



## Particle phase distribution of polycyclic aromatic hydrocarbons in stormwater — Using humic acid and iron nano-sized colloids as test particles

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1 Particle Phase Distribution of Polycyclic Aromatic Hydrocarbons in Stormwater – Using Humic Acid  
2 and Iron Nano-sized Colloids as Test Particles

3

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## 10 **Abstract**

11 The distribution of polycyclic aromatic hydrocarbons (PAHs) in different particulate fractions in  
12 stormwater: Total, Particulate, Filtrated, Colloidal and Dissolved fractions, were examined and  
13 compared to synthetic suspensions of humic acid colloids and iron nano-sized particles. The  
14 distribution of low-molecular weight (LMW PAHs), middle-molecular weight (MMW PAHs) and  
15 high-molecular weight (HMW PAHs) among the fractions was also evaluated. The results from the  
16 synthetic suspensions showed that the highest concentrations of the PAHs were found in the Filtrated  
17 fractions and, surprisingly, high loads were found in the Dissolved fractions. The PAHs identified in  
18 stormwater in the Particulate fractions and Dissolved fractions follow their hydrophobic properties. In  
19 most samples > 50% of the HMW PAHs were found in the Particulate fractions, while the LMW and  
20 MMW PAHs were found to a higher extent in the Filtrated fractions. The highest concentrations of  
21 PAHs were present in the stormwater with the highest total suspended solids (TSS); the relative amount  
22 of the HMW PAHs was highest in the Particulate fractions (particles > 0.7  $\mu\text{m}$ ). The highest  
23 concentration of PAHs in the Colloidal fraction was found in the sample with occurrence of small  
24 nano-sized particles (< 10nm). The results show the importance of developing technologies that both  
25 can manage particulate matter but also effectively remove PAHs present in the Colloidal and Dissolved  
26 fractions in stormwater.

27 **Keywords:** Colloid enhanced transport, liquid – liquid extraction, solid phase extraction,  
28 particle sorption, urban stormwater

## 29 **1 Introduction**

30 During the last decades, growing urbanization and increased anthropogenic activities have turned urban  
31 stormwater into a pollution source for receiving waters (Eriksson et al., 2007; Björklund et al., 2011;  
32 Barbosa et al., 2012; Deffontis et al. 2013). The concern of pollution of receiving waters has yielded  
33 The European Water Framework Directive (2000/60/EC) for protection and restoring of clean water  
34 across Europe to ensure its long-term sustainable use. Consequently, pressures exist for implementing  
35 efforts in urban areas to collect the stormwater and remove the pollutants closer to the pollution  
36 sources, i.e. structural best management practices (BMPs) (Liu et al. 2014). The most frequently  
37 applied techniques are construction of artificial wetlands and wet stormwater ponds for sedimentation  
38 of particulate pollution (Pitcher et. al. 2004). These treatment facilities are effective if the pollutants are

39 sorbed to particles which readily settles, i.e. particles  $> 0.45 \mu\text{m}$  (Howitt et al., 2014; Bin et al., 2011;  
40 Grolimund et al., 2005; Pettersson 1998). However, from recent research, it is clear that pollutants  
41 substantially are sorbed onto colloidal particles, and therefore cannot be effectively removed in the  
42 treatment facilities operating today (Kalmykova et al. 2013, Nielsen et al. 2015). Several stormwater  
43 priority pollutants, notably toxic metals and polycyclic aromatic hydrocarbons (PAHs), have been  
44 associated with colloidal material ( $< 1 \mu\text{m}$ ) in the water (Aryal et al. 2013, Xanthopoulos and Hahn  
45 1990). Kalmykova et al. (2013) have shown that particles  $< 0.7 \mu\text{m}$  could considerably contribute to the  
46 transport of organic pollutants in landfill leachate, stormwater from urban areas and waste-sorting sites.  
47 Despite the documented association of PAHs with colloidal particles, the related particle size  
48 distributions (PSD) have not been shown. A greater knowledge of the PSD and general particle  
49 characteristics of the colloids transporting the PAHs in stormwater would benefit the targeted  
50 development of stormwater treatment facilities, and explain the reasons why PAHs are analysed in  
51 receiving waters.

52 Higher traffic activities have shown a positive correlation with increasing levels of PAHs in stormwater  
53 (Moilleron et al., 2002; Murakami et al., 2005; Van Metre et al., 2000). Even though emission control  
54 strategies and exchange of fuels have been implemented, increased concentrations of PAHs have been  
55 found in urban sediments (Hwang et al., 2006). An important identified source of PAHs in stormwater  
56 are highly aromatic (HA) oils added to rubber tires (Wik and Dave, 2005; Norin and Strömvall, 2004).

57 The categorization of PAHs according to molecular weight follows the definitions by the Agency for  
58 Toxic Substances and Disease Registry (ATSDR), under the US Environmental Protection agency  
59 (U.S. EPA, 1995): Low-molecular weight PAHs (LMW PAHs) are naphthalene, acenaphthene and  
60 acenaphthylene (two and three ring structures), medium-molecular weight PAHs (MMW PAHs) are  
61 fluorene, phenanthrene, anthracene, fluoranthene and pyrene (three- and four ring structures). The  
62 group of high molecular weight PAHs (HMW PAHs) comprises PAHs with four to six rings, i.e.  
63 benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene,  
64 dibenzo[a,h]anthracene, benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene. Carcinogenic effects have  
65 been quantified for the MMW PAHs and HMW PAHs (Palm et al., 2011). Therefore it is important to  
66 study how the PAHs in the different groups are distributed among the Particulate, Colloidal and  
67 Dissolved fractions in stormwater. Depending on the different distribution pattern of the groups of

68 PAHs, combinations of different treatment technologies are needed for sustainable and efficient  
69 treatment approaches for the PAHs in stormwater. This may involve a step where larger particles  
70 containing most of the HMW PAHs are separated, as for example by sedimentation, combined with  
71 techniques for sorbing or oxidizing the dissolved, LMW PAHs, as well as the colloids carrying the  
72 MMW PAHs (Kalmykova et al., 2014).

73 The aim of this study is to investigate the distribution of PAHs associated to nano-sized particles,  
74 colloids and particulate matter in urban stormwater, collected at two different stormwater treatment  
75 facilities. The collected samples were analysed for the content of LMW PAHs, MMW PAHs and  
76 HMW PAHs in the fractions: Total-, Particulate-, Filtrated-, Colloidal- and Dissolved- fractions  
77 including nano-sized particles. As the chemical composition of the colloids and the particles, and the  
78 particle size distributions in the stormwater samples were unknown, and are expected to vary both in-  
79 between and within runoff events, test particles based on documented humic acid nano-sized (HA-n)  
80 colloids and nano-sized iron(III) (Fe) particles in suspensions were used as references (Nielsen et al.  
81 Submitted), to investigate the distribution of PAHs among the fractions for an organic and inorganic  
82 colloid/particle suspension.

83 The hypotheses were that: i) The PAHs will be distributed in different fractions depending on the  
84 molecular weight and, physico-chemical properties of the PAHs, i.e. the HMW PAHs will sorb to  
85 particles, the MMW PAHs will be found the colloidal phase and the LMW PAHs in the dissolved  
86 phase (Kalmykova et al., 2013), ii) A difference in the groups of PAHs sorbed to the inorganic and  
87 organic test particles is expected, due to different sorption pattern(Boyd et al. 2001; Celis et al. 2006;  
88 Luo et al. 2008), iii) The amount of PAHs found in the Total fraction will decrease from the inlet to the  
89 outlet in the sedimentation pond and the chamber sedimentation facility due to settling, whereas the  
90 PAHs in the Filtrated fractions, i.e. Colloidal and Dissolved, it is not expected to differ substantially  
91 between the inlet and outlet, since removal of these fractions is not expected in the treatment facilities  
92 currently used (Pettersson 1999 Lead et al. 2006).

## 93 **2 Materials and Methods**

### 94 **2.1 Suspensions and Samples**

#### 95 **2.1.1 Preparation of Synthetic Nano-sized Particles**

96 A colloidal suspension with particle sizes of 160 nm in hydrodynamic diameter (HA-n), and a 44 nm in  
97 hydrodynamic diameter (Fe) nano-sized particle suspension, derived from iron nitrate, were used as  
98 synthetic colloids and nano-sized particles to investigate the sorption of PAHs to an organic and a  
99 inorganic entity. Natural organic matter, often consisting of humic and fulvic acids, and quantified as  
100 total organic matter (TOC) (e.g. Badin et al., 2008) play an important role in the enhanced transport of  
101 pollutants in stormwater, and therefore are HA-n colloids relevant to use as test particles. It is also  
102 known that stormwater contains inorganic particles such as natural clay and silt (Grolimund et al. 2005)  
103 as well as break-debris particles derived from break wear (Peikertová et al., 2013), and iron has been  
104 analysed in high concentrations in road dust (Herngren et al. 2006). Accordingly the use of inorganic  
105 Fe nano-sized suspension as test particles is justified. The HA-n colloid and Fe particle suspensions  
106 were made following the procedure given by Florence (1982). The mixture of the Fe-n particles and  
107 HA-n colloids were found to agglomerate to particles > 200 nm in hydrodynamic diameter. The final  
108 HA-n colloid suspension contained 14.4 mg Non-Volatile Organic Carbon (NVOC)/L, with a pH of 7.0  
109 and colloids with an ionic strength of  $3.5 \times 10^{-6}$  mS/cm. The Fe particle suspension contained 47.6 mg  
110 Fe/L with a pH of 3.4 and an ionic strength of  $0.38 \times 10^{-6}$  mS/cm. The HA-n colloids and Fe particles  
111 are stable over a short time period (<2 months) when stored at +4 °C (Nielsen et al. 2015). For the  
112 experiments duplicate suspensions were tested, together with a mixture of the two suspensions  
113 (50%/50%), and a Milli-Q water solution (95%/5% V/V Milli-Q H<sub>2</sub>O/iso-propanol). The iso-propanol  
114 was added to the Milli-Q to better keep the PAHs in the solution, and to avoid PAH sorption to the  
115 glass surfaces.

#### 116 **2.1.2 Stormwater Sampling and Sites**

117 Stormwater was collected by multiple grab sampling at Gårda and Järnbrott, two stormwater  
118 sedimentation facilities in the area of Gothenburg, Sweden. Samples were collected during two rain  
119 events, in the spring of 2013. At the first event only inlet stormwater was sampled (n = 1 for each site),  
120 while at the second event both inlet and outlet stormwater were collected (n = 2 for each site), as

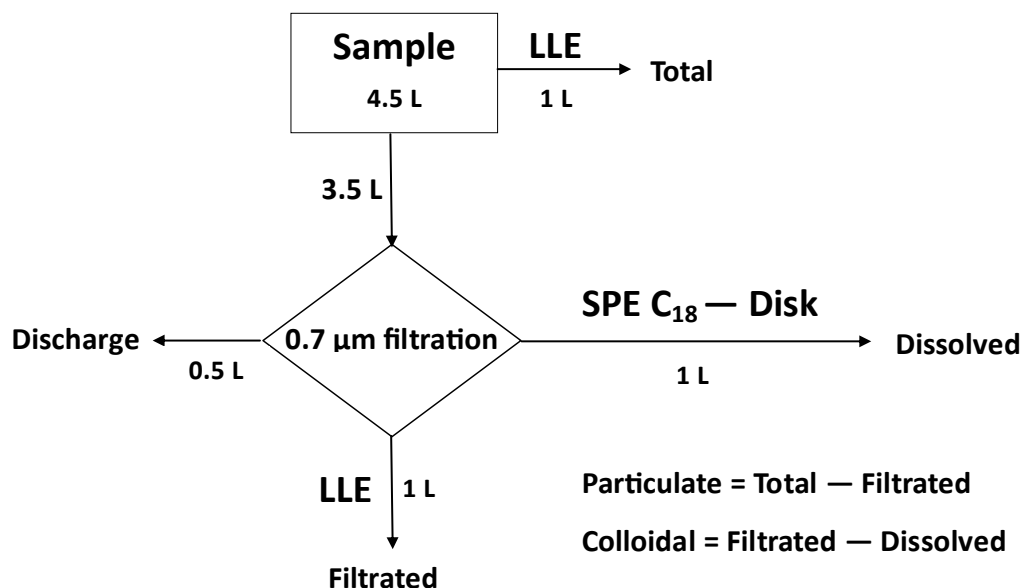
121 multiple grab samples (5 á 2 L) were pooled to yield one composite sample per event, site, and in-  
122 /outlet. All sub-samples were stored at < 8 °C in dark 2 L glass bottles and were extracted within 48 h.

123 The Gårda stormwater sedimentation facility is situated in Gothenburg city (population ~ 550,000), and  
124 is connected to the E6 highway, used by 100,000 vehicles on a daily basis. The catchment is mainly  
125 from the trafficked area with ~ 0.051km<sup>2</sup> with 40 % imperious surface. The facility manages  
126 stormwater through settling and sedimentation, in seven concrete chambers in series, with a total  
127 volume of 122 m<sup>3</sup>. The hydraulic retention time is 40 hours, after which the treated water is pumped via  
128 a draining pipe to a nearby stream (Pettersson et al., 2005). The inlet samples were collected in  
129 chamber 1, and the outlet in chamber 7.

130 The Järnbrott stormwater facility is a stormwater pond, situated 5 km outside Gothenburg, with a  
131 catchment of 30 % commercial/industrial and 70 % residential areas (Pettersson, 1999). The total area  
132 is 4.78km<sup>2</sup>, with 33 % impervious surface. The area is divided with a city motorway with an annual  
133 daily traffic of ~40,000 vehicles. The pond is located in a green area, with a surface area of 6200 m<sup>2</sup>,  
134 and can contain ~6000 m<sup>3</sup> water, with a maximum inflow of 1100 l/s , the outlet reaches a small  
135 stream, which discharges into Kattegat.

## 136 **2.2 Phase separation**

137 To determine the concentrations of PAHs in the Total, Filtrated and Dissolved fraction (see Figure 1),  
138 liquid-liquid extraction (LLE), physical filtration and solid phase extraction (SPE) was used  
139 (Kalmykova et al., 2013). Particle- and Colloidal fractions were calculated, using the amounts of PAHs  
140 found in the analysed fractions.



141

142 Figure 1: Flow-diagram for separating the nano-sized colloids in suspension, and thereby determine the  
 143 concentrations of PAHs in the fractions: Total, Filtrated and Dissolved.

144 A stock solution containing 14 selected PAHs: acenaphthene, acenaphthylene, anthracene,  
 145 benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene,  
 146 benzo[k]fluoranthene, chrysene, fluorene, fluoranthene, naphthalene, phenanthrene and pyrene, was  
 147 prepared in ethanol with individual concentrations of ~ 210 mg/L. To determine the amount of PAHs in  
 148 the different fractions, mixtures were prepared by adding 2.5 mL of stock solution to a 4.5 L Milli-Q  
 149 water or nano-sized and colloidal particle suspension.

### 150 2.3 Extraction of PAHs

151 The mixtures were equilibrated in room temperature for 24 hours, followed by homogenization by  
 152 shaking before sample aliquots were taken out. The 24 hour equilibrating time was confirmed by Birch  
 153 et al. (2010), and the biological half-time for the chosen PAHs were in the range of 2 to 2200 days  
 154 (Wang et al., 2010) assuring that no biological degradation will occur during the experiments. For all  
 155 experiments an identical filtration and extraction procedure was used following the flow-diagram in  
 156 Figure 1, and were conducted in duplicates. An aliquot of 1 L was taken for analysis of the  
 157 concentration of PAHs in the Total fraction by LLE. Here 1 ml of pyrene-d<sub>10</sub> in acetone (100 mg/L)  
 158 and 1 ml of perylene-d<sub>12</sub> in acetone (100 mg/L) were added as internal standards. For the Filtrated and  
 159 Dissolved fractions, 3.5 L was filtered through a < 0.7 µm binder free glass fibre filter (Whatman®). Of



160 the filtrated sample (3.5 L), 1 L was taken out for LLE and 1 L aliquots for SPE C<sub>18</sub>-disc; to each of  
161 these, pyrene-d<sub>10</sub> and perylene-d<sub>12</sub> were added as internal standards.

162 The PAHs in the different fractions was determined using the LLE U.S. EPA Method 3510C (1996)  
163 and SPE on the C<sub>18</sub>-disk (Brown et al. 2003). For LLE cyclohexane:ethyl acetate (1:1) was used as  
164 solvent, and the extract was cleaned up using a Florisil column to remove polar compounds in the  
165 sample (Waksmundzka-Hajnos et al. 1996). The C<sub>18</sub>-disk (Empore<sup>TM</sup>) was conditioned, using  
166 cyclohexane:ethyl acetate (1:1) and methanol. For the C<sub>18</sub>-disk a volume of 250 mL could be loaded  
167 creating quadrupole loadings in order to yield the nominated 1 L volume. The PAHs was eluted using  
168 cyclohexane:ethyl acetate (1:1). All extracts were analysed in duplicates for the 14 specific PAHs, by  
169 GC-MS-SIM. The chromatographic separation was conducted on an Agilent 6890 gas chromatograph  
170 equipped with a, 60 m x 0.25 mm i.d x 0.25 µm film thickness, ZB-5ms column with a 5 m GuardZ  
171 column (Phenomenex). Splitless mode was used, and a 2 µL sample was injected with the injector held  
172 at 300 °C. The oven was programmed with a gradient temperature program: start 70 °C, then 20  
173 °C/min to 300 °C, then 50 °C/min to 325 °C held for 10 min. Helium was used as carrier gas with a 1  
174 ml/min constant flow. Detection was achieved on an Agilent 5975C triple-axis mass-selective detector  
175 operated in SIM mode with the MS source at 230 °C and the quadrupole at 150 °C.

#### 176 **2.4. Characterization of Stormwater**

177 Dynamic light scattering (Zetasizer Nano ZS, Malvern) measuring in the range from 1 nm to 1000 nm  
178 was used to determine the particle size distribution (PSD) in the Filtrated and Colloidal fraction;  
179 particles in these fractions were expected to be in the nano-size range. A Coulter Counter, Multisizer<sup>TM</sup>  
180 II, measuring in the range from 2 µm to 50 µm was used to count the number of particles in the Total  
181 fraction. Both methods are described in Nielsen et al. (2015). The Zetasizer (Malvern) was also used  
182 for measurement of zeta potential (mV) and ionic strength (mS/cm).

183 Total suspended solids were measured using the same glass fibre filter (0.7 µm) as in the fractionation  
184 following the U.S. EPA Method no. 160.2. Element analysis were made on unfiltered samples:  
185 aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), cadmium calcium (Ca), cadmium (Cd),  
186 cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), potassium (K), lithium (Li), magnesium (Mg)  
187 molybdenum (Mo), manganese (Mn), nickel (Ni), phosphorus (P), lead (Pb), sodium (Na), selenium  
188 (Se), silicon (Si), strontium (Sr), sulphur (S), titanium (Ti), vanadium (V) and zinc (Zn), and were

189 analysed using ICP-OES: Varian, Vista MPX, after acid digestion according to the Standard DS/EN  
190 13656; NVOC was measured by Shimadzu, TOC-V wp.

## 191 **2.5. Data analysis and statistical tests**

192 The concentrations of the PAHs were derived from the calibration curve and calculated as averages of  
193 duplicates. The  $\mu\text{mol}$  loads were corrected according to the internal standard (pyrene- $d_{10}$ ). To calculate  
194 the percentage distribution (DIS%), the amount in  $\mu\text{mol}$  of the PAHs in each of the fractions  
195 Particulate, Filtrated, Colloidal and Dissolved (see Figure 1), have been divided with the amount  
196 ( $\mu\text{mol}$ ) of PAHs in the Total fraction. The recovery of the Total fraction was calculated by dividing the  
197 spiked amount of PAHs, with the quantified amount of PAHs in the Total fraction. For each fraction  
198 the relative percentage (REL%) was calculated for the low-, medium- and high-weighted PAHs based  
199 on the total sum of ( $\mu\text{mol}$ ) PAH. When nothing else is noted, the statistical comparison of  
200 measurements was conducted using Students *t*-test, where  $p < 0.05$  indicates no statistically significant  
201 difference between measurements. The statistical calculations were performed using the Graph Pad  
202 Prism Software.

## 203 **3 Results**

### 204 **3.1 PAHs extractions from synthetic nano-sized colloids and particles in suspension**

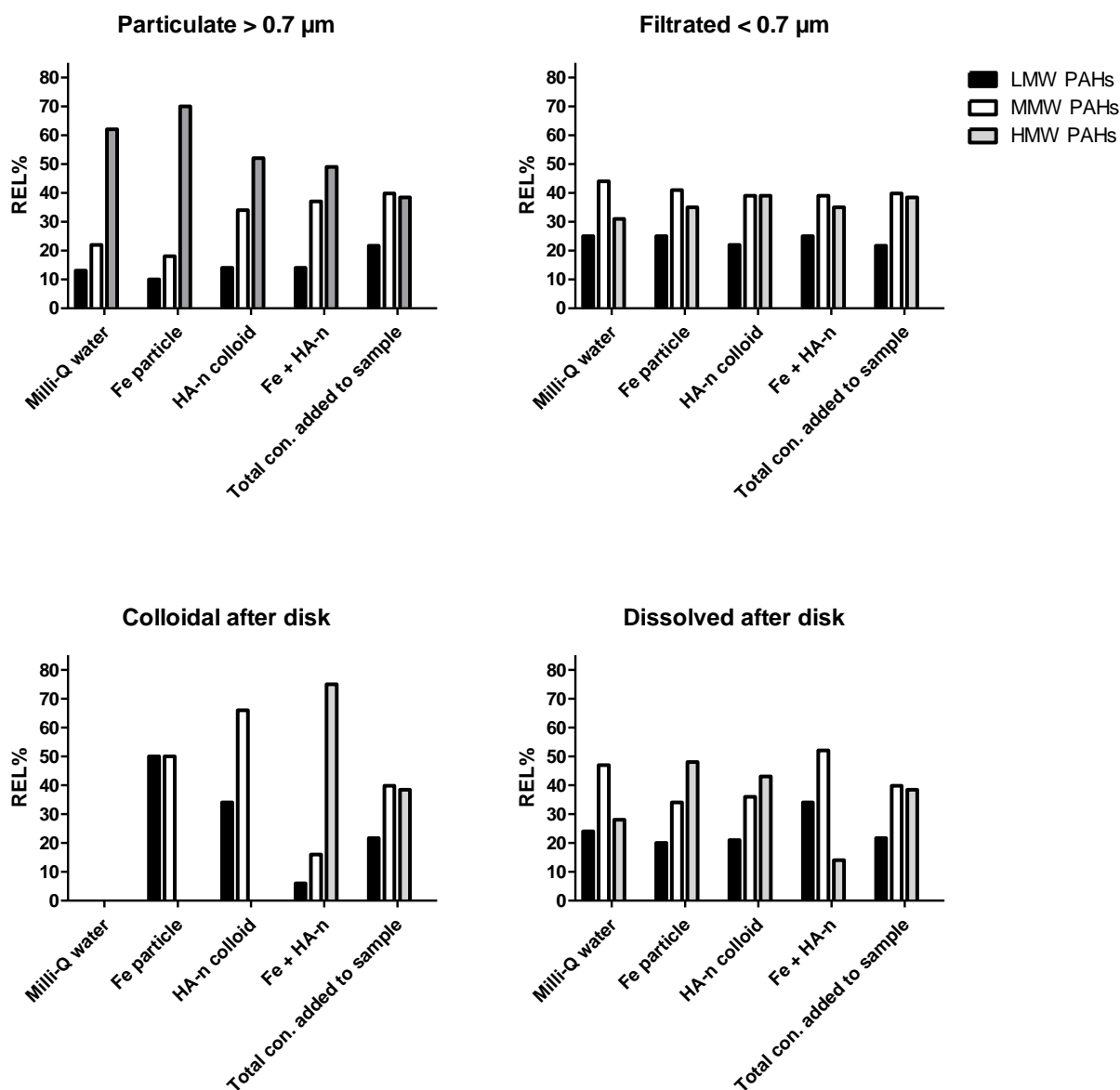
205 The distribution of PAHs among the fractions, i.e. DIS% among Total, Particulate, Filtrated, Colloidal  
206 and Dissolved, in the three synthetic suspensions containing colloids and nano-sized particles are  
207 presented in Table 1, together with the relative composition of the PAHs presented as REL% in Figure  
208 2. In the Milli-Q water spiked with PAHs without added nano-sized particles, 63% of the PAHs in the  
209 Total fraction were found in the Particulate fraction. This is explained by sorption of PAHs on the  
210 surfaces in the glass-fibre filter. Sorption of PAHs on glass surfaces is a well-known and inevitable  
211 problem (Qian et al. 2011); the sorption was shown to decrease with increasing ration of solution  
212 volume to contacted surface area (V/S), by using silanized glass and co-solvents. Humic acids were  
213 shown to act as co-solvent and increased the solubilisation of volatile organic compounds (Sato et al.  
214 2005). This may explain the lower distribution of 40% PAHs in the Particulate fraction in the  
215 suspension containing HA-n colloids. . The loss in the filters were much lower when the colloids were  
216 added; therefore it was assumed that the loss due to sorption on the glass-fibre filter will be even lower  
217 during filtration of the real stormwater samples, because the glass surfaces are quickly covered by

218 particles. Losses due to glass surface sorption is not possible to quantify; thus the figures in this study  
219 are not corrected for the sorption effect. The low recovery from the Original added (39  $\mu\text{mol}$ ) in the  
220 Total fractions of 28 – 49%, are also explained by sorption on the glass equipment.  
221 The distribution of the PAHs among the fractions showed that the highest amounts of PAHs were  
222 present in the Filtrated fractions in all the synthetic suspensions. This indicates that the PAHs were  
223 dissolved or sorbed onto the HA-n colloids and Fe-n particles and, thus, passed through the 0.7  $\mu\text{m}$   
224 filter. Notable, high amounts of the PAHs were found in the Dissolved fraction. For the sample  
225 containing Fe particles, as much as 75% of the Total fraction was distributed to the Dissolved fraction.  
226 It is possible that the Colloidal phase is underestimated and a part of it measured as Dissolved, as both  
227 the HA and Fe particles may be sorbed in the C<sub>18</sub>-material in the SPE disk.  
228

229 Table 1. Distribution of PAHs among fractions in the suspensions with different synthetic nano-sized colloids.

	Milli-Q water			Fe-n particles		HA-n colloids		Fe-n particles + HA-n colloids	
	PAHs	µmol	DIS% <sup>a</sup>	µmol	DIS% <sup>a</sup>	µmol	DIS% <sup>a</sup>	µmol	DIS% <sup>a</sup>
<b>Original added</b>	LMW	11		11		11		11	
	MMW	16		16		16		16	
	HMW	23		23		23		23	
	ΣPAHs	39		39		39		39	
<b>Total fraction<sup>c</sup></b>	LMW	3.4		2.2		2.6		3.3	
	MMW	5.9		3.7		5.1		6.1	
	HMW	9.7		5.2		6.1		6.6	
	ΣPAHs	19	100(49 <sup>d</sup> )	11	100 (28 <sup>d</sup> )	14	100 (36 <sup>d</sup> )	15	100 (38 <sup>d</sup> )
<b>Particulate fraction &gt; 0.7 µm<sup>d</sup></b>	LMW	1.5	44	0.36	16	0.8	31	1.1	33
	MMW	2.6	44	0.66	18	1.9	37	2.8	46
	HMW	7.4	76	2.6	50	2.9	48	3.7	56
	ΣPAHs	12	63	3.7	34	5.6	40	7.6	51
<b>Filtrated fraction &lt; 0.7 µm<sup>e</sup></b>	LMW	1.9	56	1.9	86	1.8	69	2.1	64
	MMW	3.3	56	3.1	84	3.2	63	3.3	54
	HMW	2.3	24	2.6	50	3.2	52	2.9	44
	ΣPAHs	7.5	39	7.5	68	8.3	59	8.4	56
<b>Colloidal fraction<sup>f</sup></b>	LMW	-		0.27	12	0.22	8	0.18	5
	MMW	-		0.27	7	0.43	8	0.46	8
	HMW	-		-	-	-	-	2.1	32
	ΣPAHs	-		0.54	5	0.65	5	2.8	19
<b>Dissolved fraction<sup>g</sup></b>	LMW	2.2	65	1.6	73	1.6	62	1.9	58
	MMW	4.4	75	2.8	76	2.8	55	2.9	48
	HMW	2.6	27	3.9	75	3.3	54	0.79	12
	ΣPAHs	9.3	49	8.2	75	7.7	55	5.6	37

230 <sup>a</sup>DIS%= distribution% calculated from the quantified ΣPAHs (µmol) as well as by **LMW PAHs, -M and -H** in each Particulate, Filtrated,  
231 Colloidal and Dissolved fractions divided with the quantified corresponding mass (µmol) in the Total fraction<sup>c</sup>Total=chemical quantified  
232 PAHs in the original sample; <sup>d</sup>The Recovery%= calculated by dividing the ΣPAHs quantified in Total in µmol with the ΣPAHs in µmol  
233 added to the original samples; <sup>e</sup>Particulate= calculated as the PAH quantified in Total – PAHs quantified in Filtrated; <sup>f</sup>Filtrated= PAHs  
234 quantified in samples after filtration through 0.7 µm glass fibre; <sup>g</sup>Colloidal= calculated as Filtrated PAHs –Dissolved; <sup>i</sup>Dissolved = PAHs  
235 quantified on disk SPE.



237

238 Figure 2: Relative composition (REL%)<sup>a</sup> of LMW, MMW and HMW PAHs, in the Milli-Q solution  
 239 and the three suspensions with Fe particles, HA-n colloids and the mixture of Fe particles and HA-n  
 240 colloids. <sup>a</sup>REL% calculated by the quantified μmol of the LMW PAHs, -M and -H divided with the quantified ΣPAHs in each  
 241 sample

242 The relative composition of the LMW, MMW and HMW PAHs were approximately the same in the  
 243 Filtrated and the Dissolved phases (except for the much lower HMW PAHs for the Dissolved in the  
 244 Fe+HA suspension). Instead, the HMW PAHs in the Filtrated Fe+HA suspension were found in the  
 245 Colloidal fraction. The concentrations of PAHs found in the Particulate fractions vs. the Dissolved  
 246 fractions followed their hydrophobic properties; of the HMW PAHs 50 – 75% was found in the  
 247 Particulate fractions, while the LMW PAHs and MMH were found to a higher extent, 50 – 75%, in

248 the Dissolved fractions (see DIS% in Table 1). This is explained by the partitioning and the higher  
 249 logK<sub>ow</sub> of the HMW PAHs and thus a higher ability to sorb to surfaces compared to the LMW  
 250 PAHs.

### 251 3.2 Physico-chemical parameters in stormwater

252 The stormwater samples were analysed for physical parameters, PSD and concentration of selected  
 253 metals, see Table 2. The quantifications of TSS from Järnbrott showed lower concentrations  
 254 compared to Gårda. At Gårda the two inlet samples were quantified to 150 mg/L and 180 mg/L  
 255 TSS, and an unexpected high TSS at the outlet of 400 mg/L (Pettersson et al. 2005). Even though  
 256 the TSS increased from the inlet to the outlet, did the PDS, neither the hydrodynamic diameter nor  
 257 the Coulter counter diameter, show any statistically difference of the sizes of the particles (Table 2).  
 258 The measurements of pH did not show any statistical difference between samples from inlet and  
 259 outlet, nor between locations (p <0.05) except for one of the inlet samples from Gårda showing  
 260 more of an unbuffered rainwater of pH 4.6. The turbidity measured in the inlet sample for Event 2  
 261 at Gårda, were found to be significantly different from the rest of the measurements. This could be  
 262 explained by high turbulence in the underground sedimentation tanks. When the outlet samples  
 263 were collected, all tanks were filled with water indicating a blockage in the outgoing water. The  
 264 high water level and heavy rain in the days before sampling could have created turbulence in the  
 265 tanks, re-suspending some of sediment and thereby given the higher turbidity for the samples.

266 Table 2: Physico-chemical parameters, particle size distribution and major and minor element  
 267 concentrations measured in the stormwater.

	Gårda			Järnbrott		
	Event 1	Event 2		Event 1	Event 2	
	<i>Inlet</i>	<i>Inlet</i>	<i>Outlet</i>	<i>Inlet</i>	<i>Inlet</i>	<i>Outlet</i>
<b>pH</b>	6.7	4.6	6.6	7.6	6.9	7.6
<b>EC (µS/cm)</b>	27000	370	290	750	370	440
<b>Ionic strength ×10<sup>-6</sup> (mS/cm)</b>	50	5.2	6.4	1.3	7.6	6.8
<b>TSS (mg/L)</b>	150±20	180±3.5	400±7.3	75±1.4	24±6.5	20±0.9
<b>Turbidity (NTU)</b>	90	220	310	90	20	27
<b>Zeta potential (mV)</b>	-18	-22	-21	-24	-22	-26
<b>Hydrodynamic diameter in nm range<sup>a</sup></b>	39-150	29-95	7.8-170	5.8-230	10-230	16-230
<b>Hydrodynamic diameter in µm range<sup>b</sup></b>	7.2	4.9	6.5	11	6.2	6.0
<b>NVOC (mg/L)</b>	300	290	270	250	290	270
<b>Concentration of elements (mg/L)</b>						

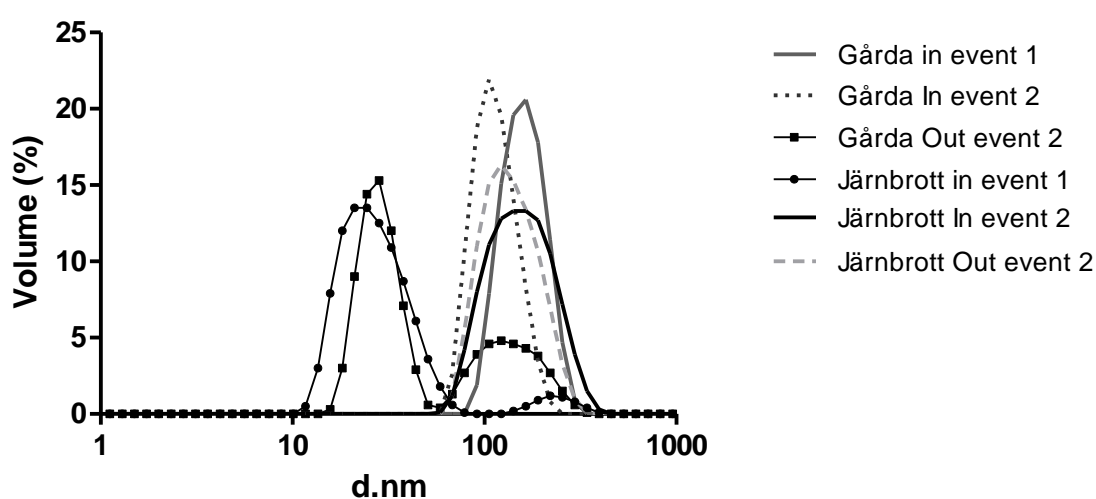
	<b>Al</b>	1.9	5.4	2.4	1.5	0.47	0.42
	<b>Ca</b>	59	9.1	15	32	23	18
	<b>Fe</b>	5.2	13	5.8	5.3	1.1	1.1
	<b>K</b>	30	5.8	5.3	6.6	46	3.5
	<b>Mg</b>	28	5.4	4.2	6.3	3.5	3.0
	<b>Na</b>	350	36	39	81	42	3.7
<b>Concentration of elements (µg/L)</b>							
	<b>As</b>	BDL	BDL	BDL	BDL	BDL	BDL
	<b>Ba</b>	110	87	54	55	26	21
	<b>Cd</b>	BDL	BDL	BDL	BDL	BDL	BDL
	<b>Co</b>	8.8	13	6.0	2.2	BDL	BDL
	<b>Cr</b>	9.4	25	16	4.8	1.4	BDL
	<b>Cu</b>	110	140	64	53	15	17
	<b>Li</b>	11	9.6	6.0	5.7	3.3	2.9
	<b>Mn</b>	270	220	110	190	58	55
	<b>Mo</b>	13	3.6	2.9	1.9	1.3	BDL
	<b>Ni</b>	9.6	12	6.2	6.1	2.8	2.4
	<b>P</b>	220	350	280	570	84	87
	<b>Pb</b>	5.8	16	7.8	6.3	2.6	2.2
	<b>S</b>	21000	1700	3200	9600	7000	5000
	<b>Sb</b>	7.9	11	6.5	2.7	BDL	BDL
	<b>Se</b>	4.0	BDL	BDL	BDL	BDL	BDL
	<b>Si</b>	8500	11000	8000	6900	6400	6000
	<b>Sn</b>	17	23	15	13	11	8.9
	<b>Sr</b>	280	50	59	100	71	57
	<b>Ti</b>	BDL	BDL	BDL	BDL	BDL	BDL
	<b>V</b>	10	19	8.7	6.7	1.5	1.8
	<b>Zn</b>	350	460	270	220	50	62

268 *BDL = Below Detection Limit (1.3 µg/L), <sup>a</sup> size at 95% accumulated volume (Nielsen et al.*  
269 *2015) measured with Coulter counter, <sup>b</sup> range given for where nano-particles were observed, when*  
270 *using volume distribution, the samples have been filtrated through a 0.45 µm filter before filtration*  
271 *measured with Zetasizer*

272 The particle size distribution, measured with the Coulter counter showed that the majority of the  
273 particles were smaller than 10 µm in diameter, though the accumulated mean diameters were 8 – 12

274  $\mu\text{m}$ . The Zetasizer measurement showed evidence of nano-particles in all of the samples, but an  
275 exact size distribution is not possible to give due to the heterogeneity of the samples (Nielsen et al.  
276 submitted). As illustrated in Figure 3, the particle size distributions showed hydrodynamic  
277 diameters around 100 nm but the suspensions were highly poly-dispersed hampering accurate  
278 interpretations of the distribution curves.

279 The zeta potential were for all samples found to be negative, though the magnitude of -25 to -17  
280 mV indicates instability (Cho et al. 2012), i.e. prone to coagulate and flocculate. A negative surface  
281 charge of the particles, is consistent with particles containing organic acids e.g. fulvic and humic  
282 acid and have been documented in literature (Kayhanian et al. 2012, Nielsen et al. 2015).



283

284 Figure 3: Particle size distribution (PSD) of nano-particles in stormwater measured with a Zetasizer  
285 on filtrated samples.

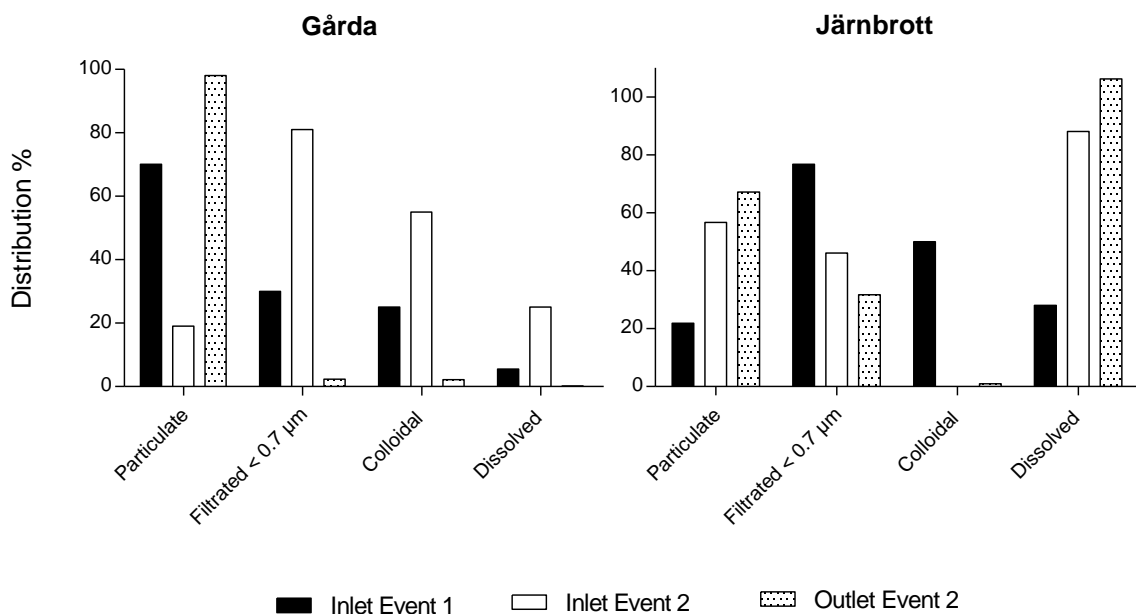
### 286 3.4 Polycyclic aromatic hydrocarbons in stormwater

287 The stormwater samples, presented in Table 3 for Gårda, and Table 4 for Järnbrott, all contained  
288 PAHs in concentrations from 3.2 to 139  $\mu\text{g/L}$ . These concentrations were higher than previously  
289 reported by Pettersson et al. (2005), where the PAHs-16 at Gårda was ranging in the inlet between  
290 2.6 – 6.9  $\mu\text{g/L}$ , and outlet, between 0.56 – 1.6  $\mu\text{g/L}$ . Comparatively, PAHs measured in urban snow  
291 at Gårda was as high as 15  $\mu\text{g/L}$  (Björklund et al., 2011). The high concentrations measured in this  
292 study are explained by the relatively long periods of dry weather before sampling, i.e. 8 days before  
293 Event 1, and 6 days of dryness before Event 2. During the dry periods, deposition of the pollutants  
294 is accumulated on the surfaces and cause high concentrations of pollutants in the stormwater of the  
295 coming rain event. Another explanation is that the samples in this study were grab sampled, and the



296 water sample in the earlier study were taken by flow proportional samplers and yielded event mean  
 297 concentrations. The PAH concentrations in this study are within the range (<0.01 – 180 µg/L)  
 298 previously found in stormwater and road runoff, though they notably are in the higher range  
 299 (Makepeace et al., 1995; Eriksson, 2002; Göbel et al., 2007; Birch et al., 2011). Both parking lot  
 300 and roof runoff have, however, been quantified with substantially higher PAH concentrations,  
 301 mainly related to site-specific pollution sources (Eriksson, 2002).

302 The distribution of PAHs among the fractions in the stormwater (Tables 3 and 4, and Figure 4)  
 303 showed that high loads of PAHs were found in several of the Particulate fractions at both locations,  
 304 but the variability was substantial, especially at Event 2 where the Gårda inlet had 32% of the PAHs  
 305 in the Particulate phase, compared to the outlet where as much as 98% of the PAHs were found on  
 306 the particles. This is explained by re-suspension of settled sediments caused by the turbulence in the  
 307 facility during the heavy rain fall, and the thereby much higher value of TSS (Table 2) found in the  
 308 Gårda outlet samples.



309  
 310 Figure 4: Distribution of PAHs among the different fractions at the two locations.

311 The PAHs in the Filtrated fractions were lower, but also had a large variability, e.g. from the Event  
 312 2 outlet Gårda of only 2.4% PAHs in the Filtrated till the 81% in the inlet sample.. In the Filtrated  
 313 fractions it was a large difference in the composition of fractions between Gårda and Järnbrott,  
 314 where samples at Gårda had most of the PAHs in the Colloidal fractions, meanwhile at Järnbrott  
 315 high concentrations were measured in the Dissolved fraction during event 2. The Gårda samples  
 316 (event 2, out) had the highest concentration of PAHs in the particulate fraction, and the high

317 concentrations are explained by the high TSS value in this sample. The Järnbrott sample (event 1,  
318 in) with a much lower TSS showed very high amount in the Filtrated and Colloidal fraction; here  
319 the occurrence of small particles (< 100 nm) may explain the high concentrations in the colloidal  
320 fraction.

321 The relative composition (Table 3 and 4) show a low proportion of LMW PAHs in the stormwater  
322 samples, and especially at the Event 1, which had a long pre-existing dry period (~ 8 days) before  
323 the sampling which caused a possible volatilization of the LMW PAHs from the urban surfaces.  
324 The samples with the highest loads of the LMW PAHs were the inlet samples at the Event 2 with  
325 heavy rain shortly before the sampling; this is as could be expected since the LMW PAHs are the  
326 most water soluble and volatile of the 14 PAHs. At both sites the MMW PAHs was dominating, and  
327 as earlier reported with a possible sources from both rubber tires and diesel exhausts (Strömvall et  
328 al., 2006). The highest amounts of the HMW PAHs were found in the outlet samples for Event 2.  
329 Otherwise, the relative loads of the HMW PAHs in the Particulate fractions were highest in the  
330 samples with high TSS and the smallest particles (Figure 2), i.e. Gårda out Event 2 and Järnbrott in  
331 Event 1. This is explained by the higher  $\log K_{ow}$  of the HMW PAHs and their higher ability to sorb  
332 to particle surfaces and the high active surfaces of the smallest particles.  
333

334 **Table 3.** Distribution of PAHs among fractions, and the relative composition, in samples from the Gårda sedimentation chamber facility.

		$\mu\text{g/L}$	In Event 1 DIS% <sup>a</sup>	REL% <sup>b</sup>	$\mu\text{g/L}$	In Event 2 DIS% <sup>a</sup>	REL% <sup>b</sup>	$\mu\text{g/L}$	Out Event 2 DIS% <sup>a</sup>	REL% <sup>b</sup>
<b>Total fraction<sup>c</sup></b>	LMW	0.062		0.15	8.9		18	11		8
	MMW	38		94	23		45	64		46
	HMW	2.4		5.8	19		37	63		46
	$\Sigma$ PAHs	40	100		50	100		139	100	
<b>Particulate fraction &gt; 0.7 <math>\mu\text{m}^{\text{d}}</math></b>	LMW	0.030		0.11	<d.l. <sup>h</sup>		<d.l. <sup>h</sup>	11		8.3
	MMW	26		92	14		88	61		45
	HMW	2.3		8.1	1.9		12	63		47
	$\Sigma$ PAHs	28	70		9.7	32		135	98	
<b>Filtrated fraction &lt; 0.7 <math>\mu\text{m}^{\text{e}}</math></b>	LMW	0.031		0.26	15		37	0.031		0.94
	MMW	12		99	8.9		22	3.2		98
	HMW	0.074		0.61	17		41	0.037		1.1
	$\Sigma$ PAHs	12	30		41	81		3.3	2.4	
<b>Colloidal fraction<sup>f</sup></b>	LMW	<d.l. <sup>h</sup>		<d.l. <sup>h</sup>	14		50	<d.l. <sup>h</sup>		<d.l. <sup>h</sup>
	MMW	11		100	8.6		31	3.0		100
	HMW	<d.l. <sup>h</sup>		<d.l. <sup>h</sup>	5.4		20	<d.l. <sup>h</sup>		<d.l. <sup>h</sup>
	$\Sigma$ PAHs	10	27		28	56		3.0	2.2	
<b>Dissolved fraction<sup>g</sup></b>	LMW	0.062		2.8	1.2		9.6	0.031		10
	MMW	0.99		44	0.30		2.4	0.23		77
	HMW	1.2		53	11		88	0.037		12
	$\Sigma$ PAHs	2.2	5.6		13	25		0.30	0.22	

335 <sup>a</sup>DIS%= distribution% calculated from the quantified  $\Sigma$ PAHs ( $\mu\text{mol}$ ) in each Particulate, Filtrated, Colloidal and Dissolved fractions  
336 divided with the  $\Sigma$ PAHs ( $\mu\text{mol}$ ) quantified in the Total fraction; <sup>b</sup>REL%= relative% calculated by the  $\mu\text{mol}$  of the LMW PAHs, -M and -H  
337 divided with the  $\Sigma$ PAHs in each sample; <sup>c</sup>Total = quantified  $\Sigma$ PAHs in the original sample; <sup>d</sup>Particulate= calculated as PAHs quantified in  
338 Total – PAHs quantified in Filtrated; <sup>e</sup>Filtrated= PAHs quantified in samples after filtrations through 0.7  $\mu\text{m}$  glass fibre filter; <sup>f</sup>Colloidal=  
339 calculated as Filtrated PAHs – Dissolved; <sup>g</sup>Dissolved = PAHs analysed on disk SPE.

340

341

342 **Table 4.** Distribution of PAHs among fractions, and the relative composition, in samples from the Järnbrott sedimentation pond.

		$\mu\text{g/L}$	In Event 1 DIS% <sup>a</sup>	REL% <sup>b</sup>	$\mu\text{g/L}$	In Event 2 DIS% <sup>a</sup>	REL% <sup>b</sup>	$\mu\text{g/L}$	Out Event 2 DIS% <sup>a</sup>	REL% <sup>b</sup>
<b>Total fraction<sup>c</sup></b>		0.06	0.08		12	17		0.031	0.96	
	LMW	57	79		19	26		1.9	59	
	MMW	15	21		20	28		1.3	40	
	HMW	71			52			3.2		
	$\Sigma$ PAHs									
			100			100			100	
<b>Particulate fraction &gt; 0.7 <math>\mu\text{m}^{\text{d}}</math></b>	LMW	0.031		0.2	8.3		29	<d.l. <sup>h</sup>		<d.l. <sup>h</sup>
	MMW	3.7		24	19		65	1.4		66
	HMW	12		77	1.6		5.5	0.77		35
	$\Sigma$ PAHs	16	22		28	57		2.2	68	
<b>Filtrated fraction &lt; 0.7 <math>\mu\text{m}^{\text{e}}</math></b>	LMW	0.031		0.06	3.9		17	0.062		6.0
	MMW	53		96	0.59		2.5	0.45		44
	HMW	2.3		4.2	19		81	0.51		50
	$\Sigma$ PAHs	55	78		23	46		1.0	32	
<b>Colloidal fraction<sup>f</sup></b>	LMW	–		<d.l. <sup>h</sup>	3.9		18	0.03		100
	MMW	34		97	<d.l. <sup>h</sup>		<d.l. <sup>h</sup>	<d.l. <sup>h</sup>		<d.l. <sup>h</sup>
	HMW	1.17		3	17		81	<d.l. <sup>h</sup>		<d.l. <sup>h</sup>
	$\Sigma$ PAHs	35	50%		<d.l. <sup>h</sup>	<d.l. <sup>h</sup>		0.3	1.0	
<b>Dissolved fraction<sup>g</sup></b>	LMW	0.031		0.15	0.031		0.07	0.03		0.9
	MMW	18		94	43		96	1.5		44
	HMW	1.2		5.8	2.0		4.4	1.9		55
	$\Sigma$ PAHs	19	28		45	88		3.5	109	

343 <sup>a</sup>DIS%= distribution% calculated from the quantified  $\Sigma$ PAHs ( $\mu\text{mol}$ ) in each Particulate, Filtrated, Colloidal and Dissolved fractions  
344 divided with the  $\Sigma$ PAHs ( $\mu\text{mol}$ ) quantified in the Total fraction; <sup>b</sup>REL%= relative% calculated by the  $\mu\text{mol}$  of the LMW PAHs, -M and -H  
345 divided with the  $\Sigma$ PAHs in each sample; <sup>c</sup>Total = quantified  $\Sigma$ PAHs in the original sample; <sup>d</sup>Particulate= calculated as PAHs quantified in  
346 Total – PAHs quantified in Filtrated; <sup>e</sup>Filtrated= PAHs quantified in samples after filtrations through 0.7  $\mu\text{m}$  glass fibre filter; <sup>f</sup>Colloidal=  
347 calculated as Filtrated PAHs –Dissolved; <sup>g</sup>Dissolved = PAHs analysed on disk SPE.

348 Moreover, the outlet sample of the Event 2 at Gårda contained 139  $\mu\text{g/L}$  PAHs, almost three times  
349 the inlet concentration. In contrast, the outlet of the Järnbrott had only about 5% (3.2  $\mu\text{g/L}$ ) of the  
350 inlet concentration (71  $\mu\text{g/L}$ ), see the Discussion section for further details on these findings.

#### 351 **4 Discussion**

352 The results obtained, for both the synthetic suspensions and the stormwater samples, showed that  
353 the amount of PAHs found in the Particulate fractions vs. the Dissolved fractions follow their  
354 hydrophobic properties. In most samples, > 50% of the HMW PAHs were found in the Particulate  
355 fractions, while the LMW and MMW PAHs were found to a higher extent in the Filtrated fractions.  
356 In the synthetic suspensions, presence of colloids caused even the most hydrophobic HMW PAHs  
357 to be found more equally represented in the Filtrated and the Particulate fractions, which supports  
358 the finding by Kalmykova et al. (2013) that PAHs partition to the Particulate fraction is reduced in  
359 the presence of colloids. This effect is in accordance with the molecular weight and hydrophobicity  
360 of the compounds i.e. the partition to the Filtrated = Colloidal + Dissolved fraction show a negative  
361 correlation with  $\log K_{ow}$ . Hypothesis (i) is strengthened by the results from the stormwater, as the  
362 samples from Event 2 with heavy rain fall before sampling, contained more of the water soluble  
363 LMW PAHs; the relative amount of the HMW PAHs were also highest in the samples with high  
364 TSS, which also contained small particles.

365 For hypothesis ii) the amount of PAHs sorbed on inorganic particles (Fe) was about 50% of the  
366 loads sorbed on the organic particles, the Fe + HA and HA suspensions, respectively (Table 1,  
367 Particulate fraction). The difference was almost entirely due to the much lower LMW and MMW  
368 PAHs sorption to Fe particles. This suggests that the most hydrophobic HMW PAHs partition to Fe  
369 particles, while the LMW and MMW PAHs remain in the Dissolved fraction, which potentially  
370 enhances their mobility. Among the Colloidal suspensions, the Fe + HA combination have resulted  
371 in the highest particulate-bound PAHs, probably due to formation of the larger particles due to Fe  
372 and HA agglomeration, as was shown in Kalmykova et.al. (2010) and Nielsen et al. submitted. The  
373 Fe-n particles had a size of 44 nm in hydrodynamic, while the HA-n colloids were found to be 160  
374 nm in hydrodynamic diameter. The Fe + HA combination have also resulted in the highest  
375 Colloidal fraction, which is even more mobile than the Dissolved fraction.

376 For the third hypothesis iii) the amount of PAHs found in the Total fraction should be decreasing  
377 from the inlet to the outlet in the settling facilities. For the Gårda facility this hypothesis can be  
378 rejected, but not for the Järnbrott pond. In fact, the highest concentration of PAHs at Gårda was

379 found in the outlet of the Event 2, and it was threefold higher than the inlet concentration for the  
380 same event. Extreme situations like event 2 at Gårda (heavy rain, and sediment re-suspension) are  
381 unthinkable to use for evaluation of the treatment efficiencies, which require data for extended  
382 seasons, different types of events as described by intensity and duration, and sampling schemes  
383 adjusted according to the systems hydraulic retention time. Here, however, the results from Gårda  
384 highlight that during extreme situations more particulate matter than anticipated can be discharged,  
385 and with it, toxic trace metals, Table 2, and PAHs in the Particulate fraction, Table 3. At Järnbrott, a  
386 tenfold decrease of the outlet concentration of PAHs compared to the inlet concentration was  
387 observed (Table 4). The biggest decrease is seen for the Filtrated fraction, where the concentration  
388 has decreased 23-fold. Low concentrations of Colloidal-bound PAHs were found in the Järnbrott  
389 outlet that indicates that the pond, during the prevailing weather conditions, was working effective.  
390 However, repeated analysis is needed to confirm the ponds efficiency due to the large variability of  
391 the inlet composition, i.e. 77% of PAH were found in the Colloidal fraction in the inlet of the Event  
392 1, which may lead to a different removal efficiency compared to the Event 2.

393 Relatively high amounts of HMW PAHs were found in the Järnbrott outlet.. Non-volatile organic  
394 carbon, representing the organic matter in the stormwater was analysed in all the samples and  
395 showed no statically significant difference between inlet and outlet samples. Therefore the higher  
396 amount of HMW PAHs in the outlet at Järnbrott can not be explained by the sorption to elevated  
397 concentration of dissolved organic matter. An increase in the NVOC concentration in the outlet  
398 compared to the inlet, due to enrichment in the pond, could otherwise have affected the result, as the  
399 presence of DOC is proven to decrease the partition of PAHs to larger particles (Kalmykova et al.  
400 2013).

401

## 402 **5 Conclusions**

403 The stormwater in this study is polluted with PAHs originating from the highway runoff with  
404 concentrations in the higher range of the previously internationally reported levels. Substantial part  
405 of this pollution has been found in the Filtrated fraction, which may be difficult to retain by the  
406 conventional stormwater techniques, presented here by the sedimentation pond (Järnbrott) and a  
407 chain of sedimentation chambers (Gårda). In the Järnbrott pond, a tenfold decrease of the outlet  
408 concentration of PAHs compared to the inlet were found. Yet, a non-negligible PAHs concentration  
409 in the outlet sample, mainly found in the Dissolved fraction, may pose a risk to the environment. On

410 the other hand, in the sedimentation chambers, the outlet concentration was higher than the inlet,  
411 due to the re-suspension of the PAHs bound to sediment during the turbulent conditions of the  
412 heavy rain. This highlights the risks of secondary pollution from the sedimentation-based systems.  
413 The study of the PAHs distribution in the synthetic suspensions has confirmed considerable  
414 distribution of the PAHs to Filtrated fractions and clarified the role of the studied particle  
415 suspensions in the PAH distribution. It has been shown that the PAHs are distributed among the  
416 fractions differently depending on the molecular weight; the LMW and MMW PAHs were mostly  
417 found in the Filtrated fractions, while more of the HMW PAHs has been found in the Particulate  
418 fractions. The Filtrated fraction was mostly constituted of the Dissolved pollutants, except for the  
419 Fe+HA suspension, where Colloidal fraction was significant. The fact of such significant presence  
420 of PAHs in Filtrated fraction potentially enhances their mobility. The amount of PAHs sorbed to the  
421 mixture of the Fe-HA particles was the highest, while to the inorganic Fe particles – the lowest.

422

423 The results with high amounts of PAHs in the Filtrated fractions, observed for both the synthetic  
424 solutions and the stormwater, show the importance of development of advanced techniques for  
425 stormwater treatment that are able to remove the PAHs in the colloidal and dissolved phases. In  
426 particular, the stormwater treatment technologies needs to be complemented with techniques that  
427 are able to reduce the dissolved PAHs, e.g. sorption filters, and colloidal-bound PAHs by for  
428 example oxidation, ozonolysis or UV-degradation.

429

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