

Elimination and accumulation of polycyclic aromatic hydrocarbons in urban stormwater wet detention ponds

Darja Istenič, Carlos A. Arias, Víctor Matamoros, Jess Vollertsen and Hans Brix

ABSTRACT

The concentrations of polycyclic aromatic hydrocarbons (PAHs) in water and sediments of seven wet detention ponds receiving urban stormwater were investigated. The ponds comprised traditional wet detention ponds with a permanent wet volume and a storage volume as well as ponds that were expanded with sand filters and other means to improve the removal of micropollutants. The concentrations of Σ PAH in the sediments varied between 6 ± 5 and $2,222 \pm 603$ ng g⁻¹ dry weight (mean \pm standard deviation), and were highest in the ponds with lower pond volume per catchment area and did not clearly reflect different activities in the catchments. In general, the concentrations of PAHs in the sediments decreased from inlet to outlet, especially in the systems with good conditions for sedimentation such as systems with flow perpendicular sand dikes and extensive submerged vegetation. High molecular weight PAHs were predominant in the sediments indicating the pyrogenic origin of the PAHs. There was no correlation between PAH species concentrations in water or sediments and their hydrophobicity ($\log K_{ow}$). PAH concentrations in water fluctuated in response to intensity and frequency of rain events, whereas concentrations in the sediments integrated the pollutant load over time. Pond systems expanded with sand filters and other technologies to enhance removal of micropollutants consistently had concentrations of PAHs in the effluents below the detection level.

Key words | micropollutant, *Phragmites*, priority pollutant, sand filter, sediment

Darja Istenič (corresponding author)
LIMNOS Company for Applied Ecology,
Podlimbarskega 31,
1000 Ljubljana,
Slovenia
E-mail: darja@limnos.si

Carlos A. Arias
Hans Brix
Department of Biological Sciences,
Aarhus University,
Ole Worms Allé 1,
8000 Aarhus C,
Denmark

Víctor Matamoros
Department of Chemistry,
University of Girona,
Campus Montilivi,
Girona 17071,
Spain

Jess Vollertsen
Section of Environmental Engineering,
Aalborg University,
Sohngaardsholmsvej 57,
9000 Aalborg,
Denmark

INTRODUCTION

Stormwater runoff generated as a result of precipitation on impervious surfaces in urbanized areas can cause several negative effects in the environment. The presence and amount of pollutants in the runoff depends on the land use in the catchment and results in a wide range of pollutants being found in stormwater runoff. Among the most common pollutants in stormwater are suspended solids, nutrients, heavy metals and micropollutants such as polycyclic aromatic hydrocarbons (PAHs). PAHs consist of two or more aromatic rings and are represented by around 100 different chemicals that usually arise during incomplete combustion of organic matter (fossil fuels, wood, cigarettes, etc.). Most PAHs have no known use but they appear in some products like coal tar, creosote, roofing tar, crude

oil, asphalt, some medicines or dyes and plastics. PAHs are potentially highly carcinogenic and mutagenic and thus 16 of the most common PAHs are listed as priority pollutants by the US-EPA (2000).

One of the most reliable and widespread technologies for the treatment of stormwater runoff are wet detention ponds. Wet detention ponds have a permanent water volume and a temporary storage volume above it. The most important treatment processes in wet detention ponds are sedimentation, microbial degradation of organic matter and plant uptake (Hvitved-Jacobsen *et al.* 1994). Earlier studies on wet detention ponds report efficient removal of suspended solids (Hossain *et al.* 2005), particulate heavy metals (Scholes *et al.* 1999) and moderate

removal of nutrients (Carleton *et al.* 2001). In this study the performance regarding PAHs of seven wet detention ponds is presented along with accumulation of PAHs in the sediment. The wet detention ponds received stormwater from different types of catchments and had different designs.

As aromatic compounds, PAHs have low water solubility/high hydrophobicity ($\log K_{ow}$), and they therefore tend to adsorb to particles (Martinez *et al.* 2004). Sorption of PAHs to soil and sediments increases with increasing organic carbon content (Evans *et al.* 1990) and the PAHs with high K_{ow} values will be partitioned to a much greater extent to organic carbon in suspended solids than PAHs with low K_{ow} (Crunkilton & DeVita 1997). Individual PAH species tends to interact differently with sediments and suspended particulate matter because of their different physicochemical characteristics (Qiao *et al.* 2008). Stenstrom & Kayhanian (2005) analysed 32 particulate and soluble PAHs in stormwater runoff and found that the majority of PAHs were in the particulate phase, while soluble PAHs rarely were found above the detection limit of 5 ng L^{-1} . Similar to this, Hwang & Foster (2006) reported that 87% of the total PAHs were bound to filterable particles in streams receiving urban runoff. Therefore the main removal mechanism of PAHs from stormwater in wet detention ponds is considered to be sedimentation. However, in the open water phase photodegradation may also contribute to the removal (Fasnacht & Blough 2002). In the sediment, especially PAHs with four or less aromatic rings can be biodegraded, while heavier PAHs (four, five or six rings) are more persistent and also tend to have greater carcinogenic and other chronic impacts (Mangas *et al.* 1998).

METHODS

Sampling site description

The study was carried out in Denmark on seven wet stormwater detention ponds receiving runoff from residential areas, highways, roads and industrial areas, and therefore receiving different loads of PAHs (Table 1). Four ponds (referred to as pond A, B, C and D) are traditional wet detention ponds with a maximum permanent water depth of 1.4 m, inflow and outflow structures and natural wetland vegetation along the edges, while the other three are newly developed systems with modified designs optimized to treat stormwater runoff. The three systems were constructed in Aarhus, Odense and Silkeborg in the framework of a LIFE Environment project. The systems include a variety of additional technologies to improve the elimination of soluble and colloidal pollutants from stormwater, namely sand filters planted with *Phragmites australis* at the outflow of each system, facilities to dose aluminium salts at the inflow to the system at Silkeborg, an iron enriched sediment in the system at Aarhus, and adsorption filters at the final outflow from the system at Odense. More information about the systems and additional technologies implemented are presented by Vollertsen *et al.* (2009).

Sampling strategy

Flow proportional water samples were taken at the inlets and time proportional samples along the flowpath in the systems at Aarhus, Odense and Silkeborg. In the traditional wet detention ponds, grab samples were taken during dry weather conditions. The organic upper sediment layers

Table 1 | Characteristics of the investigated stormwater wet detention ponds

System	Annual precipitation (mm)	Total catchment area (ha)	Impervious catchment area (ha)	Pond volume (m ³)	Pond volume per catchment area (m ³ ha ⁻¹)	Start of operation	Catchment type
Pond A	661	28.3	20.7 (73%)	7,720	273	2003	Roads, light industry
Pond B	661	109.4	42.6 (39%)	14,330	131	2003	Residential area
Pond C	661	6.4	4.5 (70%)	1,630	255	2003	Light industry, residential area
Pond D	661	74.0	46.6 (63%)	16,400	222	2003	Light industry
Aarhus	661	57.4	25.8 (45%)	6,900	120	January 2008	Urban area
Odense	657	27.4	11.4 (42%)	1,990	73	December 2007	Light industry
Silkeborg	719	21.5	8.8 (41%)	2,680	125	September 2008	Roads, residential area

that had accumulated in the ponds over time were sampled in flow-perpendicular transects. At each transect, three to six individual samples were taken with a metal grab sampler designed for scraping the surface sediment. The organic layer was from a few millimetres up to 7 cm high. The content of organic matter in the sampled sediment varied between the systems and was in general decreasing from inlet to outlet. A total of 43 sediment and 175 water samples were taken from April 2008 to September 2009 and analysed for 16 PAHs (US-EPA recommended priority pollutants). All water samples were collected in 1 L amber clean glass bottles. The samples were transported to the laboratory the same day. Surface sediments were wrapped in aluminium foil and transported to the laboratory, where they were immediately frozen and subsequently freeze-dried. Also traditional water quality parameters were analysed (results not presented here).

In order to avoid contamination with PAHs from plastic materials the samples for PAHs analysis were handled only by glass material. All glass materials used for sampling, extraction and analysis of PAHs were muffled for at least 4 h at 400 °C before use to assure the required cleanness.

Chemicals

Naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)-anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene at 10 mg/L in cyclohexane were purchased from Dr Ehrenstorfer (Augsburg, Germany).

Water PAH analysis

Liquid-liquid extraction was carried out from 200 mL of the water sample with 20 mL of dichloromethane. Prior to extraction samples were spiked with a methanolic solution of surrogates (naphthalene-d8 (99%), anthracene-d10 (98%), pyrene-d10 (98%) and benzo(a)pyrene-d12 (98%), 50 ng of each compound). Extracts were filtered through sodium sulfate in order to remove water. Sodium sulfate was activated at 400 °C for 4 h and maintained activated at 100 °C until use. The extraction procedure was repeated three times with each sample. Samples were then concentrated to 0.25 mL under a flow of N₂-gas. Internal standard (triphenylamine) was added to the concentrated samples which were then stored at -18 °C until analysis by a Shimadzu GC-MS 2010 (Shimadzu Corporation, Japan). Limit of detection

(LOD) and limit of quantification (LOQ) ranged from 1.42 to 31.4 ng L⁻¹ and from 3.75 to 75.5 ng L⁻¹, respectively. Recoveries of surrogates were always higher than 90% with a relative standard deviation (RSD) lower than 20%. Detailed temperature programme and quantification are described in [Guitard *et al.* \(2004\)](#).

Sediment PAH analysis

PAHs were extracted from ~2 g of freeze-dried sample using dichloromethane. Prior to the extraction previously described, samples were spiked with the same solution of surrogates (50 ng of each compound). Solid-liquid extraction was carried out in an ultrasonic bath (15 min) followed by centrifugation (5,000 rpm for 10 min). The supernatant was removed through a sodium sulfate filter as described previously. The extraction procedure was repeated three times for each sample and the supernatants combined. Samples were concentrated under a N₂-gas flow to a volume of about 1 mL, and then filtered through deactivated alumina to remove colour. Aluminium oxide used for the filter was activated at 400 °C for 4 h and maintained activated at 100 °C until use. Before filtering the sample, 2 mL of dichloromethane were passed through the filter, and after the filtration the filter was eluted with 12 mL ethyl acetate. Samples were then concentrated under a flow of N₂-gas to 0.25 mL. Internal standard as described before was added to the concentrated samples, which were then stored at -18 °C until analysis by GC-MS. LOD and LOQ ranged from 0.05 to 2.8 ng g⁻¹ and from 0.16 to 9.2 ng g⁻¹, respectively. Recoveries of surrogates were always higher than 80% and RSDs were lower than 20%.

RESULTS AND DISCUSSION

PAHs in water

At the four traditional wet detention ponds only one sampling campaign was carried out, hence we have no measurement of variability in concentration levels, and the analytical results only show concentrations at the time of sampling. The data are therefore not presented in detail here. In short, the light-weight naphthalene, phenanthrene and pyrene were detected in higher concentrations compared to other PAHs in all ponds, while the four-ringed benzo(a)anthracene and five-ringed chrysene and dibenzo(a,h)anthracene were below detection limit in all samples. This is in accordance with [Qiao *et al.* \(2008\)](#), who found a

domination of less hydrophobic low molecular weight (LMW) PAHs in the water of a natural shallow lake, while the high molecular weight (HMW) PAHs were below detection level. The \sum PAHs varied between 30 and 119 ng L⁻¹ but concentrations did not decrease consistently from inlet to outlet.

In the wet detention ponds at Aarhus, Odense and Silkeborg, average PAH concentrations were above the detection limit only in the water sampled at the inflow, except in Silkeborg, where average naphthalene concentration was above the detection limit in water from the middle pond (Table 2). In the outflow from the systems (after sand and/or sorption filters) as well as in the pond water itself, the average PAH concentrations were below the detection limits. This indicates an efficient removal of PAHs from stormwater in all systems. The HMW (4–6 ring) PAHs prevailed in the inflows; however a 3-ring phenanthrene was also above detection limit. There was no correlation between PAH concentrations and their octanol-water partitioning coefficients (log K_{ow}). Based on the raw data, all 16 PAHs were detected in concentrations above the detection limit at least at one sampling date in the systems at Aarhus and Odense, while at Silkeborg 11 PAHs had concentrations higher than the detection limits.

The high standard deviations of the measured PAH concentrations indicate that PAH concentrations in the stormwater fluctuate greatly as a consequence of time-dependent variability of the stormwater pollutant loads within each single rain event and among the events. The standard deviation of pollutant concentrations that originate from a series of runoff events has in other studies been found to be of the same order of magnitude as their mean value (Hossain *et al.* 2005; Stenstrom & Kayhanian 2005). The highest diversity in PAH species and PAH concentrations were found in the Aarhus system, which receives stormwater mainly from residential areas. The system at Odense, which receives runoff from an industrial area, had higher average \sum PAH concentrations while PAH levels were low in the Silkeborg system.

Sources of PAHs can be pyrogenic or petrogenic (Brown & Peake 2006) where pyrogenic PAHs generally are found in combustion-derived particles, and petrogenic PAHs are found mainly in fuel oil or light-refined petroleum products. In pyrogenic PAHs HMW 4–6 ring PAHs prevail above LMW 2–3 ring PAHs, whereas in petrogenic PAHs LMW dominate above HMW PAHs. In this study, HMW PAHs prevailed above LMW PAHs indicating a pyrogenic source of these pollutants. Similar results were reported by

Table 2 | Average (± 1 standard deviation) PAH concentrations (ng L⁻¹) in the water at different locations in the wet detention ponds at Aarhus, Odense and Silkeborg

	Århus			Odense				Silkeborg		
	Inflow (n = 16)	Pond (n = 23)	Sand filter (n = 19)	Inflow (n = 17)	Pond (n = 25)	Sand filter (n = 20)	Sorption filter (n = 18)	Inflow (n = 4)	Pond (n = 13)	Sand filter (n = 11)
NAP	<10	<10	<10	<10	<10	<10	<10	<10	14 ± 15	<10
ACY	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
ACE	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
FL	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
PHE	16 ± 23	<10	<10	16 ± 35	<10	<10	<10	10 ± 11	<10	<10
ANT	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
FLU	25 ± 39	<10	<10	28 ± 53	<10	<10	<10	11 ± 13	<10	<10
PYR	31 ± 56	<10	<10	37 ± 75	<10	<10	<10	14 ± 13	<10	<10
BaA	<10	<10	<10	14 ± 19	<10	<10	<10	<10	<10	<10
CHR	17 ± 48	<10	<10	23 ± 50	<10	<10	<10	<10	<10	<10
BbjkF	48 ± 91	<10	<10	43 ± 88	<10	<10	<10	<10	<10	<10
BaP	15 ± 29	<10	<10	17 ± 27	<10	<10	<10	<10	<10	<10
IND	13 ± 34	<10	<10	21 ± 34	<10	<10	<10	13 ± 26	<10	<10
DBA	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
BDP	44 ± 56	<10	<10	17 ± 102	<10	<10	<10	<10	<10	<10
\sum PAH	179 ± 403	<10	<10	358 ± 479	<10	<10	<10	<10	16 ± 43	<10

NAP, naphthalene; ACY, acenaphthylene; ACE, acenaphthene; FL, flourene; PHE, phenanthrene; ANT, anthracene; FLU, flouranthene; PYR, pyrene; BaA, benz[a]anthracene; CHR, chrysene; BbjkF, benzo[b + j + k]flouranthene; BaP, benzo[a]pyrene; IND, indeno[1,2,3-cd]pyrene; DBA, dibenz[a,h]anthracene; BDP, benzo[ghi]perylene.

Hwang & Foster (2006) in urban stormwater runoff. However, Qiao *et al.* (2008) found a domination of less hydrophobic (LMW) PAHs in the water of a natural shallow lake while HMW PAHs were not detected. This indicates that PAHs in the three wet detention ponds with additional treatment technologies originated from stormwater pollution and that their distribution was not correlated to their hydrophobicity but rather to their source. In contrast to that, LMW PAHs prevailed in the water in the four traditional wet detention ponds, as reported by Qiao *et al.* (2008), which might be explained by the fact that the sampling occurred during dry weather conditions with no discharge of stormwater.

PAHs in the sediment

As the majority of PAHs is known to be associated with suspended particles (Hwang & Foster 2006), the main removal mechanism of PAHs in wet detention ponds is supposed to be sedimentation with a consecutive accumulation of PAHs in the sediment accreting on the bottom of the ponds. The results of the sediment analysis clearly showed that PAHs accumulated in the sediment of the ponds and the PAH concentrations differed markedly between the ponds. Pond C had a significantly lower average Σ PAH concentration compared to ponds A and B, which may be explained by differences in catchment use or more likely by the intensity of the activities in the catchment and by the ratio between the pond volume and the catchment area (Table 1). The concentrations of PAHs were, as expected, generally highest at the influent end of the ponds, corresponding to the zone with the highest accretion rates. In pond A, B and D the lowest Σ PAH concentrations were measured at the outlet, while in pond C, the lowest Σ PAH occurred in the middle of the pond, which seemed to be a hydraulically 'dead zone' (Figure 1). Especially in pond B, concentrations of individual PAHs at the outlet were similar to the concentrations at the middle of the pond, indicating that the majority of PAH reduction appeared in the first half of the pond. Pond B was densely vegetated by submersed *Elodea canadensis*, which enhanced sedimentation. This pond also accumulated the highest Σ PAH concentrations compared to all other systems. It is known that dense macrophyte vegetation reduces hydraulic flow thus allowing greater residence time for sedimentation, filtration and bioaccumulation processes (Benoy & Kalff 1999; Hares & Ward 2004). Comparing PAH species in the four traditional wet ponds, fluoranthene, pyrene and chrysene prevailed above other analysed PAHs along with some other

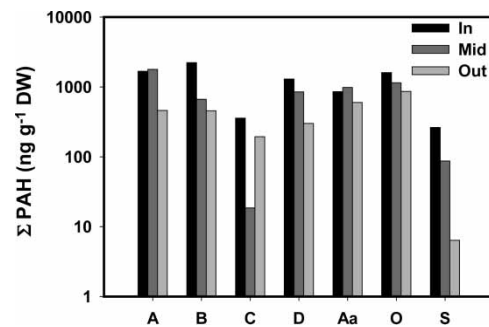


Figure 1 | Average Σ PAH concentrations (ng g⁻¹ dry weight) in the sediment at the inlet (In), halfway through (Mid) and at the outlet (Out) of traditional wet detention ponds (A–D) and in the ponds of improved stormwater systems at Aarhus (Aa), Odense (O) and Silkeborg (S).

combustion-derived PAHs. LMW acenaphthene and fluorene were not detected in pond B and C (Table 3).

The results of sediment PAH analyses of the three 'improved' stormwater systems at Aarhus, Odense and Silkeborg showed that the Odense system, which receives runoff from an industrial area, had the highest PAH concentrations followed by Aarhus and Silkeborg (Table 4). Comparing PAH species, LMW fluorene, acenaphthene and anthracene were often below detection limit in the sediment samples, which is in accordance with the results of the PAH analyses of the water. Combustion-derived PAHs like pyrene, fluoranthene and indeno(1,2,3-cd)pyrene generally occurred in higher concentrations than other PAH species.

Σ PAH concentrations in the sediment at the Aarhus and Odense systems did not show marked decrease through the ponds, while in Silkeborg there was a significant decrease in sediment Σ PAH concentrations through the pond, which is due to two flow-perpendicular sand dikes constructed in this pond in order to enhance sedimentation.

To our knowledge, there are no publications documenting changes in PAH concentrations in the sediment along the flow path in stormwater wet detention ponds. Because the main removal process of PAHs from stormwater is sedimentation, higher PAH concentrations are expected at the inlet region of the pond. In this study, a decrease in PAH concentration through the pond was found in the Silkeborg ponds, and to some extent in ponds A, B and D. In the pond at Aarhus, the highest PAH concentrations were detected in the sediment in the middle of the pond and in the pond at Odense, higher PAH concentrations in the middle of the pond were detected for half of the analyzed PAHs. The difference between the ponds in spatial distribution of accumulated PAHs is probably caused by the different hydraulics of the systems, different shapes of the ponds

Table 3 | Average (± 1 standard deviation) PAH concentrations (ng g^{-1} dry weight) in the sediment at the inlet (In), halfway through (Mid) and at the outlet (Out) of four wet detention ponds

PAH	Pond A			Pond B			Pond C			Pond D		
	In ($n = 2$)	Mid ($n = 4$)	Out ($n = 1$)	In ($n = 3$)	Mid ($n = 2$)	Out ($n = 3$)	In ($n = 3$)	Mid ($n = 3$)	Out ($n = 2$)	In ($n = 5$)	Mid ($n = 3$)	Out ($n = 3$)
NAP	40 \pm 33	59 \pm 21	43	53 \pm 4	25 \pm 5	29 \pm 16	30 \pm 16	14 \pm 7	17 \pm 12	27 \pm 24	30 \pm 9	23 \pm 9
ACY	22 \pm 6	30 \pm 16	4	24 \pm 26	5 \pm 7	6 \pm 2	1 \pm 2	<0.1	<0.1	13 \pm 14	15 \pm 4	<0.1
ACE	<0.2	1.4 \pm 2.8	4.0	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	7 \pm 14	<0.2	<0.2
FL	11 \pm 15	11 \pm 12	3	<1	<1	<1	1 \pm 1	<1	<1	20 \pm 26	2 \pm 3	<1
PHE	129 \pm 38	119 \pm 85	36	283 \pm 128	36 \pm 50	23 \pm 8	25 \pm 6	<1	10 \pm 6	172 \pm 292	37 \pm 9	<1
ANT	22 \pm 11	22 \pm 14	3	9 \pm 15	<0.1	<0.1	<0.1	<0.1	0.3 \pm 0.4	44 \pm 64	10 \pm 8	<0.1
FLU	249 \pm 71	252 \pm 146	54	252 \pm 51	72 \pm 66	53 \pm 33	43 \pm 12	<1	35 \pm 38	221 \pm 350	102 \pm 20	35 \pm 7
PYR	301 \pm 68	266 \pm 152	62	347 \pm 68	103 \pm 111	70 \pm 32	50 \pm 18	<0.1	37 \pm 41	195 \pm 243	125 \pm 12	41 \pm 6
BaA	79 \pm 24	75 \pm 39	17	46 \pm 42	29 \pm 2	17 \pm 11	21 \pm 18	<0.2	13 \pm 16	73 \pm 119	42 \pm 4	11 \pm 10
CHR	179 \pm 40	191 \pm 105	51	279 \pm 131	92 \pm 93	67 \pm 26	44 \pm 16	<1	16 \pm 14	154 \pm 133	74 \pm 34	27 \pm 25
BbF	157 \pm 65	193 \pm 127	59	261 \pm 106	92 \pm 65	53 \pm 18	39 \pm 19	1 \pm 3	5 \pm 7	107 \pm 102	118 \pm 22	44 \pm 12
BkF	59 \pm 15	69 \pm 41	24	88 \pm 15	24 \pm 10	20 \pm 11	14 \pm 6	2 \pm 4	40 \pm 48	48 \pm 51	44 \pm 15	21 \pm 9
BaP	129 \pm 50	138 \pm 111	23	223 \pm 83	75 \pm 51	43 \pm 14	27 \pm 24	1 \pm 2	21 \pm 19	84 \pm 75	89 \pm 52	34 \pm 8
DBA	25 \pm 1	28 \pm 23	<1	<1	<1	<1	<1	<1	<1	14 \pm 10	12 \pm 9	<1
IND	170 \pm 53	205 \pm 116	48	248 \pm 128	77 \pm 59	43 \pm 12	39 \pm 21	<0.2	<0.2	67 \pm 38	80 \pm 31	38 \pm 12
BGP	104 \pm 36	121 \pm 75	29	108 \pm 32	33 \pm 18	30 \pm 12	34 \pm 23	<0.1	0.8 \pm 1.1	52 \pm 42	68 \pm 13	28 \pm 6
Σ PAH	1,675 \pm 527	1,780 \pm 1,077	461	2,222 \pm 603	663 \pm 522	454 \pm 187	357 \pm 147	19 \pm 11	194 \pm 187	1,295 \pm 1,508	847 \pm 155	301 \pm 102

NAP, naphthalene; ACY, acenaphthylene; ACE, acenaphthene; FL, flourene; PHE, phenanthrene; ANT, anthracene; FLU, flouranthene; PYR, pyrene; BaA, benz[a]anthracene; CHR, chrysene; BbF, benzo[b]flouranthene; BkF, benzo[k]flouranthene; BaP, benzo[a]pyrene; DBA, dibenz[a,h]anthracene; BDP, benzo[ghi]perylene; IND, indeno[1,2,3-cd]pyrene.

(ponds A and B have a horseshoe shape) and different length to width ratios.

In most of the ponds studied, more PAH species were detected in higher concentrations in the sediment samples than in the water. In cases when PAH species were below detection limit in the sediment, they were usually some of the LMW PAHs, due to their lower concentrations in water and higher water solubility. Besides this, also microbial degradation might contribute to lower LMW PAH concentrations as LMW PAHs are more likely to be degraded over time than HMW PAHs (Mangas *et al.* 1998). Also, Kang *et al.* (2010) found root concentration factor values of pyrene about two times greater than those of phenanthrene in ryegrass, indicating that more lipophilic contaminants like HMW PAHs have a higher tendency for

plant uptake, which could contribute to the reduction of HMW PAHs in the sediment.

In all investigated ponds, HMW PAHs accumulated in the sediments in the highest concentrations. There was, however, no correlation between PAH species in sediments and their hydrophobicity ($\log K_{ow}$). Moreover the partition coefficient between sediment and water was not correlated with $\log K_{ow}$, which is in contrast to some other studies, e.g. Qiao *et al.* (2008), who reported that partition coefficients between sediment and overlying water were positively correlated with $\log K_{ow}$. Prevalence of HMW PAHs above LMW in our study indicates the pyrogenic source of these pollutants. Similar results have been reported by Jiries *et al.* (2000), Brown & Peake (2006) and Hwang & Foster (2006). Stormwater runoff typically contains PAHs that originate from pyrogenic

Table 4 | Average (± 1 standard deviation) PAHs concentrations (ng g^{-1} dry weight) in the sediment at the inlet (In), halfway through (Mid) and at the outlet (Out) of the wet detention ponds at Aarhus, Odense and Silkeborg

PAH	Århus			Odense			Silkeborg		
	In ($n = 4$)	Mid ($n = 5$)	Out ($n = 4$)	In ($n = 2$)	Mid ($n = 6$)	Out ($n = 4$)	In ($n = 6$)	Mid ($n = 9$)	Out ($n = 4$)
NAP	29 \pm 12	32 \pm 8	21 \pm 14	32 \pm 18	19 \pm 5	25 \pm 13	4 \pm 1	<3	<3
ACY	11 \pm 8	26 \pm 19	59 \pm 92	17 \pm 3	9 \pm 9	10 \pm 7	3 \pm 2	1 \pm 1	0.2 \pm 0.4
ACE	<0.2	<0.2	16 \pm 29	<0.2	1 \pm 3	<0.2	<0.2	<0.2	<0.2
FL	<1	<1	<1	18 \pm 14	6 \pm 10	<1	<1	<1	<1
PHE	81 \pm 98	47 \pm 38	32 \pm 29	111 \pm 48	73 \pm 41	40 \pm 16	27 \pm 12	9 \pm 5	4 \pm 3
ANT	7 \pm 5	7 \pm 11	1 \pm 1	16 \pm 6	8 \pm 9	1 \pm 2	2 \pm 2	1 \pm 1	0.1 \pm 0.2
FLU	81 \pm 29	111 \pm 54	46 \pm 12	217 \pm 64	153 \pm 59	117 \pm 50	33 \pm 13	12 \pm 11	<1
PYR	91 \pm 30	140 \pm 53	69 \pm 19	262 \pm 106	199 \pm 92	139 \pm 58	37 \pm 13	13 \pm 12	1 \pm 1
BaA	29 \pm 10	48 \pm 16	15 \pm 4	51 \pm 20	47 \pm 18	39 \pm 14	9 \pm 2	3 \pm 3	<0.2
CHR	59 \pm 20	133 \pm 74	65 \pm 18	178 \pm 71	149 \pm 71	107 \pm 58	30 \pm 9	11 \pm 11	<1
BbF	118 \pm 88	125 \pm 51	86 \pm 18	159 \pm 73	126 \pm 65	101 \pm 35	32 \pm 11	13 \pm 12	<0.1
BkF	39 \pm 29	43 \pm 38	23 \pm 23	53 \pm 28	41 \pm 14	34 \pm 9	12 \pm 4	5 \pm 4	<1
BaP	90 \pm 74	67 \pm 30	32 \pm 15	95 \pm 68	90 \pm 67	69 \pm 38	19 \pm 2	9 \pm 10	<0.1
DBA	19 \pm 21	2 \pm 4	BDL	80 \pm 90	5 \pm 12	8 \pm 10	6 \pm 10	1 \pm 2	<1
IND	110 \pm 67	116 \pm 39	84 \pm 20	187 \pm 81	142 \pm 83	98 \pm 48	28 \pm 9	11 \pm 10	<0.2
BGP	91 \pm 58	83 \pm 36	50 \pm 3	124 \pm 67	73 \pm 44	70 \pm 34	19 \pm 6	8 \pm 7	<0.1
Σ PAH	855 \pm 515	982 \pm 399	599 \pm 203	1,599 \pm 756	1,143 \pm 553	859 \pm 370	262 \pm 75	87 \pm 86	6 \pm 5

NAP, naphthalene; ACY, acenaphthylene; ACE, acenaphthene; FL, flourene; PHE, phenanthrene; ANT, anthracene; FLU, flouranthene; PYR, pyrene; BaA, benz[a]anthracene; CHR, chrysene; BbF, benzo[b]flouranthene; BkF, benzo[k]flouranthene; BaP, benzo[a]pyrene; DBA, dibenz[a,h]anthracene; BDP, benzo[ghi]perylene; IND, indeno[1,2,3-cd]pyrene.

sources such as incomplete combustion of fossil fuels. Combustion specific PAHs are fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(c,d)pyrene and benzo(g,h,i)perylene. Most of them, but especially pyrene and fluoranthene, occurred in high concentrations in the pond sediment as well as in the water.

In comparison with other studies (e.g. Kamalakkannan *et al.* 2004; Brown & Peake 2006) the Σ PAHs in the sediment of the ponds investigated here are low. Kamalakkannan *et al.* (2004) report a range of Σ PAH of 38,000–65,000 ng g^{-1} dry weight. This difference is probably caused by different age of the systems and high loadings from a highway with heavy traffic in the study of Kamalakkannan *et al.* (2004) and illustrates how differences in catchment characteristics can result in different pollution levels in the detention pond sediments. In the present study, the Σ PAHs in general did not differ markedly between the studied systems, despite the fact that the ponds received stormwaters from different catchments, had different loads and were of different age. The lowest Σ PAH concentrations were found in the sediment from the systems at Silkeborg and pond C. The low PAH

concentrations in the system at Silkeborg are a consequence of low inflow PAH concentrations and the relatively short period of operation for this pond as compared to the other ponds. Also microbial degradation of PAHs over time may diminish PAH accumulation over time and result in lower sediment concentrations than expected.

CONCLUSIONS

PAHs generally accumulated in the sediments of wet detention ponds and integrated pollution loads of stormwater events. Concentrations of PAHs in the pond water were highly variable. The relative concentrations of the 16 PAHs analysed differed between the systems as a consequence of differences in type of catchment and systems load. Generally, combustion derived PAHs prevailed in the water as well as in the sediment in the majority of the systems. Low molecular weight PAHs were often below detection limit in water as well as sediment samples. The distribution of individual PAH species was not correlated to their lipophilicity ($\log K_{ow}$) but rather depends on the source of pollution.

The research showed that planted wet detention ponds can efficiently remove PAHs from stormwater and hence help protect natural waters from PAH pollution. The accumulation of PAHs in the sediment implies that final sediment disposal procedures may demand additional remediation techniques for safe disposal. Further research is, however, needed in order to investigate the accumulation of PAHs with pond age, the role of microbial degradation in the sediment and plant uptake.

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