods with extensive irrigation. Gan *et al.*[44] compared the occurrence of fipronil and its metabolites in dry weather urban residential runoff collected in Southern California (Orange County, US) and Northern California (Sacramento, US). Fipronil is used in a variety of products against pests on horticultural crops, lawns, and golf courses. Fipronil is also the active ingredient in flea and tick control sprays for dogs and cats and is frequently applied for structural pest control as discussed above. Median concentrations of fipronil in dry weather runoff were 3.1–5.6 ng L^{-1} and 79–131 ng L^{-1} in Northern and Southern CA, respectively, reflecting more frequent and long-term usage of this insecticide in the south.[44] This in accordance with a survey of storm drains in which fipronil was detected at median concentrations of 33 ng L^{-1} in Northern California and 76 ng L^{-1} in Southern California (Table 2).[74] Fipronil concentrations followed seasonal trends reflecting heavier use of fipronil from spring to fall.[44] Lower fipronil concentrations in the winter season is likely due to lower applications from October to March and dilution effects during the rainy season.[44]

Urban green spaces with a stagnant or shallow pool of water (*e.g.*, rain barrels, stormwater retention ponds,

stormwater catch basins, and storm drains), can be potential mosquito breeding habitats. Hyphil-TrOCs applied for mosquito control include malathion, carbaryl, and imidacloprid. Neonicotinoids such as imidacloprid are among the most popular insecticides in the world to control a wide range of pests and disease vectors in soils, plants, and sewer systems. In California, imidacloprid was frequently found in storm drain outfalls and surface waters with maximum concentrations of 160 ng L^{-1} during the dry season and 670 ng L^{-1} during the rainy season (Table 2).[57] After rain events, imidacloprid was detected at particularly high concentrations up to 1462 ng L^{-1} in an urban creek in California.[80] Imidacloprid was also present in a Californian residential stormwater pond.[81]

In addition to pesticides, other chemicals can leach from urban green spaces but are much less studied. For instance, samples collected during rainfall from a grass field drainage in England contained bisphenol A (BPA) and bisphenol S (BPS) in the range of 100 ng L^{-1} (Table 3).[43] Moreover, litter (packaging or cigarette butts) can contribute to hyphil-TrOC concentrations in urban stormwater runoff.[12] Only one cigarette butt in 1 m^3 of water may lead to nicotine concentrations above the predicted no effect concentration (2.4 μg L^{-1}).[82]

3.4 Traffic

Street runoff is known to carry significant concentrations of per- and polyfluoroalkyl substances (PFASs).[43,83] PFASs are frequently detected in the environment and include perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) used in fluoropolymers such as Teflon, and perfluorooctane sulfonate (PFOS) a fluorosurfactant used in stain repellents and fire-fighting foams.[84] PFASs are persistent in the environment, difficult to remove in water treatment, and pose a health risk to biota and humans.[85] Concentrations of PFASs are usually <100 ng L^{-1} in surface waters but high levels of PFOA up to 3640 ng L^{-1} have been reported in a German river.[86] Street runoff and urban stormwater are reported to contain high levels of PFOA, PFOS, and PFNA with concentrations being as high as 1160 ng L^{-1},[43] 50 ng L^{-1},[83] and 648 ng L^{-1},[43] respectively (Table 3). These PFNA and PFOA concentrations were 3.0 and 8.5 times higher in street runoff than in wastewater treatment plant effluent.[43] Zushi and Masunaga[87] reported elevated PFAS concentrations in urban runoff from catchments with transport-related land use, especially in the presence of train stations. Thus, stormwater runoff from streets or other transportation-related structures can be a significant non-point source of PFASs in receiving waters.[43,65,83,88]

Street runoff may also show high levels of the plasticizers bisphenol A (BPA) and bisphenol S (BPS).[43,89] BPA and BPS are high production volume chemicals used in the production of plastic materials, epoxy resins, food packaging and many other products. BPA is frequently detected in surface waters with median and maximum concentrations of

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Table 3 Concentrations and detection frequencies of per- and polyfluoroalkyl substances (PFASs), plasticizers, corrosion inhibitors, and organophosphates in street runoff (SRO), field drainage (FD), stormwater from separate sewer systems (SW), and combined sewer overflow (CSO) in different countries. For reference, we show long-term environmental quality standards expressed as annual average concentration (AA-EQS) and short-term environmental quality standards expressed as maximum allowable concentration (MAC-EQS) for priority substances in inland surface waters as proposed by the EU Water Framework Directive.[107] For compounds not yet under EU regulation, we report chronic and acute quality standards proposed by the Swiss Ecotox Center (*).[108]

Contaminant group	Compound	AA-/MAC-EQSs ($\mu g\ L^{-1}$)	Median conc ($\mu g\ L^{-1}$)	Concentration range ($\mu g\ L^{-1}$)	Country	Sample type	Detection frequency	Source
PFASs	PFOA	—	—	0.0065–1.16	England	SRO	100%	Wilkinson et al.[43]
			0.087[a,b]	0.017–0.174	Japan	SRO	60%[b]	Murakami et al.[83]
			0.0038	0.00051–0.029	NY, USA	SRO, SW	100%	Kim and Kannan[65]
			0.0073	0.0023–0.0157	CA, USA	SW	100%	Houtz and Sedlak[88]
	PFOS	0.00065/36	—	0.0090	England	SRO	50%	Wilkinson et al.[43]
			0.0105[a,b]	0.0029–0.050	Japan	SRO	100%[b]	Murakami et al.[83]
			0.00081	0.0146[c]	NY, USA	SRO, SW	93%[b]	Kim and Kannan[65]
			0.015	0.0026–0.0263	CA, USA	SW	100%	Houtz and Sedlak[88]
	PFNA	—	—	0.0692–0.648	England	SRO	100%	Wilkinson et al.[43]
			0.030[a,b]	0.0047–0.070	Japan	SRO	50%[b]	Murakami et al.[83]
			0.00071	0.0059[c]	NY, USA	SRO, SW	93%[b]	Kim and Kannan[65]
			—	0.0003–0.0038	CA, USA	SW	100%	Houtz and Sedlak[88]
Plasticizers	BPA	0.24*/53*	—	0.0456–0.101	England	FD	100%	Wilkinson et al.[43]
			—	0.511–2.41	England	SRO	100%	Wilkinson et al.[43]
			1.4	0.24–2.5	Germany	SRO	—	Stachel et al.[89]
			0.412	0.234–0.964	France	SRO	—	Flanagan et al.[111]
			0.552[a]	0.207–0.817	France	SW	>80%	Gasperi et al.[26]
			0.056	0.158[c]	LA, USA	SW	100%	Boyd et al.[61]
			0.263	2.77[c]	USA	SW	90%	Masoner et al.[31]
			—	0.85–16.8	Sweden	SW	100%	Kalmykova et al.[112]
			—	0.20	Australia	SW	—	Tang et al.[113]
			0.321	0.140–0.400	Germany	CSO	—	Launay et al.[13]
	BPS	—	—	0.00227–0.159	England	FD	100%	Wilkinson et al.[43]
			—	0.0406–0.0502	England	SRO	100%	Wilkinson et al.[43]
Corrosion inhibitors	1H-BT	19*/160*	0.36	0.075–1.906	WI, USA	SW	100%	Burant et al.[40]
			0.403[b]	2.65[b,c]	Germany	SW	100%[b]	Beckers et al.[30]
			0.727	0.358–1.793	Germany	CSO	—	Launay et al.[13]
	Methyl-1H-BT	20*/430*	0.806	5.55[c]	MN, USA	SW	100%	Fairbairn et al.[12]
			0.861	6.79[c]	USA	SW	92%	Masoner et al.[31]
	5-MeBT	—	0.135	13.4[c]	MN, USA	SW	56%	Fairbairn et al.[12]
			0.285	0.190–1.058	Germany	CSO	—	Launay et al.[13]
	Benzothiazole	240*/250*	—	1.210[c]	RI, USA	SRO	100%	Reddy and Quinn[94]
			0.410	0.282–1.037	Germany	CSO	—	Launay et al.[13]
	Benzo. sulf.[d]	—	—	55[c]	Germany	SRO	—	Kloepfer et al.[95]
Organophosphates	TCEP	—	0.077	0.033–0.275	Germany	SRO	100%	Regnery and Püttmann[56]
			0.431	0.056–0.660	WI, USA	SW	100%	Burant et al.[40]
			0.270	0.041–0.340	Germany	CSO	—	Launay et al.[13]
	TCPP	—	0.880	0.016–5.79	Germany	SRO	100%	Regnery and Püttmann[56]
			0.854	0.275–2.074	WI, USA	SW	100%	Burant et al.[40]
			0.692	0.516–2.700	Germany	CSO	—	Launay et al.[13]
	TBEP	—	0.077	1.616[c]	Germany	SRO	—	Regnery and Püttmann[56]
			0.055	5.93[c]	MN, USA	SW	50%	Fairbairn et al.[12]
			1.060	2.750[c]	WI, USA	SW	54%	Burant et al.[40]
			1.300	0.078–4.100	Germany	CSO	—	Launay et al.[13]
	TiBP	—	0.117	0.002–1.478	Germany	SRO	100%	Regnery and Püttmann[56]

[a] Mean value. [b] Calculated from data in the respective supporting information. [c] Reported maximum concentration. [d] Benzothiazole-2-sulfonate.

140 and 12 000 ng L^{-1}, respectively.[90] BPA and BPS have been detected in street runoff in England with concentrations as high as 2410 ng L^{-1} and 50 ng L^{-1}, respectively (Table 3).[43] The concentration of BPA in street runoff was 2.7 times higher than the highest BPA levels in wastewater treatment plant effluents.[43] Similar findings were made in Germany where median and maximum BPA concentrations in highway runoff were in the range of 1400 ng L^{-1} and 2500 ng L^{-1}, respectively (Table 3).[89] Urban groundwater in Germany was found to contain comparable or even higher BPA concentrations than wastewater treatment plant effluents what is likely due to urban stormwater infiltration.[37]

1H-Benzotriazole (1H-BT), 4-methyl-1H-benzotriazole (4-MeBT), and 5-methyl-1H-benzotriazole (5-MeBT) are corrosion inhibitors that are widely used in aircraft deicing and antiicing fluids, cooling and brake fluids, and dishwasher detergents.[91] Cancilla et al.[92] analyzed stormwater runoff from a US airport during a deicer

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application event and found remarkably high concentrations of up to 1.67 mg L^{-1} and 2.16 mg L^{-1} of 4-MeBT and 5-MeBT, respectively. While airports and wastewater treatment plant effluents are believed to be the main sources of benzotriazoles to the environment, vehicular emissions can also contribute to their loads in surface waters.[93] During rain events and snowmelt, 1H-BT, 4-MeBT, and 5-MeBT were detected in two Canadian stormwater-fed creeks that were not impacted by wastewater treatment plant effluents.[93] Total time-weighted average benzotriazole concentrations were 1.3–110 times higher in a creek located in a highly urbanized watershed (up to approximately 1800 ng L^{-1}) compared to a creek in an agricultural, suburban watershed (up to approximately 280 ng L^{-1}).[93] Vehicle fluids are likely a main source of benzotriazoles in both watersheds with heavy vehicle traffic leading to elevated baseflow concentrations.[93]

Street runoff can also contain benzothiazoles which are used as corrosion-inhibitors in antifreeze liquids and as vulcanization accelerators in rubber production.[94–96] Tire abrasion from roads is a known stormwater-related input pathway of benzothiazoles into surface waters.[94] The total concentration of five benzothiazoles in German street runoff was in the range of 20–74 μg L^{-1} which was about 1 order of magnitude higher than concentrations found in untreated municipal wastewater.[95] Benzothiazole-2-sulfonate accounted for 60% of the total benzothiazole concentration and 2-hydroxybenzothiazole and benzothiazole for 25–30% and 8–13%, respectively.[95]

Traffic-impacted stormwater runoff can contain numerous other hyphil-TrOCs such as organophosphate (OP) flame retardants. Six OP flame retardants were detected in urban surface runoff in Germany with TCPP exhibiting highest concentration levels (median and maximum concentrations of 0.88 μg L^{-1} and 5.79 μg L^{-1}, respectively).[56] Also frequently detected were tris(2-chloroethyl) phosphate (TCEP, up to 0.275 μg L^{-1}), tri-iso-butyl phosphate (TiBP, up to 1.478 μg L^{-1}), and tris(2-butoxyethyl) phosphate (TBEP, up to 1.616 μg L^{-1}, Table 3).[56]

3.5 Sanitary sewer overflow

The occurrence of hyphil-TrOCs in urban stormwater has been predominantly studied in separate sewer systems (Table 1) in which storm sewers drain untreated urban stormwater into surface waters. Even though stormwater and sewage are conveyed in separate conduits, frequent detection of wastewater-derived hyphil-TrOCs in storm drains (e.g., lifestyle compounds, pharmaceuticals, and personal care products) indicate intrusion of raw sewage.[12,31,40,61] For instance, Burant et al.[40] found the wastewater indicator caffeine in all samples collected at storm sewer outlets in a residential and commercial area. Masoner et al.[31] frequently detected the prescription pharmaceutical metformin in urban stormwater. Sewage can enter storm sewers through (i) illicit connections of sewage pipes to storm sewers, (ii) sanitary sewer overflow (SSO), and (iii) cross-flow between sanitary and storm systems

due to broken sewer pipes.[12,30] Illicit connections are a continuous source of wastewater into storm drains and can lead to discharge of raw sewage also during dry weather conditions.[30] SSOs can be caused by blockage of the sanitary sewer or stormwater entering sewer lines. SSO causes raw sewage to overflow onto streets where it can intrude into storm sewers. Many sewer connections have been installed decades ago and a lack of repair or renewal can lead to leakages. Raw sewage has been found to contaminate stormwater drainage and receiving water bodies in the city of New Orleans (USA) due to aging infrastructure.[61] In two stormwater canals, pharmaceuticals (naproxen, ibuprofen) and endocrine disrupting chemicals (BPA) were present with maximum concentrations in the range of several hundred ng L^{-1} (Tables 3 and 4).[61] Wastewater-derived compounds from low-flow sources such as leaky sanitary systems have been observed to display greater concentrations in winter.[12]

Wastewater-associated contaminants may serve as indicator for human waste in separate storm sewers.[61,97,98] Sauvé et al.[98] found that caffeine concentrations of >400 ng L^{-1} were indicative of coliform counts >200 colony-forming units per 100 mL of water. As shown in Table 4, median caffeine concentrations reported in separate storm sewers in the US and Canada range from 0.207–1.07 μg L^{-1} with maximum concentrations up to 53 μg L^{-1} indicating a widespread and often overlooked impact of sewage intrusion into storm sewers.[12,31,40,98] However, the use of hyphil-TrOCs as indicator for fecal contamination in stormwater has limitations and should be carefully employed because fecal contamination can be also present in the absence of anthropogenic contaminants, e.g., when stemming from encampments or agriculture.[98]

3.6 Hyphil-TrOC mixtures in separate storm sewers

Urban storm sewer discharges can contain complex mixtures of hundreds of individual chemicals stemming from the many sources discussed above. Fairbairn et al.[12] collected 36 grab samples from stormwater conveyance pipes in the US and screened them for the occurrence of 384 organic contaminants of which 123 different individual compounds were detected (Table 1). 31 compounds were found with a frequency of ≥50% and 8 compounds with a frequency of ≥90%.[12] Most frequently detected were the herbicides 2,4-D (median concentration 0.390 μg L^{-1}) and atrazine (0.040 μg L^{-1}), the corrosion inhibitor methyl-1H-benzotriazole (methyl-1H-BT, 0.806 μg L^{-1}), the insect repellent DEET (0.120 μg L^{-1}), and the lifestyle compounds nicotine (0.205 μg L^{-1}) and caffeine (0.207 μg L^{-1}) (see Tables 2–4).[12] Masoner et al.[31] screened 50 stormwater samples collected across the US for the occurrence of 438 different organic chemicals of which 215 were detected (Table 1). 69 compounds were frequently detected in ≥50% of the samples.[31] Among the most pervasive hyphil-TrOCs were DEET, nicotine, caffeine, carbendazim, and methyl-1H-benzotriazole which is consistent with the findings of Fairbairn et al.[12,31]

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Table 4 Concentrations and detection frequencies of personal care products, artificial sweeteners, pharmaceuticals, lifestyle compounds, and transformation products in dry weather runoff (DWR), stormwater from separate sewer systems (SW), and combined sewer overflow (CSO) in different countries. For reference, we show long-term environmental quality standards expressed as annual average concentration (AA-EQS) and short-term environmental quality standards expressed as maximum allowable concentration (MAC-EQS) for priority substances in inland surface waters as proposed by the EU Water Framework Directive.[107] For compounds not yet under EU regulation, we report chronic and acute quality standards proposed by the Swiss Ecotox Center (*).[108]

Contaminant group	Compound	AA-/MAC-EQSs ($\mu g\ L^{-1}$)	Median conc ($\mu g\ L^{-1}$)	Concentration range ($\mu g\ L^{-1}$)	Country	Sample type	Detection frequency	Source
Personal care products	DEET[a]	88*/410*	0.12	0.49[b]	MN, USA	SW	97%	Fairbairn et al.[12]
			—	0.11	Australia	SW	—	Tang et al.[113]
			0.078	0.013–0.114	Germany	CSO	—	Launay et al.[13]
Artificial sweeteners	Acesulfame	—	2.370[c]	19.9[b,c]	Germany	SW	100%[c]	Beckers et al.[30]
			3.200	0.812–5.314	Germany	CSO	—	Launay et al.[13]
	Cyclamate	—	3.1[c]	32.3[b,c]	Germany	SW	100%[c]	Beckers et al.[30]
Pharmaceuticals	Lidocaine	—	0.00394	0.0199[b]	MN, USA	SW	89%	Fairbairn et al.[12]
			0.0048[c]	0.027[b,c]	Germany	SW	100%[c]	Beckers et al.[30]
			0.00925	0.242[b]	USA	SW	69%	Masoner et al.[31]
	Metformin	160*/640*	7.74[c]	89.6[b,c]	Germany	SW	100%[c]	Beckers et al.[30]
			0.0149	0.247[b]	MN, USA	SW	64%	Fairbairn et al.[12]
			0.1016	1.26[b]	USA	SW	73%	Masoner et al.[31]
	Metoprolol	8.6*/75*	0.30[c]	3.84[b,c]	Germany	SW	100%[c]	Beckers et al.[30]
			0.178	0.089–0.365	Germany	CSO	—	Launay et al.[13]
	Ibuprofen	0.011*/1700*	0.038	0.674[b]	LA, USA	SW	66%[c]	Boyd et al.[61]
			1.200	0.576–2.25	Germany	CSO	—	Launay et al.[13]
	Naproxen	—	0.0078	0.145[b]	LA, USA	SW	86%[c]	Boyd et al.[61]
			0.130	0.033–0.238	Germany	CSO	—	Launay et al.[13]
Lifestyle compounds	Caffeine	—	0.207	1.71[b]	MN, USA	SW	92%	Fairbairn et al.[12]
			0.942	32.2[b]	USA	SW	96%	Masoner et al.[31]
			1.06	0.235–5.40	WI, USA	SW	100%	Burant et al.[40]
			1.07	0.0029–53.0	Canada	SW	—	Sauvé et al.[98]
			7.600	3.495–18.54	Germany	CSO	—	Launay et al.[13]
	Nicotine	—	0.205	3.89[b]	MN, USA	SW	94%	Fairbairn et al.[12]
			0.782	18.3[b]	USA	SW	98%	Masoner et al.[31]
	Cotinine	—	0.054	0.54[b]	MN, USA	SW	100%	Fairbairn et al.[12]
			0.045	0.55[b]	USA	SW	92%	Masoner et al.[31]
			0.18[c]	0.85[b,c]	Germany	SW	100%[c]	Beckers et al.[30]
Transformation products	Fipronil sulfone	—	0.09	0.55[b]	CA, USA	SW	—	Ensminger et al.[57]
			0.026[d]; 0.077[e]	—	CA, USA	SW	36%[d]; 89%[e]	Budd et al.[74]
			0.0047–0.145	0.391[b,d]; 1.96[b,e]	CA, USA	DWR	64–100%	Gan et al.[44]
	Fipronil sulfide	—	0.004[d]; 0.009[e]	—	CA, USA	SW	2%[d]; 5%[e]	Budd et al.[74]
			0.0011–0.0198	0.054[b,d]; 0.33[b,e]	CA, USA	DWR	47–100%	Gan et al.[44]
	Fipronil desulfinyl	—	0.015[d]; 0.041[e]	—	CA, USA	SW	23%[d]; 68%[e]	Budd et al.[74]
			0.0016–0.077	0.034[b,d]; 1.12[b,e]	CA, USA	DWR	72–100%	Gan et al.[44]
	DES[f]	—	0.007–0.036[g]	—	Australia	SW	40%[c]	Rippy et al.[58]
	DIA[h]	—	0.013	0.144[b]	WI, USA	SW	92%	Burant et al.[40]
	AMPA	1500*/1500*	0.64	0.14–9.37	France	SW	93%	Zgheib et al.[59]
			0.824[g]	0.016–0.469	France	SW	40–75%	Gasperi et al.[26]
			—	0.06–1.3	Denmark	SW, CSO	100%	Birch et al.[46]

[a] N,N-Diethyl-m-toluamide. [b] Reported maximum concentration. [c] Calculated from data in the respective supporting information. [d] Northern CA. [e] Southern CA. [f] Desethylatrazine. [g] Mean value. [h] Deisopropylatrazine.

Stormwater conveyance pipes demonstrate diverse pollutant profiles that depend on (i) catchment type and land use, (ii) seasonal application of chemicals, (iii) weather dynamics, and (iv) intrusion of raw sewage. Current literature suggests no clear correlation between land use and the occurrence of specific hyphil-TrOCs. Gasperi et al.[26] analyzed hyphil-TrOCs in storm sewer outlets located in three different catchments (industrial, residential, and residential with heavy traffic) in France and did not find any significant difference between the sites. Six herbicides (glyphosate, glufosinate, AMPA, diuron, isoproturon, and 2,4-MCPA), one biocide (carbendazim) and BPA were systematically detected in stormwater from all sites.[26] Burant et al.[40] found that land use seems to affect different contaminant groups to different extents. With few exceptions, pesticide concentrations were equivalent in stormwater from a residential area and a commercial site.[40] In contrast, significant differences were observed for OP flame retardants and benzotriazoles which had higher concentrations at the residential site.[40] Future research is needed to understand how land use affects the leaching and transport of hyphil-TrOCs and whether this information can be used to predict the occurrence of hyphil-TrOCs in urban runoff.

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Seasonal use patterns of chemicals such as urban-use pesticides are reflected in stormwater.[44] The common application periods of pesticides are usually during late spring, summer, and early fall when pest pressure is high.[44] Indeed, Wittmer et al.[76] found that mecoprop concentrations in urban storm sewers were higher from May to September (up to 32 $\mu g\ L^{-1}$) compared to October and November (below 100 ng L^{-1}). For compounds with multiple applications in the urban environment (e.g., mecoprop as pesticide on lawns and in bitumen sheets on roofs), such seasonal concentrations patterns can hint to predominant sources.[76] Similar findings were made by Fairbairn et al.[12] who detected 1–2 orders of magnitude greater herbicide concentrations in spring and early summer than late summer and winter. However, compared to agricultural herbicides, urban and mixed-use pesticides (e.g., diuron and triclopyr) showed more frequent late summer or winter detections indicating seasonally independent sources.[12]

Beckers et al.[30] studied seasonal and weather dynamics of hyphil-TrOCs in a separate sewer system in Germany (Table 1). Storm sewer effluent was sampled under dry and wet weather conditions over one year.[30] Out of 149 target compounds, 67 were detected.[30] No clear seasonal dynamics could be observed, which is in contrast to Fairbairn et al.[12,30] Instead, concentrations of hyphil-TrOCs in stormwater were mainly driven by wet and dry weather conditions.[30] Urban pesticides (e.g., diuron), biocides (e.g., terbutryn, carbendazim), and insecticides (e.g., fipronil) were predominant during storm events.[30] In contrast, legacy pesticides and pharmaceuticals dominated storm sewer effluents during dry weather conditions indicating wastewater as a source.[30]

3.7 Hyphil-TrOC mixtures in combined sewer systems

Combined sewers transport stormwater as well as domestic and industrial wastewater to wastewater treatment plants (WWTPs) where the water is treated prior to discharge into the receiving water body. Mixing of stormwater with sewage complicates the study of stormwater-derived hyphil-TrOCs due to heavy dilution and potential co-occurrence of the same contaminants in raw sewage.

Frequent detections of hyphil-TrOCs in urban surface runoff suggest that stormwater contributes to the overall hyphil-TrOC load in WWTPs. Conventional WWTPs are not designed to remove hyphil-TrOCs and therefore act as major point sources of these chemicals to receiving water bodies. Approximately half of the overall TrOC load in wastewater is eliminated either by sorption (e.g., hydrophobic organic compounds like certain personal care products) or degradation (e.g., surfactants and hormones).[2,4,11] Hyphil-TrOCs that are poorly biodegradable are poorly removed.[2,11] Broad-scale implementations of advanced wastewater treatment technologies such as ozonation or powdered activated carbon have the potential to significantly enhance the removal of hyphil-TrOCs from wastewater.[11,99,100] Yet,

intense storm events will continue to challenge combined sewer systems and WWTPs. High flows reduce the hydraulic residence time of wastewater in the treatment system and reduce the treatment efficiency of biodegradable compounds.[62] Moreover, high volumes of rainwater and sewage can exceed the capacity of combined sewers and WWTPs leading to discharges of untreated storm- and wastewater as bypass flow or CSO.

Bypass flows and CSOs have been shown to significantly contribute to the hyphil-TrOC load in surface waters.[13,48,62,101,102] Bypass flows and CSOs can lead to short peaks in discharge with high loads of hyphil-TrOCs[48,76] and subsequent water quality degradation and ecotoxicological effects.[103] Phillips et al.[62] compared the relative contribution of WWTP bypass flow and treated wastewater to the load of hormones and other hyphil-TrOCs to a lake. The total volume of water discharged as bypass flow represented only 10% of the total annual water discharged (i.e., bypass flow plus treated wastewater).[62] Yet, discharges of the bypass flow accounted for 40–90% of the annual load for certain hormones and wastewater-derived hyphil-TrOCs.[62] Compounds with the highest elimination efficiencies in WWTPs (>90%, e.g., caffeine and hormones) had the highest portion of total annual load from bypass discharge.[62] At the studied WWTP, >80% of the caffeine load was attributable to bypass flow discharge.[62] In contrast, for compounds with low removal efficiency in WWTPs (e.g., BPA) the contribution of bypass flow to the overall pollutant load was not significant (<10%).[62] The concentration of hyphil-TrOCs that are poorly removed in WWTPs, generally decreased during intense rain events due to dilution of untreated wastewater with stormwater.[62,104]

4 Occurrence of transformation products

Few studies have investigated transformations of hyphil-TrOCs in urban stormwater. While we know that certain hyphil-TrOCs can undergo photolysis, oxidation, reduction, or biotransformation, knowledge on the occurrence of transformation products in urban stormwater is scarce.

Stormwater samples collected in an urban catchment in Switzerland contained the terbutryn phototransformation product desethyl-terbutryn.[68] Indeed, it is known that terbutryn is degradable by UV-irradiation.[105,106] Also octylisothiazolinone can undergo photodegradation and is likely the reason for its absence in stormwater samples collected in an urban catchment in Switzerland.[68,114] Burkhardt et al.[71] analyzed façade runoff water for N-(3,4-dichlorophenyl)-N-methylurea (DCPMU) and N-tert-butyl-6-(methylsulfanyl)-1,3,5-triazine-2,4-diamine, which are major transformation products of diuron and terbutryn or irgarol 1051, respectively. They found that concentrations of transformation products can exceed the concentration of the parent biocides especially after longer periods of façade exposure to rain.[71] However, they were not able to close the

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mass balance indicating that undetected transformation products or other unknown loss mechanisms play an important role in both the activity and longevity of biocides for material protection and their release into stormwater.[71] Also the insecticide fipronil is subject to photolysis leading to fipronil desulfinyl, which was frequently detected in dry weather residential runoff (median concentration up to 77 ng L^{-1})[44] and urban stormwater (up to 41 ng L^{-1}) in California (Table 4).[74] The presence of fipronil desulfinyl in dry weather urban runoff collected at the outfall of an underground storm sewer suggested rapid fipronil photolysis on concrete or soil.[44] Also 4-keto molinate, a photodegradation product of the herbicide molinate, has been reported in the literature.[115]

In addition to photolysis, fipronil can undergo oxidation and reduction. The oxidation product fipronil sulfone was found in residential urban runoff and stormwater with median concentrations as high as 145 ng L^{-1} (Table 4).[44,57,74] The fipronil reduction product fipronil sulfide was frequently detected in residential runoff, but in much lower concentrations (<20 ng L^{-1}) than the parent compound.[44] One of the most frequently studied transformation products in stormwater is aminomethylphosphonic acid (AMPA), the primary transformation product of glyphosate. AMPA is frequently found in stormwater runoff and CSOs.[26,46,59,116,117] Other reported transformation products include desethylatrazine,[30,40,58] deisopropylatrazine,[30,40] 2-hydroxy-atrazine,[116] and 2-hydroxysimazine[116] as well as diazinon-oxon, which is more toxic than the parent diazinon.[115]

Current knowledge suggests that transformation products can show temporally delayed concentration profiles compared to their parent compounds, but the same seasonal trends.[44] Transformation products are often reported with high detection frequencies (Table 4), indicating their so far overlooked importance. Comprehensive screenings of transformation products in urban stormwater are needed to understand their formation mechanisms, (trans)formation kinetics, transportation patterns, and contribution to stormwater toxicity.

5 Toxicological relevance of hydrophilic TrOCs in urban stormwater

While chemical analyses provide the opportunity to identify and quantify individual contaminants, they can not reveal the toxicity of complex chemical mixtures in stormwater.[118] Various studies indicate that urban stormwater runoff can be a significant contributor to increased toxicity of surface waters.[119–122] For instance, urban stormwater has been found to be acutely lethal to coho salmon (*Oncorhynchus kisutch*) and other aquatic species in the Pacific Northwest of the United States.[119,120] Coho mortality could not be linked to conventional water quality parameters such as dissolved oxygen or dissolved solids and was not correlated with pathogen-associated disease or exposure to metals, PAHs, and common pesticides.[123,124] Exposure of healthy coho spawners to untreated highway runoff collected during storm events reproduced the mortality syndrome indicating that coho salmon are vulnerable to one or more chemicals present in runoff.[124,123] Using high-resolution mass spectrometry (HRMS), Peter *et al.*[125] developed a chemical signature for the coho mortality by isolating HRMS features (*i.e.*, exact mass-retention time pairs) that co-occurred in road runoff and field samples that caused symptomatic coho. This "coho mortality signature" was then compared to chemical signatures of several motorvehicle fluids and tire wear particle leachate.[125] The chemical signature of tire wear particle leachate displayed most similarity to waters that caused coho mortality.[125] Prominent chemicals identified in the coho mortality signature were octylphenol ethoxylates, glycols, bicyclic amines, and (methoxymethyl)melamine compounds.[125] However, the presence of individual chemicals could not be linked to observed coho mortality.[125] Given that stormwater runoff may contain hundreds to thousands of different organic compounds,[119] the identified chemicals likely represent a small fraction of the overall cocktail. It remains unknown whether or not the actual toxicants were represented by HRMS features in the coho mortality signature because sample preparation and analysis inherently exclude a fraction of the chemicals present in field samples.[125] Notwithstanding, HRMS based approaches have great potential to reveal chemical patterns and similarities that may indicate (storm)water toxicity.[125] Compared to conventional LC-MS analysis, suspect and non-target HRMS screenings also provide more comprehensive insights into the occurrence of hyphil-TrOCs and allow for the identification of overlooked or unknown chemicals.

Acute coho salmon mortality is a severe manifestation of stormwater toxicity that raises public awareness and regulatory concern. Lethal effects of stormwater runoff have been reported elsewhere for other organisms including water fleas, rainbow trout, and fathead minnows.[121,122] Apart from lethal effects, stormwater can also cause sub-lethal or chronic effects that are less apparent, yet detrimental to long-term organismal fitness.[126] Zebrafish embryos exposed to urban highway runoff displayed various sub-lethal effects including delayed hatching, reduced growth, abnormal swim bladder inflation, and lateral line defects.[127,126] How these observed effects relate to the presence of complex stormwater pollutant mixtures is currently unknown.

While early studies on stormwater toxicity tried to link adverse effects to the occurrence of conventional stormwater pollutants (*e.g.*, TSS, metals, and PAHs),[121,122,128,129] there is increasing awareness of the importance of hyphil-TrOCs as shown in the case of coho salmon mortality. As discussed in sections 3 and 4, stormwater can carry numerous hyphil-TrOCs of which many are bioactive and persistent and, thus, of high concern. In a US-wide survey of trace organic contaminants in surface waters, bioactive compounds

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including pesticides, antimicrobials, and pharmaceuticals comprised 57% of 406 compounds that were detected at least once.[5] Designed bioactivity can lead to ecosystem concern and specific interactions with aquatic organisms.[5] Beckers *et al.*[30] reported that four out of seven risk drivers in storm sewer effluent were biocides. Biocide concentrations in urban stormwater often exceeded the predicted no effect concentration values as well as Swiss water regulations of 0.1 μg L^{-1}.[68] Fipronil detected in dry weather urban runoff in CA often exceeded the LC50 values for mysid shrimp and grass shrimp (0.14 and 0.32 μg L^{-1}, respectively), which are important trophic links in aquatic food webs.[44] Spills or incorrect disposal of chemicals such as the neuroactive insecticide dimethoate can significantly increase the acute toxicity of stormwater.[30] Cancilla *et al.*[92] reported increased toxicity of airport runoff during intensive application of aircraft deicing and antiicing fluids as well as the presence of 4-MeBT and 5-MeBT in whole-tissue extracts from minnows that were exposed to airport runoff. While this review article cannot provide a comprehensive compilation of TrOC-related toxicity studies, these selected examples highlight the potential impact of hyphil-TrOCs in stormwater runoff on observed acute or chronic effects as well as the need to identify relevant drivers of toxicity.

In risk assessment, analytically determined concentrations of priority pollutants are compared to environmental quality standards.[130] In Tables 2–4, we report long-term environmental quality standards expressed as annual average concentration (AA-EQS) as well as short-term environmental quality standards expressed as maximum allowable concentration (MAC-EQS) for priority substances in inland surface waters as proposed by the EU Water Framework Directive.[107] For compounds not yet under EU regulation, we list chronic and acute quality standards proposed by the Swiss Ecotox Center.[108] For certain hyphil-TrOCs (*e.g.*, imidacloprid, diuron, PFOS, and BPA), the reported median concentrations in stormwater were oftentimes greater than the chronic quality standards (Tables 2 and 3). For various pesticides (*e.g.*, carbendazim, terbutryn, dimethoate, imidacloprid, and 2,4-D), the reported maximum concentrations in stormwater oftentimes exceeded the acute quality standards (Table 2). Such observations may help to select priority contaminants in stormwater and identify candidate drivers of toxicity. However, risk assessments which are purely based on target chemical analyses may overlook analytically undetected but toxicologically relevant chemicals, transformation products of unknown toxicity and persistence, and complex mixture effects.[130]

First evidence suggests that seasonal and inter-event variations of urban stormwater composition and quality may be reflected in stormwater toxicity.[121] However, the assessment of linkages between stormwater contaminants and toxicity is complicated by (i) the vast number of chemicals (many of them unidentified), (ii) the great variability in stormwater quality over time and space, and (iii) different, predominantly unknown effects of individual chemicals and chemical mixtures on different organisms.[113,119] Conventional stormwater toxicity assessment techniques follow standardized protocols to expose different test organisms (*e.g.*, fathead minnow, *Ceriodaphnia*, or green algae) to stormwater for a predefined amount of time prior to reporting the species response to a specific endpoint (*e.g.*, survival, growth, reproduction, or biomass production).[131] The traditional approach to combine *in vivo* toxicity testings with target chemical analyses of stormwater is, however, not well suited to reveal and monitor the toxicity of rapidly changing chemical mixtures in stormwater runoff.[132–134] Little is known about the toxicity of complex chemical mixtures that may exert synergistic or additive effects, which complicates the identification of toxicants and their role in observed toxicity.[113,121]

Recently, cell-based (*in vitro*) high-throughput screening assays have been developed as effect-based method for water monitoring.[130,134] Cell-based bioassays target health-relevant biological endpoints and can serve as effect-based screening tool to assess the toxicity of stormwater and complement chemical water quality analyses.[133,134] In a given bioassay, all organic chemicals with a common mode of toxic action act together.[133] Tang *et al.*[133] applied a battery of six bioassays to characterize stormwater samples from urban, residential, and industrial areas in Australian cities in terms of their baseline toxicity, phytotoxicity, dioxin-like activity, estrogenicity, genotoxicity, and oxidative stress. The overall toxicity of stormwater samples was similar to secondary treated wastewater effluent.[133] Stormwater displayed higher effect levels than tertiary treated water, surface water, and drinking water, indicating the need for stormwater treatment prior to discharge or stormwater harvesting.[133] Some stormwater samples displayed toxicity similar to primary wastewater treatment plant effluent, which is likely due to sewage-impacted storm sewers.[133] Industrial and urban commercial sites had higher baseline toxicity compared to residential sites.[133] Road runoff displayed especially high baseline toxicity, genotoxicity, and oxidative stress response.[133] The baseline toxicity of the stormwater samples correlated significantly with their dissolved organic carbon (DOC) concentration suggesting that DOC could be used as indicator of baseline toxicity.[133] Using the combined algae test, herbicides were shown to dominate the baseline toxicity in most samples.[133] Typically, a few herbicides (including diuron, terbutryn, bromacil, atrazine, and simazine) can explain the majority of the bioassay-derived phytotoxicity.[133] Estrogenic activity was negligible in 95% of the collected stormwater samples.[133] However, some samples showed estrogenic effects similar to raw sewage suggesting that the presence of high estrogenic activity could serve as indicator of sewage contamination.[133]

Collectively, results from *in vivo* and *in vitro* studies highlight a possible significant contribution of urban stormwater runoff to acute and chronic toxicity of receiving water bodies. Toxic hyphil-TrOC mixtures can pose a threat in drinking water, especially when coupling the capture of

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stormwater to potable water supply *via* aquifer recharge.[35] Hyphil-TrOCs in drinking water supplies are of concern because (i) they can pose a risk to human health and (ii) they may be transformed to potentially more harmful byproducts during the production of safe drinking water. For instance, the herbicide diuron, which is frequently found in stormwater, is classified as "known/likely" human carcinogen.[135] During drinking water chlorination and chloramination, diuron can be transformed to *N*-nitrosodimethylamine (NDMA), which is mutagenic, probably carcinogenic to humans, and frequently detected in drinking water.[135–137] Indeed, stormwater runoff has been shown to be a source of *N*-nitrosamines and their precursor compounds.[138]

In order to choose appropriate monitoring strategies and management options for hyphil-TrOCs in stormwater, it is essential to identify the most relevant toxicants. Therefore, chemical screening tools can be complemented with cell-based bioassays to assess which of the detected chemicals drive the biological effects and which fraction of effect remains unexplained by detected chemicals.[130,139] Subsequently, an approach called effect-directed analysis can be applied to isolate and identify so-far unknown but relevant toxicants.[130,140] Monitoring of such priority substances will improve the development of efficient and cost-effective stormwater treatment technologies, which are needed to protect aquatic ecosystems and enable safe use of urban stormwater for groundwater recharge and potable water supply.

6 Fate of hydrophilic TrOCs in green stormwater infrastructure

Green stormwater infrastructure is designed to capture and treat stormwater while also providing multiple ecological and societal benefits.[141] Green stormwater infrastructure components (also called best management practices, BMPs) include permeable pavement, green roofs, detention and retention basins, constructed wetlands, and biofilters.[141] BMPs complement gray infrastructure (*i.e.*, storm drains and pipes), reduce runoff volumes, provide cost-effective stormwater treatment, and expand green spaces in highly urbanized areas.[141]

The outflow of BMPs is either discharged into receiving water bodies or infiltrated into the ground for aquifer recharge. The type and design of BMPs can significantly impact the removal of contaminants from urban stormwater. Current knowledge suggests that green stormwater infrastructure can reduce the toxicity associated with stormwater.[120,124,142] Stormwater quality improvements through BMPs are, however, only assessed by monitoring the removal of traditional stormwater pollutants such as TSS,[143] nitrate,[144–146] phosphates,[147] metals,[143,148] microorganisms,[145] and specific organic legacy compounds such as PAHs and certain pesticides.[14,149] Little is known about the fate of hyphil-TrOCs in stormwater BMPs which

are not designed to remove highly mobile and persistent organic pollutants. In the following section, we present the current knowledge on the removal of hyphil-TrOCs in detention basins, constructed wetlands, and biofilters.

6.1 Detention basins

Stormwater detention basins (also called dry ponds) are among the most adopted urban BMPs.[150] While the main purpose of detention basins is to prevent flooding, they can provide a water quality benefit when the hydraulic residence time allows for sedimentation of suspended solids and other particle-associated contaminants. However, hyphil-TrOCs with $\log K_{OW}$ values <4 (*e.g.*, atrazine, diuron, chlorfenvinphos, isoproturon, and simazine) are predominantly present in the dissolved fraction of stormwater.[26,42,59,112] As the tendency of hyphil-TrOCs to bind to particles is low, they are poorly removed through sedimentation.[3,59,150,151] In fact, Sébastian *et al.*[151,152] observed that a number of pesticides including diuron, isoproturon, simazine, atrazine, carbendazim, mecoprop, and chlorfenvinphos were not trapped in a stormwater detention basin. In two monitoring campaigns (out of three studied), high removal efficiencies of $>50\%$ were observed for 2,4-MCPA, glyphosate, and ammonium glyphosate probably due to a combination of mechanisms including transformation.[151] The more hydrophobic alkylphenols and alkylphenol ethoxylates, which were present in the dissolved and particulate phase, showed proven removal efficiencies of around 40%.[151] In fact, alkylphenols, alkylphenol ethoxylates, and BPA were also found in sediments of detention ponds.[150]

6.2 Constructed wetlands

Constructed wetlands are engineered, low-energy water treatment systems in which stormwater or CSO is directed through an open marsh land. In addition to water treatment, constructed wetlands provide volume control, ecosystem and recreational benefits. The two basic designs of constructed wetlands are: (i) subsurface flow wetlands in which water moves horizontally or vertically through the planted substrate and (ii) surface flow wetlands in which water flows mainly above the soil surface.[153] As discussed by Imfeld *et al.*[153] and Jasper *et al.*,[154] constructed wetlands can remove organic contaminants through natural (a)biotic processes including sedimentation, hydrolysis, photolysis, sorption, oxidation, biotransformation, plant uptake, and phytotransformation (Fig. 2). Removal mechanisms depend on the hyphil-TrOC being treated, the wetland type and operational design, the environmental conditions, vegetation, and the soil matrix.[153,155] Our knowledge on removal mechanisms of hyphil-TrOCs in constructed wetlands remains scarce because the majority of studies focus on removal efficiencies.

Jasper *et al.*[154] highlight that constructed wetlands provide only partial and highly variable removal of numerous pharmaceuticals and personal care products (*e.g.*, carbamazepine and clofibric acid) from wastewater effluent.

Fig. 2 Main abiotic and biotic processes that contribute to the removal or transformation of hydrophilic trace organic contaminants (hyphil-TrOCs) in a constructed wetland and subsequent geomedia-amended biofilter. Hyphil-TrOCs are depicted as pink circle, transformation products as purple symbols.

Few studies report removal efficiencies of hyphil-TrOCs in constructed wetlands for stormwater treatment. Page *et al.*[156] investigated a constructed wetland receiving stormwater from a residential and light industrial catchment and found mean removal efficiencies of 33–51% for diuron and 20–60% for simazine. Low to moderate removal of hyphil-TrOCs from a vineyard catchment was found by Maillard *et al.*[157] who reported load reductions of 36–60% for simazine, 57–72% for diuron, 77–90% for glyphosate, and 10–59% for AMPA in a surface flow stormwater wetland. Other compounds (*e.g.*, cymoxanil and terbuthylazine) were completely eliminated.[157] Plant roots and fine sediments were primary contributors to the retention of glyphosate, AMPA, and dithiocarbamates in the studied wetland.[158] Under reducing conditions in summer, glyphosate was degraded into AMPA, which was more persistent than its parent compound.[158] AMPA accumulated in the fine sediments posing ecotoxicological risks from accumulation, remobilization, and the release of not yet identified transformation products.[158] Dithiocarbamates were found to be degraded under oxic conditions in spring.[158] Complex seasonal changes in the wetlands source/sink functions are likely driven by climate conditions, storm duration and frequency, vegetative cover, root structure, and the resulting hydrochemical conditions.[157,158]

Tondera *et al.*[159] investigated the elimination of hyphil-TrOCs from CSO in a subsurface flow constructed wetland after seven years of operation. Low to medium removal rates were found for sulfamethoxazole (23 ± 10%), carbamazepine

(30 ± 9%), 1*H*-BT (40 ± 8%), and TCPP (43 ± 8%).[159] Better removal was achieved for metoprolol (60 ± 6%), BPA (69 ± 5%), and diclofenac (73 ± 3%).[159] After 10 years of operation, the studied wetland lost its efficiency to remove chemicals with no or slow biological degradability (*e.g.*, sulfamethoxazole or TCPP) likely due to exhausted adsorption capacity.[160] The abatement of BPA exhibited seasonal variations with warmer temperatures potentially promoting biotransformation.[160] More research is needed to assess the long-term functionality of constructed wetlands including changes in their hydrochemistry and underlying hyphil-TrOC removal mechanisms.

Highly fluctuating flows and pollutant loads, seasonal variability in performance, and emergence of short-circuited sections may contribute to incomplete removal of hyphil-TrOCs in constructed stormwater wetlands. Novel wetland designs may consist of a sequence of unit process cells that target the removal of specific contaminants.[154] Moreover, wetland effluents may be polished using a post-treatment unit containing engineered reactive geomedia (*e.g.*, pyrogenic carbonaceous adsorbents) as depicted in Fig. 2 and described in detail in section 7.

6.3 Biofilters

Stormwater biofilters, also known as bioretention cells, rain gardens, or bioswales, are low-energy treatment systems consisting of a planted soil-based filter media, which commonly has a high content of sand.[161] Stormwater

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percolates through the biofilter before it is discharged through an underdrain or infiltrated into the subsoil for aquifer recharge. Biofilters are among the most promising stormwater treatment technologies as they are designed to remove traditional stormwater pollutants (TSS, nutrients, and metals).[161,162] Indeed, biofilters can enhance water quality and reduce stormwater toxicity.[120,124,142] However, biofilters may fail to remove hyphil-TrOCs. Few studies have investigated the fate of hyphil-TrOCs in biofilters, which depends on the filter media, the physicochemical properties of the contaminants, the percolation rate through the filter, and the environmental conditions.[161]

Zhang et al.[161] challenged two full-scale biofiltration cells with stormwater to which a mixture of organic contaminants was dosed. Hydrophobic contaminants such as petroleum hydrocarbons and phthalates were well removed in the biofilters of which one had no submerged zone and consisted of loamy sand and the other contained a submerged zone and used sand.[161] Also glyphosate showed good removal (>80%) probably due to a combination of adsorption and transformation.[161] However, triazine herbicides (atrazine and simazine) were poorly eliminated with 20–50% load removal in the cell without a submerged zone and <20% in the cell with a submerged zone.[161] Prolonged dry periods of the filter as well as warmer temperatures in summer promoted atrazine and simazine abatement, likely due to biodegradation of the adsorbed herbicides.[161] While the validation of the treatment performance of stormwater biofilters is needed, such full-scale field challenge tests are difficult to conduct.[163] Therefore, Zhang et al.[163] developed an alternative validation method using in situ columns inserted in the biofilter media which attempted to reproduce the performance of the full-scale system.

To date, few other studies have evaluated hyphil-TrOC removal in full scale biofilters with field or in situ methods due to large biofilter sizes and highly fluctuating stormwater flows. For instance, bioswales have been shown to effectively remove TSS, metals, PAHs, and pyrethroid pesticides, but reduction of the more hydrophilic pesticide fipronil was highly inconsistent.[142] In a vegetative filter strip and a biofiltration swale treating heavily loaded road runoff, removal of dissolved organic pollutants was generally less effective than that of particles.[111,164] While BPA was relatively well removed in the vegetated filter strip (86% removal), it was less well retained in the bioswale (57% removal).[111] Other compounds such as nonylphenol monocarboxylate were poorly removed (32%) in the filter strip.[111] In the bioswale, release of nonylphenol monocarboxylate increased over time indicating leaching of this compound from biofilter construction materials (asphalt, drains, geomembranes).[111,164]

Ex situ approaches, i.e., laboratory batch and column experiments under controlled conditions, prevail to study removal mechanisms of hyphil-TrOCs in biofilters. Bester et al.[165,166] conducted a laboratory study to investigate the removal of biocides and other TrOCs in planted biofilters containing peat, sand, and gravel. While high removal of biocides (82–100%) was achieved under low flow conditions, pulses with high loads and low retention times of <1 h resulted in a significant drop in removal efficiency.[165] Other hyphil-TrOCs such as methylthiobenzothiazole were removed to a large extent independent of the flow through the biofilters.[166] Triclosan-methyl, a transformation product of triclosan, was detected in the effluent of the biofilter indicating biotransformation of certain organic contaminants.[166] While removal processes of dissolved pollutants (especially nutrients, metals, and hydrocarbons) in bioretention cells have been intensively discussed elsewhere,[18,167] information about the fate of hyphil-TrOCs in biofilters remains elusive. Current knowledge confirms that sand is not an adequate adsorbent material to remove hyphil-TrOCs. Therefore, sand-based stormwater treatment systems need modification, for instance through amendments with carbonaceous adsorbents or other reactive geomedia.[168]

7 Enhanced removal of hydrophilic TrOCs in geomedia-amended BMPs

Potential stormwater geomedia for next generation BMPs include metal oxide materials (e.g., iron filings and manganese oxide-coated sand) and pyrogenic carbonaceous materials (e.g., activated carbon or biochar).

7.1 Metal oxide materials

Iron-enhanced sand filters, consisting of sand with approximately 5% iron filings (w/w), have been shown to effectively remove particulate and dissolved phosphorus from stormwater[12,147] and may also retain hyphil-TrOCs due to polar and electrostatic interactions with iron oxide surface functional groups.[169] Fairbairn et al.[12] studied the removal of hyphil-TrOCs from urban stormwater in full-scale iron-enhanced sand filters in Minnesota, USA. Hydrophobic organic contaminants such as PAHs and sterols were effectively removed.[12] High removal (>60%) was also observed for several lifestyle compounds (e.g., caffeine and nicotine) and BPA.[12] However, removal of other hyphil-TrOCs was poor or negligible. Removal efficiencies were 36% for DEET, 23% for 2,4-D, 19% for diuron, 11% for carbendazim and metolachlor, and 4% for 5-MeBT.[12] While iron-enhanced sand filters efficiently attenuated phosphate (61% removal), the competition between different chemical species in stormwater may reduce the removal of organic contaminants through sorption.[12]

Manganese oxides (MnO_2) are natural oxidants in soils and sediments and can enhance the removal and transformation of organic contaminants through direct oxidation, adsorption, and surface catalysis.[170–172] MnO_2 can oxidize a variety of hyphil-TrOCs including antibacterial agents,[173,174] sulfonamide antibiotics,[171] glyphosate,[175] steroid hormones (estrone and 17α-ethinylestradiol),[176]

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BPA,[177] and β-blockers (betaxolol, atenolol, and metoprolol).[178] Compared to iron oxides, manganese oxides have a higher redox potential resulting in greater oxidation possibilities for organic contaminants.[179] Zhang et al.[180] studied manganese oxide-containing biofilters as a polishing treatment step for secondary wastewater. While diclofenac and sulfamethoxazole were effectively removed (>70%), carbamazepine was not abated.[180] Recently, manganese oxide-coated sand has been proposed as cost-effective and regenerative geomedia for stormwater treatment to target the removal of hyphil-TrOCs.[181,182] Grebel et al.[181] observed that birnessite (a layered MnO_2) was highly reactive towards aromatic compounds with electron-donating moieties (e.g., BPA and 2-mercaptobenzothiazole) and moderately reactive towards compounds with electron-withdrawing functional groups (e.g., diuron) or steric hindrance at the most likely reaction site (e.g., prometon). However, birnessite was unreactive towards numerous other hyphil-TrOCs (e.g., TCPP, benzotriazole, and fipronil).[181] Stormwater constituents such as dissolved organic matter or inorganic ions (e.g., calcium or carbonate) can contribute to exhaustion of the redox reactivity of manganese oxide-coated sands.[181] Charbonnet et al.[182] found that exhausted manganese oxide-coated sand could be regenerated with HOCl leading to similar reactivity and longevity than the pristine MnO_2. Geomedia regeneration in the field could be a main advantage as it prevents excavation of the exhausted material, reduces disposal costs, and helps to overcome implementation barriers. To the best of our knowledge, there are no current studies that assess the field performance and field regeneration of manganese oxide-coated sand in BMPs for stormwater treatment. As iron and manganese oxides are redox-sensitive materials, careful design and operation of the biofilter is required to minimize mobilization of Fe^{2+} and Mn^{2+} from the filter.

7.2 Pyrogenic carbonaceous materials

Engineered pyrogenic carbonaceous materials such as (regenerated) activated carbon and biochar exhibit a high specific surface area and strong affinity to adsorb hyphil-TrOCs.[183,184] Similar to activated carbon, biochar is the solid product of heating biomass under oxygen-limited conditions. However, biochar is usually not subject to energy-intensive thermal or chemical activation and is produced from renewable, locally available materials, such as wood, crop residues, and manure.[185] Biochar has recently received increased attention as a cost-effective and sustainable alternative to activated carbon for the treatment of wastewater and stormwater.[186–193]

The adsorption of hyphil-TrOCs onto biochar is mainly driven by diffusion into char pores. The presence of polar functional groups at the edges of the graphene-like layers facilitate electrostatic interactions and other forces (e.g., van der Waals and H-bonding).[189] The polyaromatic surface of biochars can also enhance sorbent–sorbate π-electron

interactions.[184,194] Moreover, biochars contain a variety of surface functional groups that likely play a key role for reactive transformation processes of organic contaminants.[195,196] For instance, it is known that biochars are redox-active and reversibly accept and donate electrons.[196–201]

Numerous studies investigated sorption of hyphil-TrOCs on activated carbon and biochar in controlled laboratory batch experiments.[191,194,202,203] Ulrich et al.[202] compared activated carbon and 18 different types of biochars in terms of their performance to remove hyphil-TrOCs (atrazine, benzotriazole, 2,4-D, diuron, fipronil, oryzalin, prometon, and TCPP) from synthetic stormwater. While activated carbon best removed hyphil-TrOCs, several biochars were also effective in sorbing these compounds (i.e., logarithmic solid–water distribution coefficients mostly ranged from 4 to 7 L kg^{-1}).[202]

Biochar-amended stormwater infiltration basins or biofilters have been simulated in column experiments to study the fate of hyphil-TrOCs under controlled flow regimes.[191,192,202,204] Ulrich et al.[202] filled columns of 15 cm length with sand – activated carbon or sand – biochar mixtures, equilibrated the filter materials over night with synthetic stormwater, and spiked the columns for four days with a mixture of hyphil-TrOCs including prometon, atrazine, TCPP, benzotriazole, and diuron. Breakthrough of all compounds was observed within less than 500 pore volumes, except diuron which was efficiently retained.[202] Breakthrough curves were used to verify a forward-prediction intraparticle diffusion model.[202] This model was applied to predict sorption-controlled atrazine breakthrough times of 54 years and 5.8 years for a full-scale infiltration basin (103 m^2) amended with 12.3 wt% activated carbon or 4.5 wt% biochar, respectively, at 1 inch per hour infiltration rate.[202] Water-shed scale simulations by Wolfand et al.[205] show that biochar-amended biofilters are also effective at reducing urban runoff concentrations and loads of fipronil and bifenthrin.

Ashoori et al.[191] combined biochar with woodchips for enhanced nitrate and hyphil-TrOC removal from urban stormwater. Woodchip bioreactors of 50 cm length were amended with 33 wt% biochar and aged for eight months with urban runoff from a creek in Sonoma, CA.[191] Subsequently, the bioreactors were challenged for five months with synthetic stormwater containing six hyphil-TrOCs (fipronil, diuron, 1H-benzotriazole, atrazine, TCEP, and 2,4-D).[191] While conventional woodchip bioreactors exhibited rapid breakthrough of hyphil-TrOCs, the compounds were effectively retained by biochar.[191] The aforementioned intraparticle diffusion model was applied to predict a breakthrough time of 26 years for the anionic herbicide 2,4-D in biochar-amended woodchip bioreactors assuming that 100% of the annual rainfall volume in the watershed is treated.[191] Ulrich et al.[206] show that biochar amendments are also effective for hyphil-TrOC removal in vegetated biofilters containing a sand-compost planting layer. It is postulated that the presence of dissolved organic carbon

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(DOC) can reduce sorption of hyphil-TrOCs onto biochar due to pore blockage and competitive sorption effects.[202] However, the presence of labile DOC in biochar systems may also stimulate the evolution of beneficial microbial communities that facilitate biotransformation of hyphil-TrOCs.[207] The type of DOC seems to play a critical role as the attenuation of hyphil-TrOCs was more pronounced when biochar-amended columns were fed with DOC extracted from compost than from straw.[207] Additional research is needed to elucidate the interplay of biochar, DOC, and microbial communities and their impact on the fate of hyphil-TrOCs in biochar-amended stormwater treatment systems.

Compared to other novel stormwater filtration media such as functionalized polymer-clay composites, biochar showed superior performance for the removal of hyphil-TrOCs.[204] While polycation-clay sorbents have been shown to successfully remove hyphil-TrOCs (*e.g.*, atrazine) from water,[208] biochar exhibited similar performance for the removal of perfluoroalkyl substances (*i.e.*, PFOA and PFOS) and superior performance for the removal of other hyphil-TrOCs including 2,4-D and TCEP.[204]

Results from controlled laboratory batch and column experiments provide evidence that biochar-amendments to conventional stormwater filters can significantly enhance the removal of hyphil-TrOCs from stormwater.[191,192,202,206,207] Moreover, biochar amendments to conventional green infrastructure can have co-benefits such as the removal of other stormwater pollutants (*e.g.*, fecal indicator bacteria,[145,209] or nitrate[191,210]) and increased water holding capacity.[210,211] Biochar-amendments to vegetated stormwater infrastructure may, thus, expand the selection of plants and may enhance the removal of hyphil-TrOCs through sorption and plant uptake.[211]

The effectiveness and longevity of (regenerated) activated carbon or biochar-amended stormwater treatment systems remain to be evaluated in actual field experiments. One major challenge is the selection of biochar, for which properties are highly dependent on the charring conditions, the feedstock, and the post-treatment handling. Standards to assess the quality of biochar are currently lacking but required to ensure a safe and effective (storm)water treatment. Moreover, we need to develop management strategies for exhausted biochar. While activated carbon is frequently regenerated at the end of its service life, very few studies have attempted biochar regeneration.[212]

8 Conclusions and future research needs

Research on the occurrence of hyphil-TrOCs in urban stormwater and their impact on stormwater toxicity is emerging. Sources of hyphil-TrOCs in the urban environment are manifold and include structural materials, pest control, urban green spaces, traffic, as well as raw sewage. Urban stormwater can carry numerous hyphil-TrOCs many of which are bioactive, persistent, and of toxicological concern.

Conventional green stormwater infrastructure is not designed to eliminate hyphil-TrOCs and often fails to remove polar and mobile organic compounds. Cost-effective amendments of conventional green stormwater infrastructure with reactive geomedia such as metal oxide-coated sands, regenerated activated carbon, or biochar show promise to enhance the removal of hyphil-TrOCs and, thus, protect aquatic ecosystems and enable safe use of urban stormwater for water supply. In the following section, we summarize specific findings and highlight future research needs to advance our understanding of the occurrence, toxicity, and treatment of hyphil-TrOCs in stormwater.

Monitoring of hyphil-TrOCs in stormwater

• The majority of studies dealing with hyphil-TrOCs in urban stormwater has been based on a small number of samples collected at few locations during a limited number of storm events. Long-term monitoring of hyphil-TrOCs in urban stormwater is needed at high temporal and spatial resolution to better understand sources as well as regional and seasonal occurrence patterns of these chemicals. Little is known about the frequency and relevance of single, high-intensity peaks due to spills or improper disposal of chemicals in comparison to background concentration levels of hyphil-TrOCs.

• The use of passive samplers for urban stormwater monitoring may cost-effectively complement traditional grab and automated sampling strategies. However, more research is needed to validate time-integrated and velocity-dependent passive samplers in the field during storm events with highly variable hyphil-TrOC loads. These research efforts should result in standardized protocols and guidance documents for the consistent use of passive sampling methods in stormwater monitoring.

• Assessment tools exist to predict runoff concentrations of sediments, nutrients, and metals in non-point stormwater runoff based on land use data.[213] More extensive monitoring data of hyphil-TrOCs in urban stormwater will help to evaluate whether such prediction tools can be developed for organic contaminants.

• Source apportionment of hyphil-TrOCs is currently difficult to accomplish. New analytical techniques such as compound-specific isotope analysis (CSIA) may be applied to identify predominant sources of relevant chemicals and develop elimination strategies.[214]

• Increasing evidence suggests that separate storm sewers can be impacted by raw sewage leading to discharge of elevated levels of hyphil-TrOCs and other pollutants. Little is known about the input pathways and the nationwide extent of storm sewer cross-contamination with wastewater.

• Stormwater samples have been predominantly analyzed for a finite set of target analytes. More than 100 different hyphil-TrOCs have been reported in stormwater indicating their frequent and divers occurrence. Suspect and non-target screenings using LC-HRMS are increasingly applied to detect

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unknown contaminants in wastewater,[38] natural or finished water.[215–217] Such screening approaches have been rarely applied for urban stormwater[119] but may significantly advance our knowledge on the presence and fate of hyphil-TrOCs.

• Not all hyphil-TrOCs are easy to detect and quantify using reversed-phase LC-HRMS. For instance, illicit disposal or spills of antifreeze from automobiles may lead to high concentrations of *N*-nitrosodimethylamine (NDMA) in stormwater.[218] As highlighted in Reemtsma *et al.*,[3] an analytical gap persists for highly polar compounds with negative $\log D_{OW}$ values. Future monitoring studies should consider the use of novel analytical approaches such as hydrophilic interaction LC (HILIC) to complement screening efforts.[3]

• Research on the significance of microplastics in urban stormwater is emerging. While microplastics have been recently found in stormwater retention ponds,[219] their role as source or sink for hyphil-TrOCs in urban stormwater remains elusive.

Assessment of stormwater toxicity and priority contaminants

• A comprehensive analysis of the occurrence of hyphil-TrOCs should be accompanied with stormwater toxicity assessments using a combination of classical laboratory *in vivo* studies as well as high-throughput cell-based bioassays.

• More research is needed to assess the toxicity of complex chemical mixtures in stormwater *e.g.*, by developing effect-based water quality trigger values.[113,130] Studies should also focus on evaluating the effects of combined exposure to hyphil-TrOCs and other pollutants, especially metals.[220]

• Research is warranted to assess the impact of urban runoff and BMP effluents on ecological health. Chemical analyses combined with cell-based bioassays may help to detect potential adverse effects from complex contaminant mixtures on freshwater aquatic life and community compositions.

• In order to develop a regulatory framework for stormwater harvesting, risk-based water quality guidance is needed. Therefore, criteria for the selection of stormwater priority contaminants need to be established based on their acute toxicity, chronic effects, concentration levels, persistence, and widespread occurrence.

Fate and removal of hyphil-TrOCs in stormwater BMPs

• To enhance our understanding of the removal, accumulation, and release of hyphil-TrOCs in conventional BMPs, a broad set of hyphil-TrOCs should be included in existing contaminant monitoring lists that so far mostly include traditional stormwater contaminants (*e.g.*, TSS, metals, PAHs). Chemical analyses should be complemented with bioanalytical tools to assess the impact of BMPs on stormwater toxicity. Knowledge on the performance of conventional BMPs can then be used to design next

generation BMPs that target the removal of hyphil-TrOCs as well as traditional stormwater contaminants.

• New cost-efficient and sustainable materials need to be developed that are able to effectively remove hyphil-TrOCs from stormwater runoff and CSO. While these materials will be designed and tested on the laboratory scale, the field performance and longevity of stormwater treatment materials are of utmost importance for their actual implementation. Geomedia-amended BMPs require optimized construction and operational parameters to avoid premature treatment failure through clogging or loss of geomedia functionality. Studies should especially focus on the impact of hydraulic conductivity and residence time on the removal of hyphil-TrOCs. Research is needed to evaluate possible retrofitting strategies for existing BMPs with geomedia. Moreover, the impact of geomedia-amended BMPs on stormwater toxicity reduction has to be assessed.

• Removal mechanisms of hyphil-TrOCs in conventional and geomedia-amended BMPs remain largely unstudied. Research is needed to understand the impact of various BMP components (*e.g.*, plants, roots, soil, engineered reactive geomedia) on hyphil-TrOC removal and elucidate potential transformation pathways. Suspect and non-target analyses can help identify transformation products which may, however, be transient or difficult to detect. Compound-specific isotope analysis (CSIA) might be a promising complementary approach to investigate natural transformation processes and elucidate reaction mechanisms of hyphil-TrOCs and their transformation products in BMPs.[221,222]

• Layered or mixed-media filters containing multiple geomedia such as carbonaceous adsorbents (regenerated activated carbon, biochar), zeolite, or manganese oxide-coated sand need testing under aging conditions in the field to assess longevity of performance. More research is needed to develop cost-effective and sustainable management strategies for exhausted stormwater treatment materials, *e.g.*, regeneration of MnO_2 or biochar replacement schedules.[182,212]

• As stormwater biofilters often face prolonged dry periods and, thus, present underused water treatment potential, dual-mode biofilters for treatment of stormwater in wet seasons and greywater in dry seasons have been proposed.[143] The fate of greywater-derived hyphil-TrOCs in conventional and geomedia-amended biofilters needs to be investigated especially for infiltrating systems.

Conflicts of interest

There are no conflicts to declare.

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