Polycyclic Aromatic Hydrocarbons (PAH) in Water and Sediment from Gully Pots

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Abstract A gully pot is often cleaned with the help of an eductor truck, which uses hydrodynamic pressure and a vacuum to loosen and remove the solids and standing liquid from a gully pot. This paper considers the polycyclic aromatic hydrocarbons (PAH) content in the gully pot mixture (water and sediment) after it has been discharged from the eductor truck. The results show that most PAH was attached to particles, and the dissolved phase represented approximately 22% of the total water concentration. No significant difference was found for the water phase between a housing area and a road, whereas a significant difference was found for NAP, ACE, FL, ANT, FLR, PYR, BaF, and BPY in the sediment at a 95% confidence level. Source identification showed that the PAH in the gully pot mixture came from mixed sources. Both the water and sediment phase exceed all or some of the compared guidelines. The result from this paper shows that not only the sediment needs to be discussed, but also the water phase created during the maintenance of different BMPs.

Keywords BMP · Catch basin · Organic content · Sources · Stormwater

1 Introduction

The major sources of PAH in stormwater are the wear and leaching of asphalt, tire wear, drips of crankcase oil, and vehicular exhaust (Neff 1979; Brandt and De Groot 2001, Brown and Peake 2006). Smith et al. (2000) reported that the total concentration of PAH was highest at the beginning of the runoff, the so-called first flush, and decreases with time. The most abundant PAHs in stormwater are phenanthrene, anthracene, fluoranthene and pyrene (Gonzalez et al. 2000; Brown 2002). Gonzalez et al. (2000) reported that these four PAHs accounted for 85% from a total 16 PAH in stormwater. Rocher et al. (2004) studied sewer deposits in a combined system and found phenanthrene, fluoranthene and pyrene to dominate. However, Smith et al. (2000) reported that naphthalene, followed by acenaphthene, was most frequently detected in stormwater in Virginia, USA. Generally, as a group, PAHs have relatively low solubility and high affinity for organic carbon, and most PAH can therefore be found attached to particles that have settled or are suspended in the water column (Simon and Sobieraj 2006; ATSDR 1995). Marsalek et al. (1997) found that PAHs in stormwater were correlated to suspended solids and only a small amount of the total load was found in dissolved form. This has also been reported in other studies, such as Hoffman et al. (1984) and Gonzalez et al. (2000). In road runoff small molecules such as three-ring PAHs tend to be enriched in the fine sand fraction, whereas the larger PAH (six-ring PAHs) are enriched in the fine silt frac-

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tion (Krein and Schorer 2000). Several PAHs are carcinogenic and mutagenic (ATSDR 1995), and are included in the United States Environmental Protection Agency (USEPA) and EU priority pollutants list. According to a Danish study, runoff-contaminated sediments from a stream and a retention basin were polluted with heavy metals and PAH, and the sediment and the pore water were toxic to algae (Christensen et al. 2006). Boxall and Maltby (1995) and Maltby et al. (1995) found that organic compounds were the source of the toxicity in runoff-contaminated sediment and that the fraction of three to five-ring PAHs were the major toxicants.

Gully pots are used to trap solids and protect the downstream sewer system or receiving waters from sediment deposition. Many workers have studied the metal concentrations in gully pot sediment and water, e.g. Birch and Scollen (2003); Grottker (1990) and Pratt and Adams (1984), though very few have studied PAH in gully pots. However, Brown and Peake (2006) found that road debris (street dust and gully pot mixture) was the major source of heavy metals and PAH in stormwater and that the gully pot mixture (water and sediment) had higher concentrations of PAH than street dust. Gully pots need to be cleaned periodically because they collect significantly large amounts of material that have been washed off the streets and other surfaces into the stormwater system. The most commonly used method to clean gully pots is to use an eductor truck, which uses hydrodynamic pressure and a vacuum to loosen and remove solids and the standing liquid from the gully pot. With this method, a large amount of liquids is produced compared with solids (Hepp 1995). The liquid created during the cleaning contains pollutants from the original standing liquid plus suspended solids that can be of concern if the liquid is disposed of back into the gully pot or receiving water. When the gully pot is cleaned and the solids and standing liquid are vacuumed into the eductor truck, this mixture becomes a slurry of standing liquid, solids and wash-water that has to be disposed of. The objective of this paper is to consider the quality of the solid and liquid phase (henceforth called sediment phase and water phase) of the slurry due to the presence of PAH after it has been discharged from the eductor truck, and to determine if any differences in concentration exist between a housing area and a road. The sources of the PAHs will be investigated using profiles and ratios. The results

are compared to guidelines from different countries to determine whether the water and sediment exceed the discharge criteria.

2 Study Area and Method

2.1 Field Site

This study was conducted in northern Sweden in the city of Luleå (N:65°36', E:22°13'), with approximately 73,000 inhabitants. Luleå has an average annual precipitation of 506 mm of which 194 mm (water equivalent) is an average annual snowfall (Alexandersson and Eggertsson Karlström 2001). No de-icing salts are used in the city of Luleå however; however, between 6,000–7,000 tons of anti skid material are used (4–8 mm) and approximately 50% is removed in the spring through street sweeping. More anti-skid material is used in the city centre compared to the outskirts of the city. Two sampling sites were selected according to the type of area and traffic intensity: housing area (500 v/d) and road (25,500 v/d). The housing area consists of detached houses with private garages located in the outskirt of Luleå. The road is located in the city centre adjacent to a gulf and consists of two lanes, paved with asphalt, in each direction with a swale in the middle. The studied gully pots are on the side closest to the water and a sidewalk is located between the gully pots and the water. The contributing areas to the gully pots are asphalted roads (both areas) and roof runoff (only housing area) i.e. the areas are impervious.

2.2 Sampling

The samples were taken during the autumns of 2004 and 2005. One gully pot from each site was emptied in November 2004 and then again in November 2005 together with six other gully pots, three from each site. Three gully pots from the road (R2, R3, and R3) were emptied once during the summer, making the accumulation period only four months in this study. The gully pots were totally emptied with a washed eductor truck using hydrodynamic pressure and a vacuum to loosen and remove the sediment and water. The eductor truck has a capacity of 390 l/min at 13,000 kPa. Different amounts of water were added to the gully pots due to the hardness of the sediment.

The mixture of standing water, sediment and wash-water was mixed together in the eductor truck. When this mixture was discharged from the eductor truck, water samples representing the water that could be poured back into the cleaned gully pot, storm sewer, sanitary sewer, or surface water were collected for immediate analysis. However, the water was not poured back into the gully pots in this study and the entire mixture was dumped into a clean container and the sediment samples were collected after the over-laying water was pumped away. Between every sampling occasion, the eductor truck was washed. All gully pots were made of concrete.

Table 1 gives information about the eight gully pots regarding sampling year, cleaning interval, impervious area in the catchment, amount of standing liquid, and amount of water added during the cleaning. The whole grit chamber in gully pots H1a, H2 H3, and R1a were filled with sediment and water was therefore used during the emptying process to remove all the sediment.

2.3 Laboratory Analyses

The method used for suspended solids (SS) was the standard method SS-EN 872:1996 – a standard based on filtering through a glass-fibre filter with a pore size of 1.6 μm (SIS 1996). The water and sediment were analysed for a suite of 16 PAHs; Naphthalene (NAP), Acenaphthylene (ACY), Acenaphthene (ACE), Fluorene (FL), Phenanthrene (PHEN), Anthracene (ANT), Fluoranthene (FLR), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CHY), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Dibenz(a,h)anthracene (DBA), Benzo(ghi)perylene (BPY) and Indeno(1,2,3-cd)pyrene (INP). All chemical analyses were performed by the accredited lab-

oratory Analytica AB. The water concentrations were performed according to the methods US EPA 610 and 550 and determined by High Performance Liquid Chromatography (HPLC) with a UV- and fluorescence detector. The total concentration was extracted with hexane prior to analysis and analysing the content of the filtered samples (0.45 μm) yielded the dissolved concentration. Both external calibration and five internal standards (d8-naphthalene, d10-acenaphthene, d10-phenanthrene, d12-chrysene, d12-perylene) were used. The calibration ranges were from 10 to 2,000 ng/ml ($\mu\text{g/l}$). Limits of determination were 0.1 $\mu\text{g/l}$ for NAP, 0.01 $\mu\text{g/l}$ for ACY, ACE, ANT, BaA, CHY, BbF, BkF, INP, DBA, BPY, 0.02 $\mu\text{g/l}$ for FL and BaP, 0.03 $\mu\text{g/l}$ for PHEN and FLR, and 0.06 $\mu\text{g/l}$ for PYR. The sediment concentrations were performed according to the method US EPA 8270. The PAH concentration in the sediment was determined by Gas Chromatography–Mass Spectrometry (GC–MS) after extraction with *n*-hexan/acetone (1:1).

The suspended particulate concentration was calculated by subtracting the dissolved concentration from the total concentration and then dividing the result by the concentration of SS in the sample. To perform the calculations, values below the detection limit were replaced by half of the detection limits value, as discussed in Tsanis et al. (1994). Statistical analyses were performed using the program Statgraphics to evaluate data.

3 Results and Discussion

3.1 Total PAH Concentration

The pH, temperature, conductivity, total and dissolved concentration, mean, standard deviation, median and

Table 1 Physical characteristics for the gully pots

Gully pot	Housing area					Road				
	H1a	H1b	H2	H3	H4	R1a	R1b	R2	R3	R4
Sampled (year)	-04	-05	-05	-05	-05	-04	-05	-05	-05	-05
Cleaning interval (year)	>25 ^a	1	>25 ^a	>25 ^a	>25 ^a	>5 ^a	1	0.3	0.3	0.3
Impervious area (m^2)	418	–	305	429	560	208	–	212	197	216
Standing liquid (l)	<20	70	<20	<20	>30	<20	100	90	85	75
Water added (l)	420	–	40	80	–	600	–	–	–	–

^a According to the city of Luleå; n.d. = No data

range in the water phase are summarized in Table 2. The Canadian environmental quality guidelines (CEQ 2003), Australian Water Quality Guidelines for Fresh and Marine Waters (ANZECC 1992), British Columbia Provincial water quality criteria for polycyclic aromatic hydrocarbons (O'Riordan 1993), guideline values from the Dutch circular about contaminated soils and groundwater (DEM 1994) and the EU guidelines for drinking water (EU 1998) are shown in Table 3. The results for pH, temperature and conductivity showed that the values between the gully pots varied, though small. For the metals the mean and median values show relatively similar values, while the standard deviation shows high values indicating large variations between the gully pots. The sum of carcinogenic PAH (BaA, CHY, BbF, BkF, BaP, DBA, and INP) had a mean concentration of 3.3 ± 2.5 $\mu\text{g/l}$ in the total phase and 0.5 ± 0.9 $\mu\text{g/l}$ in the dissolved phase. The dissolved phase for the each individual PAH could be detected in most of the gully pots. FL and PHEN were the only PAHs detected in the dissolved phase in all gully pots. Most PAH were attached to particles; the dissolved fraction was between 4 and 65% for the 16 PAH in the gully pots, with a mean of

22%. However, some of the individual PAH show high percentages in the gully pots, e.g. for BaP the dissolved phase was as high as 73% of the total concentration in gully pot H3, which is of interest since BaP is strongly carcinogenic (Neff 1979) and in gully pot R2 all of the NAP was in dissolved phase. These results are higher than reported for stormwater in Marsalek et al. (1997), where around 11% in the dissolved phase and only 3 individual PAH (PHEN, PYR and FLR) were found in the dissolved phase. Hoffman et al. (1984) reported that high molecular PAH was associated with particulate matter, averaging from 79 to 93%. However, Brown (2002) reported a high percentage of dissolved PAH with low molecular weight, whereas PAH with high molecular weight were associated with particulate matter. This has also been somewhat observed in the present study. Brown (2002) also reported a higher total concentration of the total 16 PAH (similar sampling techniques) compared to this study.

In the total phase, the most abundant PAH was NAP, which accounted for 55% of the total sum of 16 PAH, followed by PHEN (10%), FLR (7.5%), and PYR (7%) of the total sum of 16 PAH. These four

Table 2 Mean-, standard deviation-, median-, maximum- and minimum concentration for pH, temperature, conductivity, suspended solids, total and dissolved PAHs in the water phase ($n=10$), ($\mu\text{g/l}$)

		Mean	St. dev	Median	Max	Min
pH		7.4	0.4	7.6	8.0	6.8
Temperature ($^{\circ}\text{C}$)		7.4	0.5	7.2	8.2	6.8
Conductivity (μS)		392	171	430	578	126
SS (mg/l)		6,681	6,170	3,700	18,000	2,000
NAP	Tot./Diss.	105/28	95/52	94/11	240/170	<0.34/<0.34
ACY	Tot./Diss.	1.4/0.3	1.0/0.5	1.4/0.1	2.9/1.6	<0.25/<0.25
ACE	Tot./Diss.	6.5/1.0	5.7/1.5	7.0/0.6	17/5.2	<0.025/<0.025
FL	Tot./Diss.	6/1.0	5.2/1.5	5.3/0.6	15/5.2	0.057/0.04
PHEN	Tot./Diss.	12/1.5	11/2.3	8.6/0.8	31/7.9	0.6/0.08
ANT	Tot./Diss.	1.9/0.3	1.7/0.5	1.6/0.1	5/1.6	0.05/<0.013
FLR	Tot./Diss.	8.4/1.0	8/1.8	5.8/0.4	22/6.1	0.8/<0.03
PYR	Tot./Diss.	5.9/0.7	5.5/1.2	3.9/0.3	16/4.1	0.6/<0.037
BaA	Tot./Diss.	0.4/0.05	0.5/0.08	0.2/0.02	1.1/0.3	0.1/<0.01
CHY	Tot./Diss.	1.1/0.2	1/0.4	0.5/0.1	3.4/1.2	0.3/<0.016
BbF	Tot./Diss.	0.7/0.08	0.5/0.1	0.5/0.02	1.7/0.4	0.2/<0.027
BkF	Tot./Diss.	0.2/0.03	0.2/0.05	0.1/0.01	0.6/0.2	<0.01/<0.01
BaP	Tot./Diss.	0.4/0.06	0.3/0.1	0.4/0.01	1.1/0.4	0.04/<0.026
DBA	Tot./Diss.	0.1/0.02	0.1/0.03	0.07/0.01	0.3/0.1	0.03/<0.012
BPY	Tot./Diss.	0.7/0.09	0.5/0.2	0.5/0.03	1.8/0.5	0.15/<0.01
INP	Tot./Diss.	0.3/0.04	0.3/0.07	0.2/0.01	1/0.2	0.06/<0.01
$\Sigma 16$ PAH	Tot./Diss.	151/34	131/60	127/15	340/200	4.6/0.7

Table 3 Threshold values for five PAH guidelines

	CWQG	BCG	ANZECC	DEM	EU
NAP	1.1	1 ^a	16	70	–
ACY	–	–	–	–	–
ACE	–	6 ^a	–	–	–
FL	–	12 ^a	–	–	–
PHEN	0.4	0.3 ^a	0.6	5	–
ANT	0.012	4 ^a /0.1 ^b	0.01	5	–
FLR	0.04	4 ^a /0.2 ^b	1.0	1	–
PYR	0.025	0.02 ^b	–	–	–
BaA	0.018	0.1 ^a	–	0.5	–
CHY	–	–	–	0.2	–
BbF	–	–	–	–	–
BkF	–	–	–	0.05	–
BaP	0.015	0.01 ^a	0.1	0.05	0.01
DBA	–	–	–	–	–
BPY	–	–	–	0.05	–
INP	–	–	–	0.05	–
Σ4 PAH ^c	–	–	–	–	0.1
Σ16 PAH	–	–	3	–	–

^a Fresh water (chronic); ^b Fresh water (phototoxic); ^c Sum of BbF, BkF, BPY and INP

individual PAH represented 80% of all 16 PAH measured in the total phase. NAP was also the most abundant PAH in the dissolved phase, 82% of the 16 PAH, followed by PHEN at only 5% of the 16 PAH.

Unfortunately, no threshold values for the individual PAH ACY, BbF and DBA were included in the five different guidelines. The mean dissolved concentrations for the individual PAH, viz. NAP, PHEN, PYR, and the sum 16 EPA-PAH all exceeded the limit for the three fresh and marine waters guidelines. The mean dissolved concentration for FLR, CHY, BaP, BPY, and the sum of 4 EU-PAH exceeded the guidelines for groundwater and drinking water; however, all of the maximum dissolved concentrations exceeded the threshold values reported in the Dutch groundwater guidelines.

Table 4 shows the mean, standard deviation, median, and range for the sediment as well as the guidelines for soil and sediment from the Canadian environmental quality guidelines (CEQ 2003) and Ontario Provincial Sediment Quality Guidelines (Environment Ontario 1993). All individual PAH, except ACY, were found in all or a few of the gully pots. The sum of carcinogenic PAH (BaA, CHY, BbF, BkF, BaP, DBA, and INP) had a mean concentration in the sediment of 0.3 ± 0.1 mg/kg dw. Table 4 shows that only NAP exceeded the CWQG for soil (residential/parkland

use), and NAP, ACE, and FL exceeded the CWQG for sediment. Compared to OMOE, those that exceeded the lowest effect levels were FL, PHEN, FLR, PYR and the sum 16 EPA-PAH. However, the maximum value for ANT and BPY exceeded the guidelines for sediment. The mean concentration of the sum 16 EPA-PAH was higher in this study compare to a New Zealand study with a similar sampling technique (Brown 2002). Another Swedish study on gully pot sediment from roads with higher traffic intensities had lower concentrations for NAP, ACE, PHEN, ANT, FLR, and PYR than this study, and the sum of 16 EPA-PAH shows the same mean value, i.e. 10 mg/kg dw (Larsson 2006). Stout et al. (2004) investigated surface sediment (0–10 cm) in 9 US waterways, with 6 showing lower sediment concentrations for the sum 16 EPA-PAH than the sediment from the gully pots. The most abundant PAH in the sediment was NAP, at 58% of the total sum of 16 PAH, followed by FLR (11%), PHEN (9%), and PYR (7%).

3.2 PAH Concentration in Different Areas

To study if any differences exist between the sites, the results were divided into two different sites: the housing area (500 v/d) and road (25,500 v/d). Table 5 shows the mean, median, and standard deviation for

Table 4 Mean-, standard deviation-, median-, maximum- and minimum concentration for suspended solids, total and dissolved PAHs in the sediment phase ($n=10$), (mg/kg dw)

	Mean	St.dev	Median	Max	Min	CWQG		OMOE
						Soil	Sediment ^a	Sediment ^b
NAP	6.8	5.7	6.3	15	0.6	0.6 ^c /22 ^d	0.391	–
ACY	<0.25	–	–	<0.25	<0.25	–	0.128	–
ACE	0.5	0.4	0.5	1	0.036	–	0.0889	–
FL	0.4	0.2	0.4	0.7	0.06	–	0.0212	0.19
PHEN	0.8	0.4	0.9	1.4	0.2	5 ^c /50 ^d	0.515	0.56
ANT	0.2	0.1	0.2	0.3	0.02	–	0.245	0.22
FLR	0.9	0.4	0.9	1.3	0.2	–	2.355	0.75
PYR	0.5	0.2	0.6	0.8	0.2	10 ^c /100 ^d	0.875	0.49
BaA	0.06	0.01	0.06	0.07	0.04	1 ^c /10 ^d	0.0748	0.32
CHY	0.03	0.03	0.02	0.1	<0.037	–	0.862	0.34
BbF	0.2	0.07	0.2	0.2	0.06	1 ^c /10 ^d	–	–
BkF	0.03	0.01	0.02	0.04	0.02	1 ^c /10 ^d	–	0.24
BaP	0.01	0.01	0.01	0.03	<0.01	0.7 ^c /0.7 ^d	0.782	0.37
DBA	0.01	0.01	0.01	0.03	<0.01	1 ^c /10 ^d	0.135	0.06
BPY	0.09	0.06	0.09	0.2	0.03	–	–	0.17
INP	0.02	0.01	0.02	0.05	<0.034	1 ^c /10 ^d	–	0.2
Σ16 PAH	10	7.4	9.9	20	1.4	–	–	4

^a Freshwater, Probable effect level; ^b Lowest effect level; ^c Residential/Parkland use; ^d Commercial land use

the water concentrations for both sites. The housing area had higher mean concentrations than the road for almost all individual PAH in both total and dissolved phases; only BaP had the same total concentrations in

both areas. Both areas had high standard deviations, though the housing area appeared to be higher because the road area is a more homogenous than the housing area. However, statistical analyses were

Table 5 Mean-, standard deviation-, and median concentration for suspended solids, total and dissolved PAHs in the water phase in a housing area and a road (μg/l)

		Housing area			Road		
		Mean	St. dev	Median	Mean	St. dev	Median
SS (mg/l)		6,662	6,790	3,000	6,700	6,288	4,100
NAP	Tot./Diss.	121/41	111/73	180/8.9	89/15	87/16	57/12
ACY	Tot./Diss.	1.5/0.4	1.3/–	2/0.1	1.2/0.2	0.7/0.1	1.1/0.1
ACE	Tot./Diss.	8.1/1.3	7.6/2.2	11/0.3	4.9/0.7	3.2/0.5	4.9/0.9
FL	Tot./Diss.	7.7/1.3	7/2.2	11/0.3	4.4/0.8	2.5/0.5	4.4/0.7
PHEN	Tot./Diss.	16/2	14/3.3	23/0.6	7.6/1	3.7/0.6	7.1/0.8
ANT	Tot./Diss.	2.5/0.4	2.2/0.7	3.3/0.09	1.3/0.2	0.8/0.1	1.3/0.1
FLR	Tot./Diss.	12/1.4	10/2.6	18/0.4	4.9/0.6	2.5/0.4	4.5/0.4
PYR	Tot./Diss.	8.4/1.0	7/1.7	11/0.3	3.4/0.4	1.5/0.3	3/0.3
BaA	Tot./Diss.	0.7/0.07	0.5/0.1	0.9/0.03	0.2/0.03	0.1/0.02	0.1/0.02
CHY	Tot./Diss.	1.6/0.3	1.2/0.5	1.7/0.1	0.6/0.1	0.6/0.1	0.4/0.05
BbF	Tot./Diss.	0.9/0.1	0.7/0.2	0.9/0.03	0.5/0.05	0.1/0.05	0.5/0.01
BkF	Tot./Diss.	0.2/0.04	0.3/0.07	0.1/0.01	0.09/0.01	0.03/0.007	0.08/0.01
BaP	Tot./Diss.	0.4/0.09	0.4/0.2	0.2/0.01	0.4/0.04	0.1/0.003	0.4/0.01
DBA	Tot./Diss.	0.2/0.02	0.1/–	0.1/0.01	0.1/0.009	0.07/0.004	0.06/0.01
BPY	Tot./Diss.	0.9/0.1	0.7/0.2	0.7/0.02	0.5/0.06	0.1/0.05	0.4/0.04
INP	Tot./Diss.	0.5/0.06	0.4/0.1	0.4/0.01	0.1/0.02	0.03/0.02	0.1/0.01
Σ16 PAH	Tot./Diss.	183/48	162/86	270/11	118/19	98/16	84/19

performed (two-sample comparison of the means, a *t*-test) indicating no significant difference between the two sites, at a 95% confidence level for either total or dissolved concentrations. The sum of carcinogenic PAH in the housing area had a mean concentration of $4.5 \pm 3 \mu\text{g/l}$ in the total phase and $0.8 \pm 1.3 \mu\text{g/l}$ in the dissolved phase, and the road had a mean concentration of $2 \pm 1 \mu\text{g/l}$ in the total phase and $0.2 \pm 0.3 \mu\text{g/l}$ in the dissolved phase. Compared to the guidelines presented in Table 3, the dissolved concentrations for both areas exceeded all or a few of the guidelines, and only FL had concentrations below the limits.

Table 6 shows the mean, standard deviation, and median for the sediment concentrations of the two sites. The mean concentration of the road was higher for all individual PAH except for BaP. The standard deviation was higher for the housing area, though generally lower in the sediment than for the water phase. According to statistical analyses (a *t*-test), a significant difference between the two sites existed for NAP, ACE, FL, ANT, FLR, PYR, BaF, and BPY, at a 95% confidence level, whereas no significant difference could be found for BaA, BbF, and BkF. Unfortunately, no statistical analysis could be made for the following PAH, since most of their concentrations were below the detection limit, i.e. ACY $<0.25 \text{ mg/kg dw}$, CHY <0.037 , BaP <0.01 ,

DBA <0.01 , and INP <0.034 . Similar differences between sites were previously reported, such as Murakami et al. (2005) who studied the PAH content in road dust in Japan for a residential area and a heavy traffic area and found a significant difference in the PAH profiles between both locations rather than between size-fraction, density-fraction and period of sampling. Lau and Stenstrom (2005) showed that street particles in a residential area had lower concentrations than commercial, road and industrial land use. The sum of carcinogenic PAH had a mean concentration in the sediment of $0.2 \pm 0.05 \text{ mg/kg dw}$ for the housing area and $0.4 \pm 0.05 \text{ mg/kg dw}$ for the road. Compared to the guidelines for soil and sediment in Table 4, only the NAP concentration exceeded the limit for soil (residential/parkland use), while the concentrations of ACE and FL, in both sites, and the concentrations of PHEN, ANT, FLR, PYR, and 16 EPA-PAH for the road exceeded the guidelines for sediment.

3.3 Sources

The major source of PAH in stormwater comes from combustion of fossil fuels or wood (pyrogenic source) and drips of petroleum products (petrogenic source) (Neff 1979; Brown 2002). Many studies, e.g. Hoffman

Table 6 Mean-, standard deviation-, and median concentration for suspended solids, total and dissolved PAHs in the sediment phase in a housing area and a road (mg/kg dw)

	Housing area			Road		
	Mean	St. dev	Median	Mean	St. dev	Median
NAP	1.8	1.2	1.7	12	3	11
ACY	<0.25	—	—	<0.25	—	—
ACE	0.2	0.1	0.2	0.8	0.2	0.8
FL	0.2	0.09	0.2	0.6	0.07	0.6
PHEN	0.4	0.2	0.5	1.3	0.1	1.2
ANT	0.09	0.05	0.1	0.3	0.03	0.3
FLR	0.6	0.3	0.7	1.2	0.1	1.2
PYR	0.3	0.1	0.4	0.7	0.04	0.7
BaA	0.05	0.02	0.05	0.07	0.005	0.06
CHY	0.03	0.01	0.02	0.04	0.05	0.02
BbF	0.08	0.03	0.07	0.2	0.02	0.2
BkF	0.02	0.005	0.02	0.03	0.01	0.03
BaP	0.02	0.01	0.02	0.007	0.004	0.005
DBA	0.01	0.01	0.005	0.02	0.007	0.02
BPY	0.04	0.03	0.03	0.1	0.04	0.1
INP	<0.034	—	—	0.03	0.02	0.03
$\Sigma 16 \text{ PAH}$	3.8	1.9	4	17	2.9	17

et al. (1984); Rocher et al. (2004); Brown and Peake (2006), have divided the 16 EPA-PAH into 2 different groups depending on their physical, chemical and biological properties; low molecular weight (LMW) and high molecular weight (HMW) PAH. The LMW PAH have 2–3 rings (naphthalene to anthracene) and are acutely toxic to many aquatic organisms; the HMW PAH have 4–6 rings (fluoranthene to Indeno(1,2,3-cd)pyrene) and are strongly carcinogenic, especially BaP (Neff 1979; Brown 2002). Pyrogenic sources have a high abundance of HMW PAH, and LMW PAH dominates petrogenic sources. However, some sources are in-between pyrogenic and petrogenic profiles, e.g. used lubricating oil and asphalt (Brown and Peake 2006).

The relative distribution of individual PAH can be used to study the source of the PAH (Brown and Peake 2006; Stout et al. 2004). The individual profiles for the gully pots are plotted in Fig. 1 together with the profile for atmospheric emissions from the steel industry (Wahlberg 2007, pers. comm.), gasoline (Marr et al. 1999), diesel fuel (Mi et al. 2000), used lubricating oil (Wang et al. 2000), bitumen (Brandt and De Groot 2001) and tire rubber (Lindgren 1998). All three profiles for the gully pots show a very high abundance of NAP; 83% for dissolved, 66% for

suspended particles, and 65% for sediment phase. Gonzalez et al. (2000) found that NAP contributed 66% to the total atmospheric fallout in a study in Paris, and Yang et al. (1998) showed that the concentration of NAP is much higher than other PAH from various industrial stacks. A major steel industry located in Luleå discharged approximately 0.99 ton/year of sum of 16 PAH into the atmosphere, where NAP is the most abundant individual PAH (Alatalo 2006). Regardless of NAP, the gully pots are enriched in LMW PAH both in the water and sediment phase. The suspended particles and the sediment show similar profiles even though the sediment had slightly more FLR than the water phase. The profile for gasoline shows a high abundance of NAP while that of diesel fuel shows high abundance of LMW PAH. The profile for the used lubricating oil has a high abundance of PHEN, ANT, NAP, and PYR, i.e. mostly LMW PAH. HMW PAH dominates the bitumen profile more, though it has high abundance of some LMW PAH (NAP and PHEN), while the tire rubber profile shows a high abundance of PYR. The gully pot mixture seems to be a mix between atmospheric fall out, gasoline, diesel fuel, used lubricating oil, and to some extent, bitumen (asphalt). The gully pots are depleted

Fig. 1 Relative distribution of individual PAH for the dissolved, suspended particles and sediment phase for the gully pot mixture and atmospheric emission from steel industry (Wahlberg 2007, pers. comm.), gasoline (Marr et al. 1999),

diesel fuel (Mi et al. 2000), used lubricating oil (Wang et al. 2000), Bitumen (Brandt and De Groot 2001), Tyre rubber (Lindgren 1998)

in HMW PAH, which mainly comes from combustion, and are regarded as fine particles (Krein and Schorer 2000). Because the gully pot poorly retains fine particles (Morrison et al. 1988), the fine particles have probably followed the stormwater out from the gully pot.

Another approach to study the sources is to use different parent (non-alkylated) PAH ratios; commonly used ratios are LMW/HMW, PHEN/ANT (or ANT/ANT+PHEN), and FLR/PYR (or FLR/FLR+PYR) (Soclo et al. 2000; Yunker et al. 2002; Rocher et al. 2004; Brown and Peake 2006). LMW PAH dominate petrogenic contaminations (spilt oil or petroleum products) with an LMW/HMW ratio >1 , whereas HMW PAH dominate pyrogenic contaminations (incomplete combustion of fossil fuels or wood) with an LMW/HMW ratio <1 (Neff 1979; Soclo et al. 2000). The gully pots had high LMW/HMW ratios of 20.4 for the dissolved phase the ratio, 4.2 for the suspended particles and 5.9 for the sediment. LMW PAHs are more soluble than HMW PAHs (Neff 1979), a characteristic that might explain why the LMW/HMW ratio was higher for the dissolved phase than the particulate phase. The ratio for the suspended particles and sediment phase was also high, indicating a petrogenic source. The LMW/HMW ratio for gasoline was 91, diesel fuel was 22, used lubricating oil was 1.2, and bitumen 0.5 (Marr et al. 1999; Brandt and De Groot 2001; Mi et al. 2000; Wang et al. 2000). The ratio can differ between different brands of gasoline, diesel and oil, depending on the difference in crude oil properties, refinery operations or both (Marr et al. 1999). Even if the ratios for gasoline and diesel were higher than the

gully pot ratio, they are most likely a source for PAH in the gully pot mixture. Dividing the gully pots into different areas (housing and road) the results showed that the road had a higher ratio than the housing area, in the suspended particles phase 3.6 vs. 8.3 and in the sediment 2.2 vs. 6.1, indicating a larger contribution of petrogenic sources for the road. In this study the sources of the road are most likely atmospheric deposits and traffic, while the sources from the housing area are more dependent on the activities in the area. Some studies, e.g. Soclo et al. (2000), have excluded the lowest weight PAH due to their higher volatility than higher weight PAH. Several studies (e.g. Smith et al. 2000; Gryniewicz et al. 2002; Brown 2002) have detected high concentrations of low weight PAH in stormwater, indicating that these PAH should not be disregarded, since they are acutely toxic to many aquatic organisms (Neff 1979). However, if NAP is excluded from the calculations the LMW/HMW ratio still shows a value >1 , indicating a petrogenic source.

The PHEN/ANT ratio is high when petrogenic sources are dominant, since PHEN is more stable than ANT and the ratio is lower when pyrogenic sources are dominant (Soclo et al. 2000). Budzinski et al. (1997) has defined two classes; PHEN/ANT >10 for petrogenic sources and PHEN/ANT <10 for pyrogenic sources, though the boundary between the sources can fluctuate. FLR and PYR are often associated and are considered as typical pyrogenic products because they are primarily produced during combustion processes (Neff 1979; Soclo et al. 2000). However, the ratio differs for the combustion of different coals, e.g. Polish and French coal gives a ratio

Fig. 2 PAH cross plots for the ratios of ANT/ANT+PHEN vs. FLR/FLR+PYR in the gully pot sediment, suspended particulate phase and dissolved phase

between 4.4 and 6.5 and Australian coals gives ratios between 0.3 and 0.7 (Masclat et al. 1987). PHEN/ANT ratios in the gully pot were similar for sediment 5.3 and suspended particles 6.2, and the dissolved phase had a ratio of 9.8. The sediment and suspended particles indicated pyrogenic sources, while the dissolved phase was in the boundary zone. For example, the PHEN/ANT ratio was higher in the gully pots than for used lubricating oil (1.7), petrol engine soot (1.8) and wood smoke (3.4) (O'Malley et al. 1996; Wang et al. 2000), but lower than crude oil (13.6) (Benner et al. 1990). The gully pots FLR/PYR ratio was 1.6 for the sediment, 1.4 for the suspended particles and 1.2 for the dissolved phase indicating a pyrogenic source. The ratios for all three phases are similar to combustion sources like petrol engine soot (0.9) and wood smoke (0.95) (O'Malley et al. 1996).

Yunker et al. (2002) classified the ratios ANT/ANT+PHEN and FLR/FLR+PYR according to several references. As seen in Fig. 2, the ratio ANT/ANT+PHEN <0.1 designates petrogenic sources, while ratios >0.1 specifies pyrogenic sources. The ratio FLR/FLR+PYR <0.4 indicates petroleum sources, the ratio between 0.4 and 0.5 is a mixed zone with both petroleum and combustion sources and ratios >0.5 indicate grass, wood, coal combustion or a combination thereof. The ANT/ANT+PHEN ratio in the gully pots specifies combustion sources, though most of them are very close to the boundary line between combustion and petroleum (Fig. 2). A few gully pots also designate petroleum sources for the water phase (suspended particles and dissolved phase). The FLR/FLR+PYR ratio, however, shows grass, wood, coal combustion or a combination thereof for most of the gully pots, but some gully pots show mixed sources in the water phase.

The different approaches to identify the sources discussed in this paper give different answers depending on which is used, though all approaches indicate that the mixed sources dominate the gully pot mixture. PAH ratios work best for samples dominated by a single source, but because most environmental samples contain PAH from mixed sources (Yunker et al. 2002), it is difficult to identify the sources through ratios or profiles.

A large amount of contaminated water is formed when the gully pots are cleaned with help of an eductor truck. Sometimes this water is poured back into the gully pot to transport more solids (Hepp

1995), which can cause problems in the receiving water (Crowley 2006). Christensen et al. (2006) showed that the suspension of sediment particles is more toxic than pore water and that the suspension may cause toxic effects in the receiving water. The PAH concentrations in the gully pot mixture exceed the different guidelines, meaning that the mixture (especially the water phase) must be treated before it reaches the environment.

4 Conclusions

All measured PAH were found in the gully pot mixture. The results show that in the water phase most PAH were attached to particles and approximately 22% of the total 16 PAH were in dissolved phase. The most abundant PAH in the gully pot mixture were NAP, PHEN, FLR and PYR. In the water phase no significant difference between the two sites could be found at a 95% confidence level. There was a significant difference in the sediment phase between the two sites for NAP, ACE, FL, ANT, FLR, PYR, BaF, and BPY, at a 95% confidence level, whereas no significant difference could be found for BaA, BbF, and BkF. Both the water and sediment phases exceeded one or more of the compared guidelines. The identification of the sources gave different answers depending on which are used, though all showed that the PAH in the gully pot mixture came from mixed sources. The results from this paper show that not only the sediment but also the water phase created during the emptying process of the different gully pots need to be discussed. The water should not be poured back to the gully pot, storm sewer, sanitary sewer, or surface water; instead, it should be treated in a sustainable way before it reaches the environment.

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