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1	A look down the drain: Identification of dissolved and particle					
2	bou	nd organic pollutants in urban runoff waters and				
3	sedi	iments				
4	Hanna	E. Fuchte ^{1,*} , Natascha Beck ¹ , Evelyn Bieg ² , Viviane J. Bayer ³ , Christine Achten ³ , Martin				
5	Krauss ⁴ , Andreas Schäffer ^{1,5} and Kilian E. C. Smith ⁶					
6	1	Institute for Environmental Research, RWTH Aachen University, Worringerweg 1, 52074				
7		Aachen, Germany				
8	2	Umwelt-Mikroskopie Evelyn Bieg, Greppstraße 64, 52159 Roetgen, Germany				
9	3	Institute of Geology and Palaeontology – Applied Geology, University of Münster,				
10		Corrensstraße 24, 48149, Münster, Germany				
11	4	Helmholtz Centre for Environmental Research – UFZ, Permoserstraße 15, 04318 Leipzig,				
12		Germany				
13	5	State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment,				
14		Nanjing 210093, PR China				
15	6	Department of Water, Environment, Construction and Safety, University of Applied Sciences				
16		Magdeburg-Stendal, 39114 Magdeburg, Germany				
17	*	Correspondence: <u>hanna.fuchte@bio5.rwth-aachen.de</u>				
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21 Abstract

22 Urban runoff contains a range of organic micropollutants which, if not removed during wastewater 23 treatment, pose a risk to aquatic environments. These mixtures are complex and often site-specific. Street drains provide an ideal sampling point given they collect the runoff from local and defined 24 25 catchments. In this study, runoff was collected and sampled in five street drains located in a medium 26 sized town in Germany. A specially constructed trap was used to collect the particulate and total water 27 fractions of the runoff. In addition, passive samplers were deployed to determine the freely dissolved 28 concentrations of selected compounds in the runoff. In sum, 187 polar organic micropollutants could 29 be quantified using LC-HRMS. Thirty of these could only be detected by the use of passive samplers. Traffic derived pollutants such as corrosion inhibitors, rubber- and plastic additives, but also pollutants 30 31 of industrial origin were strongly represented with sum median concentrations of 100 µg/kg dry weight 32 (DW) in the sediment and 400 ng/L in the water fraction. Several of these substances are of concern 33 due to their environmental persistence and mobility. Perfluorinated compounds and pesticides 34 occurred at lower levels of several µg/kg DW sediment or ng/L water. A number of substances including 35 pharmaceuticals, sweeteners and stimulants indicated domestic wastewater influences. Furthermore, a total of 62 parent and alkylated PAHs were quantified by GC-MS and contributed 30-70% to the sum 36 37 concentrations of the micropollutants. Non-EPA PAHs dominated the carcinogenic PAH toxicity. The 38 increased PAH alkylation indices (0.7-0.9) showed these primarily came from combustion sources. The 39 runoff particles were additionally microscopically characterized, and correlations were found between 40 the rubber particle counts and the PAH alkylation-index as well as the levels of 41 2-(methylthio)benzothiazole, a marker compound for tire leaching.

43 1. Introduction

Micropollutants released into the urban environment (from traffic, building materials, industry etc.) 44 45 can eventually contribute to the impairment of aquatic ecosystems (Müller et al., 2020). During rainfall 46 the pollutants are collected in the runoff water, where they partition between particles and the water 47 phase depending on their physico-chemical properties. This runoff may subsequently be discharged to surface waters or seep into ground water (Masoner et al., 2019). Several of the pollutants are 48 49 persistent, mobile, can bioaccumulate and have harmful effects on aquatic and other organisms 50 (Langenbach, 2013; Reemtsma et al., 2016). Some may even cause public health risks when entering 51 the freshwater supply (Schwarzenbach et al., 2006). In Germany, the quality of surface and groundwater is regularly surveyed in monitoring programs (European Commission (EC), 2013; German 52 53 Environment Agency (UBA), 2017). However, many pollutants are not monitored (e.g., due to site-54 specificity or insufficient data on their adverse health properties (Baat et al., 2019; Krauss et al., 2019)). These need to be identified and their fate and effects investigated. To date, there is no specific 55 56 regulatory framework for runoff pollutants and studies are required to identify newly emerging 57 compounds and to select priority pollutants from the complex mixtures present in such runoff 58 (Eriksson et al., 2007; Spahr et al., 2020). Traffic is one major source, with the pollutants being emitted 59 as exhaust gases, via oil and other leakages or from abrasion of vehicle components and road surfaces 60 (Markiewicz et al., 2017). Pollutants that have been found in traffic environments include 61 benzothiazoles used as rubber vulcanization accelerators (Asheim et al., 2019; Grung et al., 2021; 62 Klöckner et al., 2020; Liao et al., 2018; Wever and Verachtert, 1997), benzotriazoles used as corrosion inhibitors (Asheim et al., 2019; Giger et al., 2006) and organophosphates emitted from car interiors 63 and lubricants (Grung et al., 2021; Marklund et al., 2005). 64

65 One important group of traffic pollutants are the polycyclic aromatic hydrocarbons (PAHs), some of 66 which are known carcinogens. Sixteen representatives, including benzo[a]pyrene, have been listed by 67 the US-Environmental Protection Agency (EPA) and well-studied in runoff (Grynkiewicz et al., 2002; 68 Jartun et al., 2008; Karlsson and Viklander, 2008; Zgheib et al., 2012). In contrast, more research is 69 needed concerning the many non-EPA PAHs (Andersson and Achten, 2015). Some exhibit particularly 70 high benzo[a]pyrene-equivalent carcinogenicities of up to 10 or 20 (Richter-Brockmann and Achten, 71 2018). Analyzing an expanded set of PAHs not only provides a more accurate estimate of the PAH 72 toxicity, but also allows to determine whether they originate from pyrogenic or petrogenic sources. 73 These are associated with a different health impact and environmental fate (Hindersmann et al., 2020; 74 Lima et al., 2005; Richter-Brockmann and Achten, 2018). Here, consideration of the alkylated PAH 75 distribution (i.e., the alkylation-index) in combination with the degree of aromatic condensation (i.e., 76 Mellitic acid (B6CA)/sum of Benzenepolycarboxylic acids (BPCAs)) has proven to be suitable, as it allows 77 even mixed PAH sources to be distinguished (Hindersmann et al., 2020; Wiedemeier et al., 2015).

A limited number of studies show that street runoff can also contain micropollutants that are typically
associated with municipal wastewater, such as pharmaceuticals, personal care products and food
ingredients (Fairbairn et al., 2018; Masoner et al., 2019; Sauvé et al., 2012).

Street drains are a major collection point for runoff, and therefore provide an ideal sampling point for
studying the nature of urban pollution.

The objectives of this study were to provide insights into the main types and concentrations of organic micropollutants in urban run-off as well as their sources, fate and potential toxicity. To this end, we (1) determined the levels of predominantly polar organic micropollutants in the aqueous and particulate phases of runoff via wide-scope target screening with LC-HRMS, (2) analyzed up to 62 parent and alkylated PAHs in these phases by GC-MS and (3) characterized the nature of the particles in the runoff via microscopic and chemical analytical methods. For this purpose, we collected and analyzed the particulate and water fractions in runoff of five street drains.

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91 2. Materials and Methods

92 2.1.Study site

Field sampling was carried out in the center of Aachen, a city in Western Germany with approximately 93 94 250,000 inhabitants. A dense building structure and high traffic intensity negatively affect ventilation 95 and air quality in some places (Merbitz et al., 2012). Five drains were chosen along an inner ring-road 96 (section S1). Two drains are characterized by the absence of green structures (mainly sealed surfaces) 97 and are located at the entrance (drain 1) and in the middle (drain 2) of a street canyon. Drains 3 and 4 are situated next to a grassy verge with high trees that gives way to a park area where drain 5 is located. 98 99 All street sections are frequented by trucks, buses as well as cars with similar total vehicle numbers 100 (Table S1b), but are remote from industrial areas (Bezirksregierung Köln, 2015). Adjacent buildings are 101 mainly residential houses with several stories.

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103 2.2. Sampling techniques

104 *Runoff traps.* For the collection of surface runoff, specially constructed sediment traps were placed in 105 the drains in August 2018 and recovered after one month. Three types of samples were obtained, 106 including (1) runoff sediment particles, (2) the overlying runoff water and (3) Passive Samplers (PS) 107 targeting the freely dissolved pollutants in the water phase. The runoff entering the drains was 108 directed via a series of sieves into a bucket-like trap, which retained up to 3 L of runoff-water and 109 collected the suspended particles via sedimentation (see Table 1). Water flow through the traps was 100 determined by coating the outer walls with plaster and measuring the weight loss due to dissolution (O'Brien et al., 2012) (S3). The water collected in the bottom bucket served as a reservoir for thecollected runoff, for the grab samples but also for the installation of the PS.

113 Passive sampling. Each trap was equipped with six silicone PS for the determination of time-weighted 114 average dissolved concentrations of the pollutants in the runoff water. The sampler material was polydimethylsiloxane (Specialty Silicone Products type M823), obtained from Shielding Solutions Ltd. 115 (Great Notley, United Kingdom). The silicone sheets were cut into 5 x 5 cm squares and pre-cleaned by 116 117 Soxhlet extraction with ethyl acetate for at least 100 hours. PS were used in kinetic mode. For 118 calibration, two methods were compared (i) a new approach using the concentration mass ratios 119 (CMR) of samplers with different thickness (Fuchte et al., 2020) and (ii) an established approach based 120 on the release rates of performance reference compounds (PRC) (Booij and Smedes, 2010). Thin 121 samplers consisted of one sheet with a nominal thickness of 0.2 mm while for the thick samplers two 122 sheets with a nominal thickness of 1 mm were pressed together. Each sheet was preloaded with a standard mix of 16 deuterated PAHs (1 μ g/sheet) as PRCs following the ICES guideline for silicone 123 124 samplers (Smedes and Booij, 2012). Triplicate samplers of both thicknesses were fixed between two pieces of stainless-steel mesh and these hung in the bottom bucket by suspending them from the sieve 125 126 above. Additional PRC-loaded sheets (3 of each thickness) that were not deployed were used as 127 process and blank controls and to determine the starting PRC concentrations. The levels accumulated 128 in the PS allowed investigation of additional urban micropollutants present in the runoff that could not 129 be measured in either the grab water or sediment samples. However, only the concentrations of 130 selected PAHs were converted to dissolved concentrations due to the lack of reliable silicone-water 131 partition coefficients and/or sampling rates for the other micropollutants.

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133 2.3. Sample preparation

An overview of the sample preparation and analytical methods with the corresponding references isgiven in Table 1 and the following sections. See section S2 for more details.

- 137 Table 1. Overview of the different types of samples collected as well as their preparation and analysis. The figure on the left
- 138 shows the three-part sediment trap with the passive samplers suspended in the bottom bucket. The outside of the trap was
- 139 coated with a layer of plaster to determine the volume of water flowing through.

Тгар	Sample	Analyte	Preparation	Analysis
		Sediment		
		16 EPA PAH	Soxhlet (acetone:n-hexane, 1:1) + SPE ¹	GC-MS
		62 PAH	PLE (dichloromethane) + SPE ¹	GC-MS
		Polar organic micropollutants	PLE (ethyl acetate:acetone, 1:1) + SPE ²	LC-HRMS
		BPCA	Acid digestion (nitric acid 65%) ³	LC-MS
		TOC/soot	Acidification (1M HCl)/ + oxidation (375°C) ⁴	CHN analysis
		Sample composition	Embedding in epoxy resin	Microscopy
		Passive samplers (C _{w-free})		
		16 EPA PAH	Shake out in methanol	GC-MS
		Polar organic micropollutants		LC-HRMS
		Grab samples (C _{w-total})		
		Polar organic micropollutants	Direct injection	LC-HRMS
		Water flow estimation		
	Land Per	Water volume	Drying plaster until weight constancy ⁵	Weighing loss

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Protocols taken/adapted from: ¹(Richter-Brockmann and Achten, 2018); ²(Machate et al., 2021); ³(Hindersmann and Achten, 2017); ⁴(Gustafsson et al., 1997); ⁵(O'Brien et al., 2012).

143 Abbreviations: BPCA: Benzene polycarboxylic acid; EPA: Environmental Protection Agency; PAH: Polycyclic aromatic

144 hydrocarbon; PLE: Pressurized Liquid Extraction; SPE: Solid phase extraction; TOC: Total organic carbon.

145 Chart of the trap designed by Natascha Beck; photos taken by Eva Germann.

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2.3.1. Sediment characterization

148 **CHN analysis.** Total organic carbon (TOC) and black carbon (BC) are two phases in which particularly 149 more hydrophobic organic micropollutants accumulate (Accardi-Dey and Gschwend, 2002). Carbon 150 analysis was based on the chemothermal oxidation method (CTO 375), and sample preparation is 151 described in (Gustafsson et al., 1997). For TOC determination this included inorganic carbon (IC) 152 removal by acidification. For BC determination, it required both, IC removal and non-BC (organic 153 carbon) removal by thermal oxidation at 375°C. Sediment amounts extracted for LC-HRMS and BPCA 154 analysis were based on the proportion of TOC to ensure comparable matrix effects.

BPCA analysis. Following the sample preparation steps of (Hindersmann and Achten, 2017), about
19 mg of dry ground sediment were weighed into glass reaction tubes and digested in nitric acid (65%)
overnight at 170°C. Extracts were dried, fully re-dissolved in 6 mL of MeOH and concentrated. A final
volume of 1 mL was spiked with the appropriate volume of a recovery standard (deuterated phthalic3,4,5,6-d4 acid, CDN Isotopes, Canada) to give a final standard concentration of 1 µg/mL for the LC-MS

analysis.

Microscopic analysis. For each drain sample, a small amount (around 0.8 g) of homogenized, dried sediment was embedded in epoxy resin. The resulting block was ground and polished perpendicular to the sedimentation level and thoroughly rinsed with water.

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2.3.2. Organic micropollutants in runoff

166 Sediment. Preparation of the sediment samples slightly differed according to the different analytical 167 methods. These typically included (1) homogenization of the sediment by stirring, (2) drying of the 168 sediment using sodium sulphate or by lyophilizing, (3) spiking with a deuterated 16 EPA PAH mix as 169 recovery standard, (4) solvent extraction and (5) a clean-up step by solid phase extraction. Sample 170 preparation for LC-HRMS samples followed (Machate et al., 2021) and for GC-MS was adapted from 171 (Meyer et al., 2013) for the 62 PAHs and from the EPA methods 3540C and 3630C for the EPA PAHs. 172 Three replicates per drain were analyzed for the EPA PAHs to check for homogeneity of the sediment. 173 Subsequently, 62 PAHs and 311 polar organic micropollutants were analyzed in one single sample per 174 drain.

175**Passive samplers (PS).** Silicone PS were carefully cleaned with a water-soaked tissue and extracted by176shaking three times overnight at 100 rpm in methanol. Sheets of 0.2 mm were extracted in 3 mL, sheets177of 1 mm in 15 mL of methanol. Extracts from the three repeat extractions were combined,178concentrated to 1 mL, filtered, and dried by passing through a pipette with sodium sulphate. For the179LC-HRMS screening 10 μ L of an internal standard mixture containing 40 isotope-labelled compounds180(1 μ g/mL) were added to 100 μ L of the extract.

181 **Water.** After removing the PS from the traps, the water collected in the bottom bucket was carefully 182 decanted into 2 L bottles such that the sediment remained in the bucket. For each drain an aliquot of 183 exactly 1 mL was taken from the top layer of water in the bottle and directly transferred into a 2 mL 184 autosampler vial and stored in the freezer until analysis. For the LC-HRMS screening 10 μ L of 2 M 185 ammonium formate buffer, 25 μ L of methanol and 25 μ L of an internal standard mixture containing 40 186 isotope-labelled compounds (40 ng mL⁻¹) were added to 1 mL of sample.

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188 2.4. Analytical methods

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2.4.1. Sediment characterization

190 **CHN analysis.** TOC and BC fractions were analyzed using a CHNOS element analyzer Vario EL III 191 (Elementar Analysensysteme GmbH). Four replicates of 20-25 mg ground sediment from each drain 192 were analyzed for carbon (C), hydrogen (H) and nitrogen (N). A standard reference soil was used to 193 check for measurement accuracy. BPCA analysis. LC–MS analysis was conducted on a Prominence XR UFLC (Shimadzu) equipped with a
 Poroshell 120 SB-C18 column (2.1 mm × 150 mm, 2.7 μm, Agilent) and coupled to a Maxis 3G UHR
 QTOF MS (Bruker Daltonik). Method parameters correspond to those used in (Hindersmann and
 Achten, 2017).

Microscopic analysis. Counting of the sediment components (1,000 counted points) was done following ISO 7404-3 with a reflected light microscope at 700 x magnification under both white and blue (fluorescence) light. In addition, the surface areas of the rubber particles (rubber abrasion) were determined with the software program 'Fossil' (Carl H. Hilgers Technisches Büro).

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2.4.2. Organic micropollutants in runoff

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2.4.2.1. LC-HRMS target screening of polar organic micropollutants

Using a target screening approach, 311 micropollutants were analyzed in the sediment, 503 in the PS and 497 in the water grab samples using an Ultimate 3000 LC system (Thermo Scientific) coupled to a QExactive Plus MS (Thermo Scientific), via a heated electrospray ionization source. Compounds were separated on a Kinetex EVO C18 (50 × 2.1 mm, 2.6 µm, Phenomenex) column equipped with a precolumn (C18 EVO 5 × 2.1 mm) and inline filter.

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2.4.2.2. GC-MS analysis of PAHs

16 EPA PAHs. Analysis was performed using an Agilent7890 A GC system with a 5975 C inert XL MSD
in selected ion mode (SIM). The compounds were separated on a DB-5ms column (30 m × 0.25 mm,
0.25 μm, DuraGuard, 10 m, Agilent). Method parameters are described in (Fuchte et al., 2020).

215 62 PAHs including alkylated PAHs. For analysis of the extended set of PAHs, a QP2010 Plus GC-MS 216 system (Shimadzu) with a Rxi-PAH GC column (60 m, 0.25 mm ID, 0.1 µm film thickness, Restek, USA) 217 was used. Analytical method details are described in (Hindersmann and Achten, 2018; Meyer et al., 218 2013). A set of 62 two to seven ring PAHs and 16 deuterated EPA PAHs as recovery standards were 219 quantitatively analyzed in SIM. In addition, a number of parent PAHs (CO) as well as their alkylated 220 homologs (C1–C4) were semiquantitatively analyzed in full scan mode using their molecular ion mass 221 to charge ratios (m/z) within defined retention time windows (Hindersmann and Achten, 2018; Stout 222 et al., 2015). PAH carcinogenicity was calculated by multiplying the PAH toxic equivalency factors (TEFs) 223 listed in Table S4 (Nisbet and Lagoy, 1992; Richter-Brockmann and Achten, 2018) by the respective 224 PAH compound concentrations. The PAH alkylation-index was calculated as sum of parent PAHs/(sum 225 of parent PAHs + sum of dialkylated PAHs) (Hindersmann et al., 2020).

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227 **2.5.** Quality assurance

Process controls of the PS and method blanks for the sediment extraction were used to check for contamination during sample processing and spiked deuterated PAH standards served for recovery control (Table E1).

For both GC-MS and LC-HRMS measurements, quality assurance procedures included solvent blank and check standard measurements, as well as the use of internal standards. For the analysis of the 16 EPA PAHs, external calibration was performed since the 16 deuterated EPA PAHs were used as PRCs. Final sample volumes were calculated by weight. Naphthalene has been excluded from the PS results due to variable contamination of naphthalene in the process controls. In LC-HRMS analysis, the internal standards were used for monitoring mass accuracy and retention time stability.

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238 3. Results and discussion

3.1. Site characteristics and sampling performance

240 Site parameters. Sediment amounts collected in the traps were highest for drain 3 at almost 500 g dry weight (DW) and ranged between 80 and 180 g DW in the other four drains. Water volumes passing 241 242 through the traps estimated using the dissolution of the plaster coating varied between 1000 and 243 2500 L. The highest volumes were observed for drain 2, which is exclusively surrounded by sealed 244 surfaces. The PRC- and the CMR-techniques applied for PS calibration (Booij and Smedes, 2010; Fuchte 245 et al., 2020) resulted in similar sampling rates (R_s; Table S2), which were applied to determine the 246 freely dissolved concentrations (C_{W-free}) of 15 EPA PAHs (excluding Naphthalene, Table E3). In drain 2, 247 the PAH amounts in the thin samplers could not be determined and R_{S-PRC} was calculated from the thick 248 samplers. All details on the site characteristics are given in Table S2.

Sediment characterization. TOC fractions in the sediments from the different drains ranged between
9 and 23%. Similar percentages of TOC have been measured in the sediments collected from tunnel
wash waters (8-9%; (Allan et al., 2016) and in harbor sediments (0.4-39%; (Jartun et al., 2008) in
Norway.

BC fractions ranged between 0.26 and 0.64%. Similar proportions of BC were measured via CTO 375 in Boston Harbor sediments (0.26-0.6%; (Accardi-Dey and Gschwend, 2002). Much higher BC contents were measured in pure traffic related matrices such as car tires (30%) and diesel particulate matter (80%) (Gustafsson et al., 1997). Overall, the BPCA measurements confirm the determined range of BC contents, but suggest slight differences between vegetated (drain 3, 4 and 5) and non-vegetated (drain 1 and 2) sites (Table S2; E7).

Microscopic analysis of the sediment composition (Table S5) revealed higher percentages of plant remains in drains 4 and 5 (64-67%) compared to the other drains (36-52%). In drain 3, the plant remains were highly decomposed. In fact, this sample stood out since the percentages of decomposed plant 262 material were two to four times higher compared to the other sites. In contrast, drains 1 and 2 without 263 vegetation in the nearby surroundings could be distinguished by their three to six times higher 264 percentages of rubber, e.g., from tire wear. This difference was further confirmed by the 265 measurements of the rubber particle surface areas (total per drain), which were found to be up to 266 three times higher in these two drains. Combustion residues were highest in drain 3 (3.6%), which 267 might be due to its location at a green space with a parking area (Table S1a). Here, cold engine starts 268 could have led to increased emissions. Also worth mentioning was a number of cyan pigment particles 269 of unknown origin, which fluoresced remarkably strongly, and were observed in all five drains (see 270 Figure S7 for microscopic pictures of particle classes).

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3.2. Organic micropollutants in runoff

273 From the set of 564 micropollutants analyzed as part of the LC-HRMS screening, 187 compounds 274 were detected in one or more drains in at least one of the sampled matrices: sediment (92), water 275 (87) or PS (128) (Table E5). Additionally, 62 PAHs were quantified in sediment and 15 in the PS using 276 GC-MS. The micropollutants included typical traffic-derived groups such as corrosion inhibitors, 277 rubber additives and the PAHs, but also groups that would rather be expected in domestic 278 wastewater (e.g., pharmaceuticals, lifestyle products and sweeteners). Besides determination of 279 their environmental levels, the group of PAHs was further used as model substances for sediment-280 water partitioning (3.2.3) and as markers for source identification (3.3).

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3.2.1. Traffic derived micropollutants

283 Polar organic pollutants. In all matrices the benzothiazoles, benzotriazoles and organophosphates, all 284 known as urban and traffic-derived pollutants, were strongly represented, and when summed up 285 accounted for up to 80% of the total polar organic micropollutant loads (see Figure 1). In sediment the most prominent substance was dicyclohexylphthalate (median of 5 drains = 3.3 mg/kg DW), a plastic 286 287 additive that has been observed in indoor air from cars, buses, taxis and subways (Chi et al., 2017). In 288 addition, 2-(methylthio)benzothiazole (MTBT, 1.6 mg/kg DW) which is a transformation product of the 289 vulcanization agent 2-mercaptobenzothiazole (and its derivatives), was found at high concentrations. 290 In the PS, dicyclohexylphthalate (median 2.1 mg/kg silicone) and two organophosphate flame 291 retardants, tri-isobutylphosphate (TiBP, 1.6 mg/kg silicone) and tris(1-chloro-2-propyl)phosphate 292 (TCPP, 1.6 mg/kg silicone) were dominant. TCPP has been suggested to stem from car interiors and has 293 been found in snow samples close to a road intersection (Marklund et al., 2005). Both, TiBP and TCPP 294 have also been found in two highway sedimentation ponds close to Oslo, but generally at lower 295 concentrations (Grung et al., 2021).

296 In the water fraction, the most abundant substance was 2-benzothiazolesulfonic acid (BTSA, median 297 52.2 µg/L), an oxidative transformation product of 2-mercaptobenzothiazole and its derivatives. BTSA 298 concentrations stand out clearly in the group of benzothiazoles, which goes along with the findings of 299 (Kloepfer et al., 2005), who observed it to be dominant in runoff from an inner-city motorway in Berlin 300 with concentrations of up to 55 μ g/L. Comparably dominant in the water fraction was 1,3-301 diphenylguanidine (DPG, 42.9 µg/L). Its concentrations were slightly above the predicted no effect 302 concentration for freshwater (30 μg/L) (European Chemicals Agency (ECHA), 2021). Good correlations 303 were observed between rubber particles (in Vol. %) and MTBT concentrations in the water phase, 304 normalized to the sum of micropollutants (R-value of 0.92, see Figure S3a). This is in accordance to the 305 findings of (Asheim et al., 2019), who proposed MTBT as a suitable marker for tire leaching. 306 Interestingly, the MTBT water concentrations in this study were markedly higher (1.5-8.8 μ g/L) than 307 those observed by (Asheim et al., 2019) (17-195 ng/L). A reason could be the different sampling 308 approaches, since the more integrative nature of the sediment trap would allow for longer leaching 309 times than a wet collector with subsequent filtration. The above mentioned traffic-related pollutants, 310 as well as further representatives, should be considered for urban spaces as they can occur at high 311 concentrations, and after leaching (e.g., from tire wear) may become mobile and pose a risk to aquatic 312 environments (Müller et al., 2021). Tris(2-chloroethyl)phosphate (TCEP) and benzotriazole have been 313 classified by the German Environment Agency as potentially persistent, mobile and toxic (PMT) and 314 very persistent and very mobile (vPvM), respectively. Furthermore, DPG and benzothiazole have also 315 been identified as potential PMT pollutants (Neumann and Schliebner, 2019). A further group of 316 pollutants that are often present in street runoff are perfluorinated compounds (PFCs) (Spahr et al., 317 2020). PFCs are of concern as persistent contaminants in soil and water, even in drinking water. In this 318 study, Perfluorooctanesulfonic acid (PFOS) was detected in drain 1 with water concentrations (2.6 319 ng/L) 4 times higher than the annual average Environmental Quality Standard (AA-EQS) set by the 320 Water Framework Directive. Perfluorooctanoic acid (PFOA) is not regulated as a priority hazardous 321 substance but was detected in the runoff water of all five drains (3.0-7.5 ng/L). Concentrations were 322 comparable to or lower than those reported from earlier runoff studies, and similar to the 323 concentration levels observed for rainfall (Murakami et al., 2009; Nguyen et al., 2011; Wilkinson et al., 324 2016). A frequently detected PFC precursor, 6:2 fluorotelomer sulfonic acid, was sporadically found in 325 the sediment (15-90 μ g/kg) and the water phase (5-10 ng/L). Similar water concentrations have been 326 found in an urban catchment in Singapore (median values of 0.7-7.8 ng/L) (Nguyen et al., 2011).



Figure 1. Polar organic micropollutant concentrations in (a) runoff particles [µg/kg DW] and (b) water grab samples [ng/L] 328 329 examplarily shown for drain 1. The graphs include only those substances that were detected in at least one drain. See 330 section S4 for the corresponding diagrams of the other drains and for the list of substances to which the numbers refer. See 331

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Polycyclic aromatic hydrocarbons. From the total pollutant concentrations of 12-43 mg/kg DW 333 334 measured in the runoff particles, the PAHs represented a significant portion. The PAH contribution to 335 the total concentration in drain 3 was 71% (which is consistent with the high microscopical counts of 336 soot, combustion material, soft brown coal and bitumen/pavement), and 34 – 57% in the other drains. 337 The total concentrations of the 62 PAHs measured in the particle fractions (ΣPAH_{62}) were relatively 338 similar, ranging between 7 and 23 mg/kg DW. These concentrations are in line with earlier studies 339 investigating urban runoff in stormwater traps, a storm sewer outlet or sedimentation ponds (Girardin 340 et al., 2020; Jartun et al., 2008; Zgheib et al., 2012). When compared to the Interim Sediment Quality 341 Guideline (ISQG) of the Canadian Council (Canadian Council, 1999; Zgheib et al., 2012), PAH concentrations exceeded the ISQG-values in almost all cases by factors of up to 50. This was especially 342 343 true for more hydrophobic PAHs. High molecular weight (HMW) PAHs (≥ four rings) comprised the major proportion, with 79% (drain 4) up to 92% (drain 5). This suggests a mainly pyrogenic source for 344 345 these compounds, especially at drain 5. When examining the individual PAHs, these showed the typical pattern for traffic-related/urban samples (Gasperi et al., 2012; Lohmann et al., 2011). Fluoranthene 346 347 (10-14% of the sum of PAHs) and pyrene (10-13%) dominated the PAH patterns followed by 348 benzo[b]fluoranthene, benzo[ghi]perylene, chrysene and phenanthrene (despite this varying more 349 between 3-11%). Cyclopenta[cd]pyrene concentrations were particularly high at the street canyon sites (1.6-1.9%) compared to those drains surrounded by vegetation (0.2-0.9%) (Figure 2a, E6). This 350 351 might be due to higher levels of gasoline combustion (Larsen and Baker, 2003) at these sites with high 352 traffic loads and probably also less aeration. In addition to the combustion of fuels, automobile tires

can be a potential source of PAHs, including the dibenzopyrene isomers with their known highcarcinogenicities (Sadiktsis et al., 2012).



Figure 2. (a) Runoff particle concentrations of 62 PAHs (mg/kg dry weight (DW)) measured in drain 1 as an example. Most dominant PAHs included phenanthrene (Phe), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd)pyrene (IndP), benzo[ghi]perylene (BghiP), coronene (Cor) and cyclopenta[cd]pyrene (CcdP). See section S4 for the corresponding diagrams of the other drains and for the list of substances to which the numbers refer. See E5 for the table of measured concentrations. HMW PAH=High molecular weight PAHs; LMW PAH=low molecular weight PAHs.

361 (b) Contributions of the EPA-PAHs (EPA), 7H-benzo[c]fluorene (BcFlu), the dibenzopyrene isomers (DBPyr) and the remaining 362 PAHs to the total concentration (Σ PAH 24) vs. the toxic equivalents (TEQ PAH 24) in drain 1.

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PAHs are often responsible for the major portion of any observed sediment toxicity (Durant et al., 1998; Markiewicz et al., 2017). Potential carcinogenic toxicity was estimated from a set of 24 PAHs for which toxicity data were available (Richter-Brockmann and Achten, 2018). Figure 2b shows that the largest contribution to the toxicity comes from the non-EPA PAHs, particularly from 7*H*benzo[*c*]fluorene and the dibenzopyrene isomers. The EPA PAHs account for only 19 to 36% of the toxic equivalents (TEQ₂₄). This highlights the importance of monitoring and regulating those additional non-EPA PAHs that are particularly relevant for human health.

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3.2.2. Micropollutants from other urban sources

The above sections concentrated on micropollutants derived from traffic-related sources. In the following compounds from other sources are considered. 375 Industrial substances. Industrial pollutants often occurred at high concentrations, in sum accounting 376 for 8-27% of the total polar organic micropollutant loads (see Figure 1). As there are mainly residential 377 houses present in the direct catchment area of the drains, it is likely that these chemicals were at least 378 partly released from households. Other sources such as long-range transport or leaching from garbage 379 should also be considered. Those substances with the highest concentrations in the PS 380 (hexa(methoxymethyl)melamine; 1-2 mg/kg), water (N-butylbenzenesulfonamide; 4-5 μ g/L) and 381 sediment (o-toluidine; 0.3-1.8 mg/kg DW) are also used in rubber or plastic manufacturing and may 382 thus additionally stem from vehicles. Some of the industrial substances, namely 2,4-dinitrophenol, 2,4-383 dichlorophenol, hexa(methoxymethyl)melamine, N-butylbenzenesulfonamide, N-methyl-2-384 pyrrolidone and triphenylphosphine oxide, have been listed by the Norman network as potentially 385 relevant for ecosystem health (Brack et al., 2012). They have been detected earlier in the environment 386 in varying concentrations (Blum et al., 2018; Emadian et al., 2021; Kandie et al., 2020; Krauss et al., 387 2019; Mohammadi et al., 2017; Peng et al., 2018), but have not been included to date in routine 388 monitoring programs at EU level.

389 Pesticides. A large number of pesticides was found in the runoff (see Figure 1). These generally 390 occurred at low concentrations (medians of 4 µg/kg in sediment (DW), 13 ng/L in water and 2 µg/kg in 391 silicone). Furthermore, depending on their physico-chemical properties these were mostly found in 392 only one of the three sampled matrices. Urban parks and roadside vegetation are possible sources of 393 pesticides, such as herbicides, fungicides and insecticides (Spahr et al., 2020), but no particular 394 patterns could be observed when comparing the greened and non-greened sites (Table S1a). 395 (Bollmann et al., 2014) considered leaching from construction materials, such as building facades and 396 roofs, as an important emission source of biocides including carbamates, phenylureas, triazines and 397 triazoles. Regarding these classes, carbendazim (log K_{ow}=1.8) and isoproturon (2.6) were mainly found 398 in water but also in the PS. In contrast, terbutryn (2.9), epoxiconazole (3.7), tebuconazole (3.7), 399 propiconazole (4.3) and prosulfocarb (4.2) were found mainly in the sediment and PS, which is 400 expected given their higher octanol water partition coefficients (all log Kow based on calculations from 401 Chemxaxon Calculator Plugins). Diuron (2.5) was found in all three matrices. Water concentrations in 402 this study were in the same range or below those for stormwater or sewer overflows reported in earlier 403 studies (Bollmann et al., 2014; Paijens et al., 2021; Spahr et al., 2020). The most abundant pesticide in the sediment phase was fenpropimorph (8-31 μ g/kg DW), a fungicide generally applied as a wood 404 405 preservative that was phased out in April 2019. In the water phase the insect repellents icaridin and 406 DEET were most prominent with concentrations of around 100 ng/L. The latter is known to be 407 ubiquitous (Masoner et al., 2019), and has even been detected in rain water but at around ten times 408 lower concentrations (Ferrey et al., 2018). The presence of pesticides in all five drains raises the 409 question of whether road runoff is a significant source of pesticides in urban environments. Pesticides are bioactive compounds for which a specific interaction with aquatic organisms must be considered.
Some of the pesticides detected in water are regulated by the (European Commission (EC), 2013)
(terbutryn, diuron, isoproturon and atrazine) or as river-basin-specific pollutants in Germany (OGewV,
2016) (bentazone, flufenacet, mecoprop, flurtamone, carbendazim and epoxiconazole). However, EQS
were not exceeded in any of the runoff water samples.

415 Domestic compounds. Several pharmaceuticals were present in water (6-11 ng/L), sediment (13-36 416 µg/kg DW) and/or the PS (2-8 ng/kg silicone). These included acetaminophen (sediment, PS), 417 diclofenac (PS, sediment), lidocaine (PS), carbamazepine (water, PS) and tetracaine (water). The 418 pharmaceuticals, the sweeteners cyclamate and acesulfame (1-2 µg/L), the bittering agent 419 denatonium (0.5-1.5 μ g/L) and the stimulants caffeine and cotinine (a human metabolite of nicotine) 420 measured in the water phase, point to possible influences of human waste in the runoff water. This 421 influence is rather surprising, as in this study the runoff water was collected directly below the gully 422 cover and could not get in contact with any wastewater from households. A rise in the level of the 423 sewer water to the level of traps only happens in exceptional cases and can be excluded during the 424 four weeks of the sampling campaign. Some of these substances have been found in earlier studies 425 investigating storm water in canals, pipes or storm sewers (Beckers et al., 2018; Fairbairn et al., 2018; 426 Masoner et al., 2019). Caffeine and cotinine were measured at rather high levels in this study (3-45 427 μ g/L and 1.7-4.2 μ g/L, respectively) compared to the median values reported by (Masoner et al., 2019) 428 $(0.9 \text{ and } 0.05 \mu g/L)$ and (Fairbairn et al., 2018) (0.2 and 0.5 $\mu g/L$). Here, the improper disposal of coffee 429 (cups) and cigarettes, but also urination, might be a reason, particularly since the drains are located 430 directly at the sidewalk. (Sauvé et al., 2012) measured fecal contaminants as well as caffeine and 431 carbamazepine in an urban storm water collection system and proposed that caffeine concentrations 432 of >400 ng/L are a good indicator of a contamination by sanitary sources (i.e. coliform counts >200 433 colony forming units per 100 mL water). In addition to contamination by organic contaminants, this 434 could thus imply a further risk to surface waters and public health due to enteric pathogens (Sauvé et 435 al., 2012; Sidhu et al., 2013).

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437 3.2.3. Micropollutant partitioning among different matrices

As visible in Figure 1, measuring in different matrices appears to be crucial for capturing the full range of organic pollutants that are present in urban environments. Industrial chemicals and the bittering agent denatonium, for instance, were predominantly measured in the water phase whereas food ingredients were mainly found in the sediment fraction. Interestingly, around 30 substances, present at low concentrations, were detected uniquely in the PS. These included for instance surfactants (including mostly long-chain aliphatic amines), the pharmaceuticals diclofenac and lidocaine, several pesticides and industrial chemicals, as well as the rubber additive benzothiazole and the plasticizer triisobutylphosphate. Therefore, PS is a promising tool for substances that are difficult to quantify
directly in the water phase.

447 Relating the TOC normalized sediment concentrations to the freely dissolved concentrations (C_{S-TOC}/C_{W-} _{free}) revealed differences in the sorption behavior of the EPA PAHs in the different runoff sediments. 448 449 Figure S5 shows the in-situ $\log K_{OC}$ values plotted against the respective $\log K_{OW}$ values of the PAHs 450 obtained from (Smedes et al., 2009). The slopes were similar for all five drains with the linearity 451 suggesting equilibrium between both phases. However, the absolute K_{OC} values of the pollutants 452 detected in drain 5 were markedly higher than those from the other four sites. One reason might be 453 that the composition of the sediment matrix, and in particular the organic fraction, differed in drain 5. 454 The higher sorption fits to the observation of the most pyrogenic PAH alkylation-index in drain 5. In 455 contrast, the BC fraction (Table S2) and degree of aromatic condensation did not provide indications 456 for a notably increased soot content in drain 5. Differences in particle size were not visible from the 457 microscopic analysis (Figures S6). Another possibility is that rubber particles might hamper the 458 extraction efficiency of PAHs even when using harsh extraction methods as suggested by (Wagner et 459 al., 2018). The number of rubber particles was lowest in drain 5, which might have led to relatively 460 higher extractable PAH amounts.

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462 3.3.PAH sources – petrogenic or pyrogenic?

Two methods were applied to identify whether the PAHs had a petrogenic or pyrogenic source. Firstly, 463 464 quantification of a number of non-alkylated parent PAHs (C0) and their alkylated homologs (C1-C4). 465 Secondly, the analysis of benzene polycarboxylic acids (BPCA) (Hindersmann et al., 2020; Wiedemeier 466 et al., 2015). Regarding the distribution of the alkylated PAH isomers in the sediment fraction, high 467 concentrations of parent compounds and decreasing concentrations of the C1 to the C4 homologs 468 were observed for all drains (Figure 3b; Figure S4 in detail). Proportions of the C0 ranged between 48% 469 and 68% and were highest in drain 3 and 5. The PAH alkylation-index [$\Sigma CO/(\Sigma C0+\Sigma C2)$] (Hindersmann 470 et al., 2020) was 0.79 and 0.73 for drains 1 and 2 and between 0.83 and 0.89 for drains 3 to 5. This 471 indicates that in all drains, but especially in drains 3, 4 and 5, the PAHs can be mainly attributed to pyrogenic sources. With regards to the BPCA analysis, relatively high B6CA/BPCA ratios of 0.47-0.64 472 473 were calculated, pointing to a high degree of aromatic condensation. This ratio was also highest in 474 drains 3, 4 and 5. In a study on urban soils and other PAH source materials, (Hindersmann et al., 2020) 475 combined both analytical outputs in a single graph by plotting the B6CA/BPCA ratio (degree of aromatic 476 condensation) against the PAH alkylation-index. Samples with known pyrogenic origin plotted in the 477 upper right and samples from primary petrogenic sources in the lower left corner. When charting the 478 data coming from the five drains in this graph (Figure 3a) the drain samples all plot in the upper right 16



Figure 3. (a) Classification of PAH sources for the five sampling sites obtained by plotting the PAH alkylationindex [$\sum CO/(\sum CO + \sum C2)$] against the degree of aromatic condensation [B6CA/BPCA] (classification by colors, lines and labels are adopted from the original graphic in (Hindersmann et al., 2020). All runoff samples plot in the upper right area, indicating a mainly pyrogenic source. (b) The alkylated distribution pattern is depicted at the bottom, showing the typical pyrogenic slope shape, with high percentages of parent compounds (CO) and decreasing percentages of their alkylated homologues (C1-C4). Each bar expresses the share of the respective homologue to the sum of concentrations.

479 corner, as was observed by (Hindersmann et al., 2020) for different kinds of solid pyrolyzed residues.
480 Even if their position in the diagram clearly points to a pyrogenic origin, drains 1 and 2 show somewhat
481 lower values on both axes. It might be suggested that the two sites are influenced by petrogenic
482 sources or that the presence of vegetation at drain 3, 4 and 5 had an impact. In terms of sediment
483 composition (Table S5), the three drains stand out slightly due to higher plant residues (drain 4 and 5)
484 or higher amounts of decomposed organic matter (drain 3). It remains to be clarified, if differences in

biogenic carbon contents had an influence. Humic substances have been observed to lead to the
formation of B6CA and could thus have shifted the ratio towards a more pyrogenic source (Chang et
al., 2018; Gerke, 2019; Poot et al., 2009).

488 With a view to drains 1 and 2 without vegetation, higher microscopic counts of rubber particles suggest 489 higher traffic impacts at these two sites. (Stout et al., 2004) reported petrogenic PAH signatures in 490 diesel soot, used motor/hydraulic oil, and petroleum-based road asphalt. An influence of these as a 491 source of particles might have led to the slight shift in the signatures of drains 1 and 2 to the lower left 492 (Figure 3a). (Grung et al., 2021) observed a dominance of alkylated PAHs (i.e. a petrogenic pattern) in 493 road runoff from Norway, where asphalt- and tire abrasion was high due to the use of studded winter 494 tires. Abrasive particles as the cause of the higher petrogenic influence in drains 1 and 2 might thus 495 also be considered as a factor. As visualized in Figures S3b, the alkylation-index shows a relatively good 496 correlation with either the microscopically determined volume (R=0.75) or total surface area (R=0.87) 497 of the rubber particles.

498

499 **4.** Conclusions

500 A huge range of organic micropollutants, including large numbers of PAHs, was found in the road 501 runoff, providing new insights into urban pollutant mixtures, their sources as well as a more realistic 502 assessment of the combined PAH toxicity. The amounts and composition of these pollutants differed 503 significantly, depending on the sampled matrix (i.e., the runoff sediment or water phase). Some 504 substance groups occurred at high levels such as the rubber and plastic additives or even exceeded 505 regulatory limits (PAHs). However, given the collected runoff is subject to additional processes (e.g., 506 contaminant degradation, dilution) before entering surface waters, such elevated levels do not 507 automatically imply a risk to surface waters. Nevertheless, their presence emphasizes that additional 508 purification and dilution processes are necessary for negating any potential harmful effects prior to 509 release. Not all environmentally relevant substances that were detected are in fact considered in 510 existing regulations. In this study we highlight, for instance, the non-EPA PAHs such as 7H-511 benzo[c]fluorene and the dibenzopyrene isomers which have a marked impact on the total PAH 512 toxicity. Pollutants leaching from tire wear are also worth emphasizing as some of them are highly 513 mobile in aqueous environments. MTBA was confirmed as a tire leaching marker in this study. A 514 correlation was also found between the rubber particle number and alkylation-index, and it could be 515 valuable to evaluate this in more detail with a hydrophobic and robust tire particle marker and to 516 additionally determine the alkylation-index of pure tire or asphalt abrasion. Under the study 517 conditions, the runoff trap proved to be a suitable tool for obtaining local samples from well-defined 518 drain catchments. The addition of PS in the water phase was useful, e.g. for the assessment of priority 519 and other pollutants with low environmental quality standards and for determining bioavailable

- 520 concentrations. However, when using PS to provide quantitative levels, it is crucial to have accurate
- 521 silicone-water partition coefficients for the compounds.
- 522 In summary, for monitoring and controlling pollution in urban runoff we suggest to:
- include environmentally relevant non-EPA PAHs, PFOA as well as mobile and persistent organic
 pollutants (e.g., some of the rubber additives). For this, the sampling of different runoff matrices,
- as well as passive sampling, are recommended.
- regularly remove and properly dispose of particles collecting on road surfaces to avoid these being
 washed into the sewers. This could be achieved through road sweeping (Breault et al., 2005),
 frequent cleaning of the sludge trapping buckets commonly installed in street drains and a well designed stormwater management regime.
- 530 3) develop quality guidance for stormwater priority pollutants as proposed by (Spahr et al., 2020) via
- 531 a combination of ecotoxicological testing and studies on their distribution and fate in the 532 environment.

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- 547

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