



Occurrence, concentration, and distribution of 38 organic micropollutants in the filter material of 12 stormwater bioretention facilities



Robert Furén^{a,d,*}, Kelsey Flanagan^a, Ryan J. Winston^{b,c}, R. Andrew Tirpak^b, Jay D. Dorsey^b, Maria Viklander^a, Godecke-Tobias Blecken^a

^a Urban Water Engineering, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, 971 87 Luleå, Sweden

^b Department of Food, Agricultural, and Biological Engineering, The Ohio State University, Columbus, OH, United States

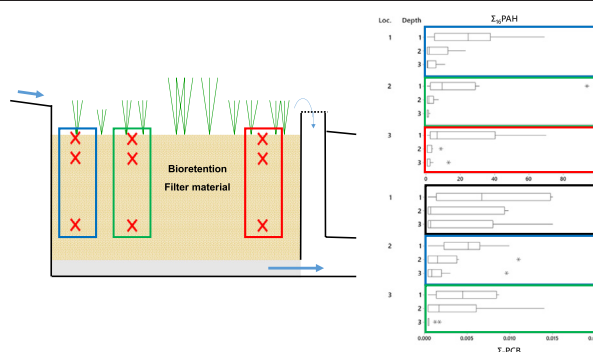
^c Department of Civil, Environmental, and Geodetic Engineering, The Ohio State University, Columbus, OH, United States

^d NCC Sverige AB, Department of Research & Innovation, 170 80 Solna, Sweden

HIGHLIGHTS

- Large scale field study of accumulation of organic micro pollutants in bioretentions
- Most PAHs and PCBs were frequently detected.
- Of 13 phthalates and two alkylphenols, DEHP and nonylphenol were quantified regularly.
- Large inter and intra-site variations with highest levels in filter top layers
- Pollution was detected in all filters regardless age, size and catchment land use.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Dimitra A. Lambropoulou

Keywords:

Stormwater biofilter
Micropollutants
Biofiltrations
Low impact development
Road runoff
Filter media

ABSTRACT

The increased use of bioretention facilities as a low impact development measure for treating stormwater runoff underscores the need to further understand their long-term function. Eventually, bioretention filter media must be (partly) replaced and disposed of at the end of its functional lifespan. While there are several studies of metal accumulation and distributions in bioretention media, less is known about organic pollutant pathways and accumulation in these filters. The present study considers the occurrence and accumulation of 16 polycyclic aromatic hydrocarbons, 7 polychlorinated biphenyls, 13 phthalates, and two alkylphenols throughout 12 older bioretention facilities (7–13 years old) used for stormwater treatment in Michigan and Ohio, USA. These pollutant groups appear to behave similarly, with greater instances of detection and higher concentrations in the upper media layers which decrease with increased depth from the surface. The patterns of detection and concentration in the filter material may be explained by characteristics of the pollutants, such as molecular structures and solubility that affect the removal of the organic pollutants by the filter material. There is also a large variation in concentration magnitudes between the bioretention sites, most likely due to differences in pollutant sources, contributing catchment size and/or land uses.

1. Introduction

Significant pollutant loads are generated and stored on urban surfaces which are subsequently conveyed to receiving water bodies by surface runoff from rain events and/or snowmelt (Müller et al., 2020). The impacts of untreated stormwater runoff are recognized as a main driver of

* Corresponding author at: Urban Water Engineering, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, 971 87 Luleå, Sweden.
E-mail address: rober.furen@associated.ltu.se (R. Furén).

environmental degradation in urban watersheds (Davis et al., 2009; Walsh et al., 2005).

While contaminants such as metals, nutrients, and sediments are ubiquitous in stormwater, recent studies have pointed to organic micropollutants (OMPs) as a pollutant group of emerging concern that may detrimentally affect receiving water bodies, aquatic life and humans (Barbosa et al., 2012; Markiewicz et al., 2017), e.g. some phthalates, alkylphenols and polycyclic organic hydrocarbons are considered as genotoxic substances (Markiewicz et al., 2020), nonylphenols and phthalates as endocrine disrupting (Björklund et al., 2009) and petroleum hydrocarbons as suspected human carcinogens (Fent, 2003; LeFevre et al., 2012; Mastrangelo et al., 1996). Polychlorinated biphenyls are classified as persistent organic pollutant (Stockholm Convention, 2008) that may increase risk for certain cancers and cause negative reproductive effects also on humans (Helmfrid et al., 2012).

Field studies have detected OMPs such as polycyclic aromatic hydrocarbons (PAHs) (Smith et al., 2000), polychlorinated biphenyls (PCBs) (Hwang and Foster, 2008), phthalates (Björklund et al., 2009) and alkylphenols (Lamprea et al., 2018) in urban runoff. Numerous diffuse sources contribute these contaminants to runoff, such as coal tar sealant, traffic, and leaching from construction materials including polyvinyl chloride (PVC) (Bergé et al., 2013; Brown and Peake, 2006; Crane, 2014; Lamprea et al., 2018; LeFevre et al., 2012). Besides these, a wide variety of organic contaminants has been frequently detected in stormwater, many of which are hydrophilic compounds with a wide application spectrum (e.g. herbicides, biocides, flame retardants, anti-icing) (Masoner et al., 2019). A study with the aim to identify organic priority pollutants, PAHs alkylphenols and phthalates were listed out of 1100 compounds in priority order among the 4 highest ranked (Markiewicz et al., 2017).

As the awareness of stormwater pollution and its impacts has increased over the past decades (Makepeace et al., 1995), the interest in stormwater quality treatment has concurrently grown (Fletcher et al., 2015). Stormwater bioretention facilities, also known as stormwater biofilters are an increasingly popular treatment technology (Davis et al., 2009). Bioretention facilities typically consist of an engineered (often sandy soil) filter media drained by a perforated underdrain enveloped in gravel. They are often topped with mulch and/or top soil planted with a variety of plant species. Studies show that bioretention facilities provide efficient removal of numerous pollutants, such as total suspended solids (TSS) (Hsieh and Davis, 2005) and metals (Blecken et al., 2009a). Their removal often exceeds 70–80 %. Particulate metals, which have been evaluated comprehensively in bioretention studies, are mainly removed through filtration (Tedoldi et al., 2016) and primarily retained in the 5–10 cm top layer of the filter (Li and Davis, 2008; Blecken et al., 2011). Similar trends have been observed for dissolved metals: Al-Ameri et al. (2018) reported 70 % of dissolved metals were trapped in the top 7 cm of filter media. This is likely due to rapid adsorption of dissolved metals to the filter material (Søberg et al., 2019). Previous studies of bioretention facilities indicated good removal of phosphorus (70 to 85 % provided that a suitable filter material is implemented) (Søberg et al., 2020), while nitrogen behavior is complex due to the biogeochemical complexity of the nitrogen species and insufficient removal or even leaching of nitrogen has been reported for facilities without a submerged zone (Biswal et al., 2022).

Compared to other pollutants, limited research has evaluated the removal of OMPs by bioretention. Although less data is available with respect to OMPs than metals or nutrients, bioretention efficiently removed a wide range of OMPs (Zhang et al., 2014). Field studies of OMP removal from stormwater in bioretention facilities show high concentration reductions (>90 %) for PCBs and PAHs (David et al., 2015; Flanagan et al., 2018; Gilbreath et al., 2019) and mass load reductions of 87 % for PAHs (DiBlasi et al., 2009). Flanagan et al. (2018) found more variable performance with respect to alkylphenols and phthalates (–49–76 % and 8–74 %, respectively). While there are several studies of metal distribution in bioretention filter media (Al-Ameri et al., 2018; Jones and Davis, 2013), less is known about OMP pathways and accumulation in the filter material. Most studies on OMP fate in bioretention facilities focus on hydrocarbons, particularly

PAHs. LeFevre et al. (2012) showed that raingarden soils contained bacteria capable of mineralizing petroleum hydrocarbons (TPH), limiting the accumulation of TPH to concentrations below regulatory limits. On the other hand, PAHs, particularly those with high molecular weights, tend to accumulate in the top layer of soil, sometimes reaching concentrations well above regulatory limits (DiBlasi et al., 2009; Flanagan et al., 2018; Tedoldi et al., 2017).

In summary, these studies highlight that further studies are needed to understand the accumulation and distribution of a wider range of OMPs in the soil of bioretention facilities, with a specific focus on older facilities, both to gain perspective on the long-term function of these facilities and to characterize maintenance needs and measures. Indeed, bioretention filter media must be replaced and disposed of when they reach the end of their functional lifespan. Characterizing the accumulation of pollutants in the filters is essential to evaluating the risks associated with managing bioretention media throughout its lifecycle. High OMP concentrations in (parts of) the filter material could further pose a risk for humans or wildlife due to acute or chronic toxicity.

To address these research needs, the present study characterizes the occurrence and accumulation of 16 PAHs, 7 PCBs, 13 phthalates, and two alkylphenols in 12 field-scale bioretention systems used for stormwater treatment. These bioretention systems had been filtering stormwater for 7–13 years at the time of sampling. To the best of our knowledge, this is one of the most comprehensive studies investigating the occurrence, accumulation, and distribution of OMPs in bioretention filter media to date.

2. Methods

A field study of organic pollutants in the filter media of bioretention systems used for stormwater treatment was carried out in Ohio and Michigan (US) in November 2019. Filter material samples were collected from 12 bioretention systems and analysed for 38 different organic pollutants.

2.1. Field sites

This study focused on twelve 7–13 years old vegetated bioretention facilities treating runoff from dense urban catchments with different land uses characteristics in Michigan (MI) and Ohio (OH), USA. These included roads, highly urban and industrial/commercial areas, as well as residential areas. At the time of sampling, the facilities varied in age from 7 to 13 years and filter areas ranged from 10 m² to approximately 2000 m². The contributing catchment areas varied from approximately 50 m² to 318,000 m² (Table 1).

2.2. Sample collection

Following a methodology similar to that used by Tedoldi et al. (2017), nine filter material samples were collected from three different locations in each bioretention facility (i.e. different distances from the inlet) and at three depths (0–5 cm, 10–15 cm and 35–50 cm), as illustrated in Fig. 1. While the samples from the two shallower depths were always taken at 0–5 and 10–15 cm, the filter material in some facilities (i.e., sites #3 and #11) was shallower than 50 cm. In these cases, the deepest sample was collected in the filter layer between 35 cm and the depth of the bottom of the filter material. This resulted in a total of 108 samples. For each sample a replicate were also taken.

The three locations along each bioretention facility were situated approximately 1 m, 3 m and 6 m from the inlet. However, for sites #2 and #6, which were smaller, the distances were scaled down (approximately 0.5 m, 1.5 m and 3 m) to permit three separate sampling locations within the facilities. Further, some filters had multiple inlets; for these sites, the sampling locations were positioned based on the inlet most likely to contribute the majority of the inflow. Therefore, the field work for each site started with a visual examination and mapping of the site. Catchment areas, inlets, and patterns of sediment deposition and erosion were studied to define a “main inlet” from which the sampling points were then measured out.

Table 1

Site characteristics of sampled bioretention facilities. Ratio is the percentage of the filter area in comparison to the contributing catchment area.

Site nr	Age [yr]	Location	Catchment area characteristics	Catchment area [m ²]	Filter area [m ²]	Ratio [%]	Mulch layer/top soil
1	9	Upper Arlington, OH	Residential/commercial	318000	950	0.3	Yes
2	8	Upper Arlington, OH	Commercial	750	40	5.3	Yes
3	10	Columbus, OH	Industrial	6000	300	5.0	No
4	7	Westerville, OH	Commercial	4000	170	4.3	Yes
5	9	Columbus, OH	Downtown urban	300	40	13.3	Yes
6	8	Columbus, OH	Downtown urban	50	10	20.0	Yes
7	12	Hamilton, OH	Industrial	4500	300	6.7	Yes
8	12	Lansing, MI	Downtown urban	600	50	8.3	Yes
9	11	Lansing, MI	Downtown urban	500	50	10.0	Yes
10	8	Parma, OH	Fueling station	2500	200	8.0	Yes*
11	13	Twinsburg, OH	Fueling station	2000	70	3.5	Yes
12	12	North Canton, OH	Fueling station	1250	180	14.4	Yes

* Indicate mulch layer of wood chips.

Samples were collected using a steel spade to cut out a core of filter material which was poured into diffusion-tight plastic bags (18 cm × 35 cm) for organic samples. The bags were sealed shut with cable ties. Approximately 1 kg of material was collected at each sampling point. The outdoor temperature during sampling was between −12 to +6 °C and the samples were refrigerated prior to laboratory analysis.

2.3. Chemical analysis

The samples were analysed for their concentrations of organic compounds that included four groups of pollutants: 16 PAHs, seven PCBs, 13 phthalates and two alkylphenols. The OMP concentrations were analysed using gas chromatography–mass spectrometry. Concentrations of 16 PAHs (i.e., naphthalene (Nap), acenaphthylene (Acyl), acenaphthene (Acen), fluorene (F), phenanthrene (Phen), anthracene (A), fluoranthene (Fluo), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chry), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DahA), benzo(g,h,i)perylene (Bper), and indeno(1,2,3-cd) pyrene (IP)) were analysed according to US EPA 8270 (Pitt et al., 1994) and ISO 18287 (ISO, 2006). The Σ_{16} PAH was calculated as the sum of the concentrations of all 16 PAHs. The sum of PAHs with low molecular weights (PAH-L) was calculated as the sum of naphthalene, acenaphthylene and acenaphthene, PAHs with medium molecular weights (PAH-M) as the sum of fluorene, phenanthrene, anthracene, fluoranthene, and pyrene, PAHs with high molecular weights (PAH-H) as the sum of benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene. Concentrations of seven PCBs indicator congeners (i.e., PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180) were analysed following DIN ISO 10382 (DIN ISO, 2002). The grouping Σ_7 PCB was calculated as the sum of these seven PCBs. Concentrations of

13 phthalates (i.e., dimethylphthalate (DMP), diethylphthalate (DEP), di-n-propylphthalate (DPP), diisobutylphthalate (DIBP), di-n-butylphthalate (DBP), di-n-pentylphthalate (DNPP), di-n-octylphthalate (DNOP), di-(2-ethylhexyl)phthalate (DEHP), butylbenzylphthalate (BBP), dicyclohexylphthalate (DCP), diisodecyl phthalate (DIDP), diisononyl phthalate (DINP) and di-n-hexylphthalate (DNHP)) were analysed following E DIN19742 (E DIN, 2014). The concentrations of two alkylphenols (i.e., 4-tert-octylphenol (OP) and 4-nonylphenols (NP)) were analysed. All OMP detection limits (DL) are presented in Table 2.

Besides the OMPs, total organic carbon (TOC) was measured using CSN EN 13137 (CSN EN, 2018) and CSN ISO 10694 (CSN ISO, 1995). Loss on ignition (LOI) was measured using gravimetric analysis based on CSN EN 12879 (CSN EN, 2014), CSN 720103 (CSN, 2009), and CSN 465735 (CSN, 1991). Dry matter (DM) were measured using appropriate methods for each pollutant group. Specific surface area (SSA) was measured following BS ISO 9277:2010 (BS ISO, 2010) (gas adsorption — BET method).

One sample (Site #6, location 2, depth 35–50 cm) of the total 108 collected samples could not be analysed for PAHs or alkylphenols due to insufficient sample volume.

2.4. Statistical analysis

Boxplots were used to illustrate pollutant distribution and their concentration in the bioretention filter material. Since parts of the data were non-normally distributed and others censored, the nonparametric Kruskal-Wallis test was used, after censoring data at the highest reporting limit (Helsel, 2012), to test statistical significance of differences between the examined parameters (i.e., depth and location). To test the cross-correlations between pollutant concentrations, the non-parametric Kendall's-tau (τ) correlation test, applicable for the analysis of censored data, was performed using the NADA package in R for

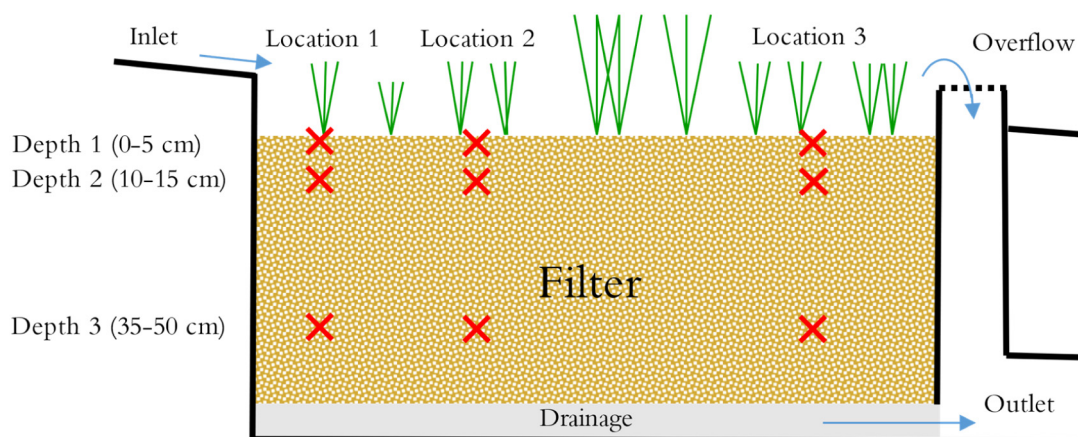


Fig. 1. Cross-section of a bioretention facility illustrating the nine sampling points (at three locations and at three depths) used in this study.

Table 2
Summary of the occurrence and concentrations of analysed OMPs above detection limits (DL).

Group/units	Substance name	Nr of samples	Occurrence		DL	Concentrations				
			Nr > DL	% > DL		Top layer/layer 1 median		All data		
						Median	Max	Median	Min	
PAH [mg/kg, DM]	Naphthalene (Nap)	107	13	12 %	0.10	<0.10	<0.10	1.49	<0.10	
	Acenaphthylene (Acyl)	107	0	0 %	0.10	–	–	–	–	
	Acenaphthene (Acen)	107	15	14 %	0.10	<0.10	<0.10	6.98	<0.10	
	Fluorene (F)	107	14	13 %	0.10	<0.10	<0.10	8.98	<0.10	
	Phenanthrene (Phen)	107	51	48 %	0.10	0.29	<0.10	127	<0.10	
	Anthracene (A)	107	24	22 %	0.10	<0.10	<0.10	19.4	<0.10	
	Fluoranthene (Fluo)	107	76	71 %	0.10	1.02	0.32	186	<0.10	
	Pyrene (Pyr)	107	74	69 %	0.10	0.83	0.25	138	<0.10	
	Benzo(a)anthracene (BaA)	107	73	68 %	0.05	0.52	0.11	45.9	<0.05	
	Chrysene (Chry)	107	81	76 %	0.05	0.92	0.18	58.7	<0.05	
	Benzo(b)fluoranthene (BbF)	107	83	78 %	0.05	1.56	0.33	52.7	<0.05	
	Benzo(k)fluoranthene (BkF)	107	68	64 %	0.05	0.41	0.08	18.5	<0.05	
	Benzo(a)pyrene (BaP)	107	76	71 %	0.05	0.67	0.16	32.9	<0.05	
	Dibenzo(a,h)anthracene (DahA)	107	44	41 %	0.05	0.14	<0.05	3.98	<0.05	
	Benzo(g,h,i)perylene (Bper)	107	67	63 %	0.10	0.78	0.20	24.5	<0.10	
	Indeno(1,2,3-cd)pyrene (IP)	107	76	71 %	0.05	0.63	0.16	15.0	<0.05	
	PAH sum Low weight (PAH-L)	107	16	15 %	0.15	<0.15	<0.15	7.80	0.11	
	PAH sum medium-weight (PAH-M)	107	76	71 %	0.25	2.10	0.57	480	0.12	
	PAH sum high-weight (PAH-H)	107	83	78 %	0.23	5.90	1.30	240	0.07	
	PAH 16 sum (Σ_{16} PAH)	107	83	78 %	0.63	8.00	1.90	730	0.07	
PCB [μ g/kg, DM]	PCB 28	108	18	17 %	(0.20–0.40)	<0.10	<0.10	18.00	<0.06	
	PCB 52	108	55	51 %	0.10	0.33	<0.10	19.00	<0.10	
	PCB 101	108	66	61 %	0.10	0.71	0.19	39.00	<0.10	
	PCB 118	108	65	60 %	0.10	0.65	0.22	46.00	<0.10	
	PCB 138	108	78	72 %	0.10	1.05	0.37	36.00	<0.10	
	PCB 153	108	80	74 %	0.10	1.20	0.42	42.00	<0.10	
	PCB 180	108	73	68 %	0.10	0.76	0.28	27.00	<0.10	
	Sum of 7 PCBs (Σ_7 PCB)	108	81	75 %	0.40	4.90	1.75	210.00	0.11	
	Phthalates [mg/kg, DM]	Dimethylphthalate (DMP)	108	1	1 %	0.05	<0.05	<0.05	1.40	<0.05
		Diethylphthalate (DEP)	108	0	0 %	0.05	–	–	–	–
Di-n-propylphthalate (DPP)		108	2	2 %	(0.05–0.50)	<0.05	<0.05	<0.50	<0.05	
Diisobutyl phthalate (DIBP)		108	5	5 %	(0.05–1.00)	<0.05	<0.05	<1.00	<0.05	
Di-n-butylphthalate (DBP)		108	2	2 %	(0.05–0.30)	<0.05	<0.05	<0.30	<0.05	
Di-n-pentylphthalate (DNPP)		108	0	0 %	(0.05–1.00)	–	–	–	–	
Di-n-octylphthalate (DNOP)		108	0	0 %	(0.05–0.25)	–	–	–	–	
Di-(2-ethylhexyl)phthalate (DEHP)		108	50	46 %	0.05	0.26	<0.05	6.10	<0.05	
Butylbenzylphthalate (BBP)		108	4	4 %	(0.05–0.30)	<0.05	<0.05	<0.30	<0.05	
Dicyclohexylphthalate (DCP)		108	0	0 %	0.05	–	–	–	–	
Diisodecyl phthalate (DIDP)		108	0	0 %	2.50	–	–	–	–	
Diisononyl phthalate (DINP)		108	6	6 %	2.50	<2.50	<2.50	6.80	<2.50	
Di-n-hexylphthalate (DNHP)		108	2	2 %	(0.05–0.10)	<0.05	<0.05	0.11	<0.05	
Alkylphenols [mg/kg, DM]	4-Tert-octylphenol (OP)	107	1	1 %	(0.01–0.03)	<0.01	<0.01	0.03	<0.01	
	4-Nonylphenols (tech.mixture) (NP)	107	19	18 %	(0.10–0.20)	<0.10	<0.10	106	<0.10	

pollutants detected in at least 42 % of the samples (the pollutants not included in this analysis were quantified in <23 % of samples). The concentrations of organic pollutants and factors potentially affecting these were also examined using principal components analysis (PCA) performed in the software SIMCA 15 for visualization of the main characteristics and correlations of the analysis results. The PCA included concentrations from the laboratory analysis with the parameters Depth, Location (Fig. 1), specific surface area (SSA), loss on ignition (LOI), total organic carbon (TOC), age, ratio between filter area and catchment area), land use Commercial-, Industrial-, down town urban- and fuel stations areas. The model where UV scaled and log transformed (auto transformed) on skewed variables. For discussion of a practical end use of the data, concentrations of PAH-H, PAH-M, PAH-L and PCB 7 were compared to the Swedish national guidance limits for classification of soil, “soil for sensitive land use” (abbreviated KM) and “soil for less sensitive land use” (abbreviated MKM), published by the Swedish Environmental protection agency (Swedish EPA, 2009).

3. Result and discussion

In total, 32 of the 38 analytes were detected in at least one of the 108 samples while six substances (five phthalates and one PAH) were never detected (Table 2). The most frequently detected pollutants in the study were

PAHs and PCBs, while phthalates and alkylphenols were less frequently detected. A summary of results and descriptive statistics are presented in Table 2, while the complete results from the analysis of the sampling campaign are presented in the Supplementary Table 4.1.

3.1. PAHs

PAHs were detected at all twelve sites examined, with at least one type of PAH above the detection limit in 78 % of all samples. Of the 16 analysed PAHs only acenaphthylene was never detected. PAHs were mainly present in the upper layer of the filter material, but were also detected in the deeper layers, though less frequently and at lower concentrations (Fig. 2 and Supplementary Fig. 2.1). The most frequently occurring PAHs, benzo(b)fluoranthene and chrysene, were found in 78 % and 76 % of all samples, respectively, followed by fluoranthene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene, all of which occurred in 71 % of samples. The occurrence and concentrations of PAHs decreased with increased depth from the surface and with increased distance from the inlet (Fig. 2). PAHs with high molecular weights (i.e., PAH-H) and PAHs with medium molecular weights (i.e., PAH-M) were present in at least one sample from all 12 sites, while PAHs with low molecular weights (i.e., PAH-L) were less frequently detected (Table 2). PAH-H and PAH-M appeared in higher concentrations than PAH-L. The concentrations of Σ_{16} PAH ranged from 0.07 mg/kg to

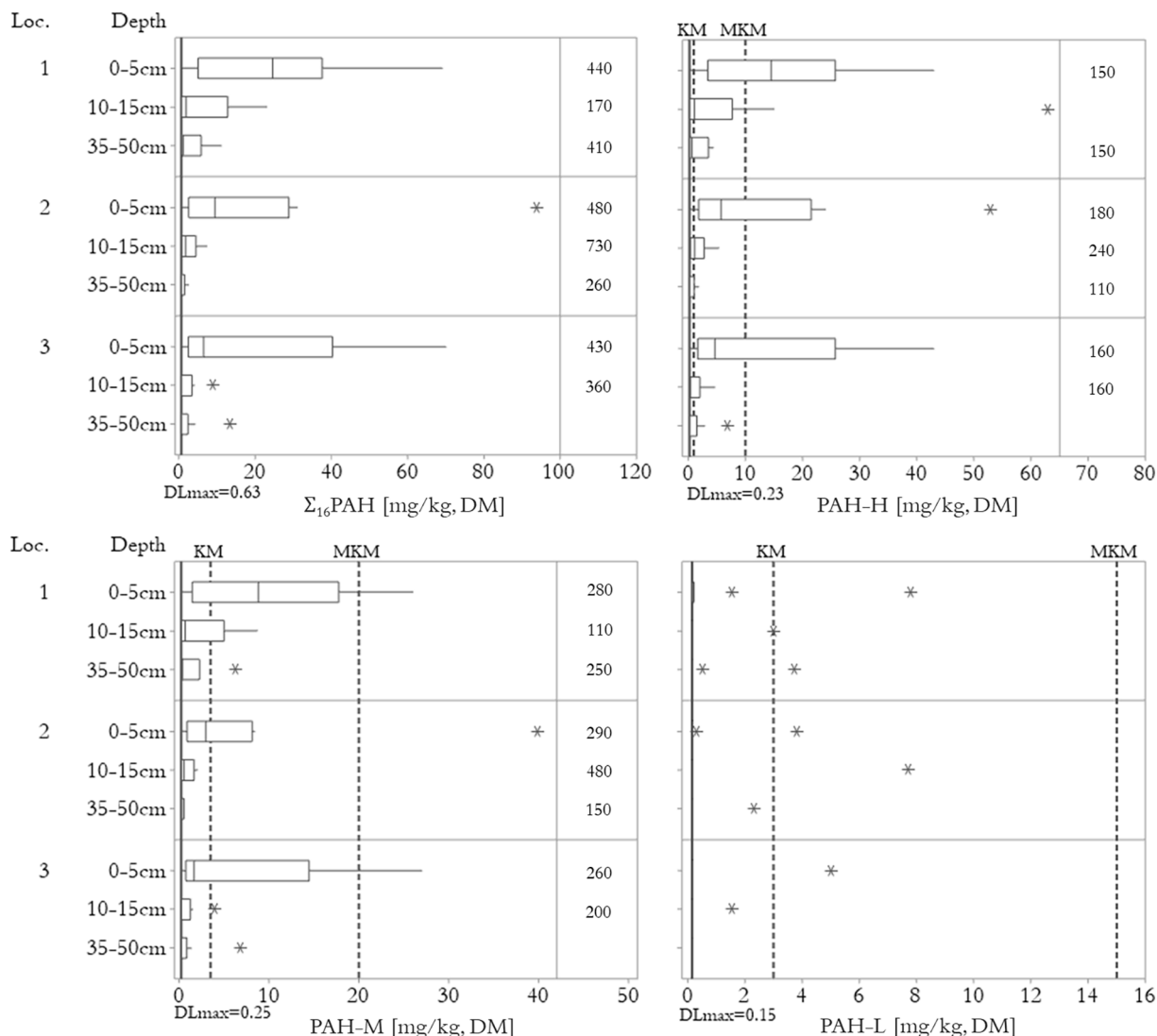


Fig. 2. Boxplots of concentrations of $\Sigma_{16}\text{PAH}$, PAH-H, PAH-M and PAH-L (mg/kg, DM) for different distances from inlets (Locations, Fig. 1) and distance from surface (Depth, Fig. 1). In addition to those plotted as asterisks (*), outliers above 100 mg/kg, DM are indicated as text to the right for plotting purposes. The concentrations of PAH-H, PAH-M and PAH-L are compared to the Swedish guidelines for pollutant concentrations relating to soil classification (KM (soil for sensitive land use) and MKM (soil for less sensitive land use)). For PAH-H concentrations above MKM are mainly present in the upper layers or close to the inlet and for PAH-M concentrations above KM are mainly present in the upper layers or close to the inlet.

730 mg/kg, with an overall median of 1.9 mg/kg; the median concentration in the top layer was found to be 8 mg/kg (Table 2), significantly higher (Kruskal-Wallis $p < 0.05$) than the layers below (Fig. 2). Also with increased distance from the inlets the median concentrations decreased; however, this trend was not statistically significant. Concentration boxplots for all 16 PAHs are presented in the Supplementary Fig. 2.1. Most of the extreme outliers shown in Fig. 2 were detected at one single facility (site #1) and here in nearly all samples were extraordinarily high ($\Sigma_{16}\text{PAH}$ 273-fold larger, PAH-H 151-fold larger and PAH-M 526-fold larger median concentration compared to the other 11 sites).

3.2. PCBs

PCBs were detected in 75 % of all samples and were the second most frequently observed group of substances in this study. In total, PCBs were not detected at just two of the 12 sites (sites #3 and #7, Table 1). Aside from PCB 28, all PCBs were found in the same 10 sites, while PCB 28 was detected in four out of 12 sites. The most frequently

occurring PCBs were PCB 153, detected in 74 % of all samples, followed by PCB 138 (72 %), PCB 180 (68 %), PCB 101 (61 %), PCB 118 (60 %), and PCB 52 (51 %). The least frequent PCB (PCB 28) was detected in just 17 % of all samples.

Although the median concentrations of PCBs were higher in the upper layer, PCBs were also detected in the deeper layers in nearly all facilities (Fig. 3). The median $\Sigma_7\text{PCB}$ concentration of all samples was 1.75 $\mu\text{g}/\text{kg}$, compared with 4.9 $\mu\text{g}/\text{kg}$ in the top layer, 1 $\mu\text{g}/\text{kg}$ in the middle layer and 0.4 $\mu\text{g}/\text{kg}$ in the bottom layer. The top layer (0–5 cm) concentrations were about 5 to 12 times higher than in the deeper layers (depths of 10–15 cm and 35–50 cm), differences which were statistically significant (Kruskal-Wallis, $p < 0.05$). The highest concentrations of PCBs were found in downtown/city center areas with high population density and traffic, while lower concentrations were found in less-densely-populated suburban residential areas with more green space. A trend of decreasing concentrations with increased distance from the inlet was observed; however, due to the large variation of concentrations within and between different sites, ranging from 0.1 $\mu\text{g}/\text{kg}$ to 210 $\mu\text{g}/\text{kg}$, no significant

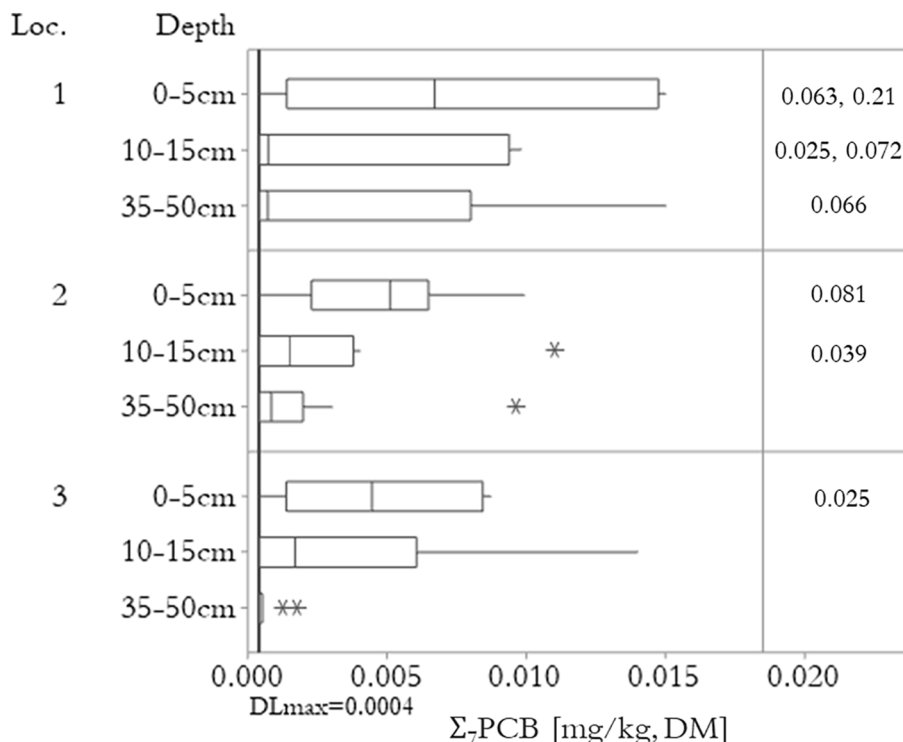


Fig. 3. Box plot of Σ_7 PCB for different distances from inlets (Locations, Fig. 1) and distance from surface (Depth, Fig. 1). In addition to those plotted as asterisks (*), outliers above 0.02 mg/kg, DM are indicated as text to the right for plotting purposes.

difference between the concentrations at different distances from the inlet was detected.

3.3. Phthalates

Phthalates were detected in eleven sites and in 52 of 108 samples (48 %). Eight of the 13 different phthalates (Table 1) were detected in at least one sample. The most frequently detected phthalate, di-2-ethylhexyl phthalate (DEHP), was detected in 46 % of samples. The remaining phthalates were only detected occasionally: DINP was found in 6 %, DIBP 5 %, BBP 4 %, DDP 2 %, DBP 2 %, DNHP 2 %, and DMP in 1 % of all samples. When detected, the concentrations of phthalates were significantly

higher (Kruskal-Wallis, $p < 0.05$) in the upper layers of the filter material and decreased with increased depth (e.g. DEHP, Fig. 4). The other detected phthalates were only found in few samples from the top layer (e.g. DINP, Fig. 4). Though not statistically significant, concentrations also tended to be higher at locations closer to the inlets and decreased with increased distance from the inlets.

3.4. Alkylphenols

As a group, alkylphenols had the lowest occurrence rate in the study. 4-Nonylphenol (NP) was detected in seven out of 12 sites and in 19 out of a total of 107 samples (18 %) and was mainly identified in the top filter

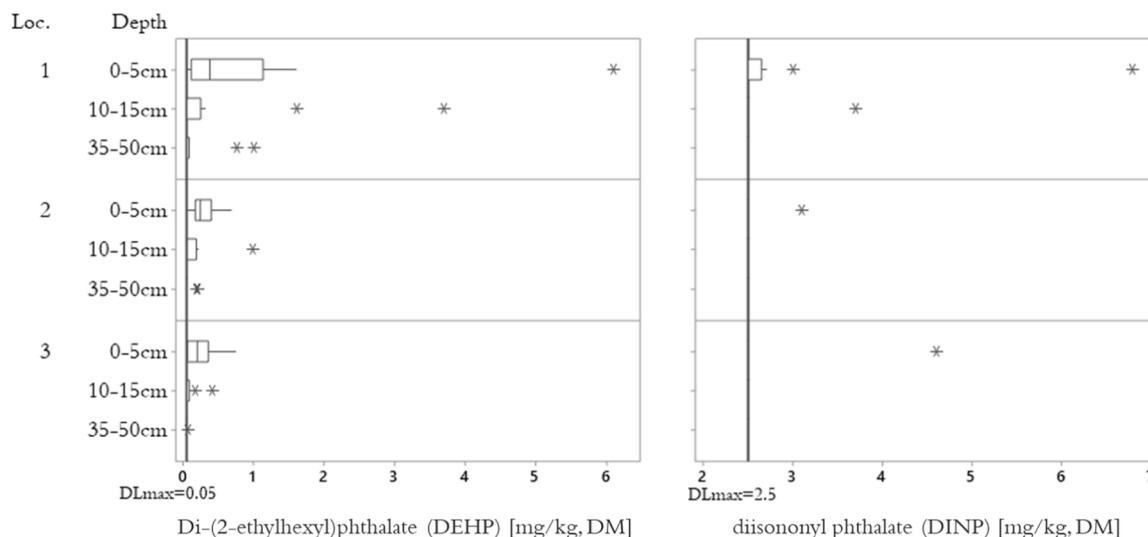


Fig. 4. Concentrations (mg/kg, DM) of di-(2-ethylhexyl)phthalate (DEHP) and phthalate with high occurrence (46 %) in the study and diisononyl phthalate (DINP) and phthalate with lower occurrence (6 %).

layers. 4-Tert-octylphenol was only found above the detection limit in one sample out of 107 (<1 % detection frequency). NP had a higher occurrence rate and higher concentrations in the top layer and at locations closer to the inlet; like other pollutants, concentration of NP rapidly decreased with increased distance from the surface and inlets (Fig. 5).

3.5. Principle component analysis

The PCA had 7 components with $R^2X_{cum} = 0.90$ (cumulative X-variation modelled after all seven components) and $Q2(cum) = 0.41$ (cumulative overall cross-validated R^2X). However, most variations were explained in the first and second component ($R^2X(p1) = 0.446$ and $R^2X(p2) = 0.124$). A summary of the results from the PCA is shown in the score plots and loading plots in Fig. 6.

In the loading plot, PAHs and PCBs, which were frequently detected, are clustered separately from the other pollutant groups. The less frequently or never-detected phthalates (except DEHP) and alkylphenols (except NP) are located closer to the center of the plot. The most influential parameters on pollutant concentration are Depth, TOC and LOI. Further, there seems to be also some impact from SSA and Location. TOC and LOI are closely correlated to each other but also to PAHs and PCBs. Reasons could be that filter materials with higher TOC contents and/or LOI tend to adsorb more PAHs and PCBs (Björklund and Li, 2017) and/or the commonly-occurring mulch layer at the biofilter surface where many (especially particulate) pollutants are trapped and accumulated. Despite the positive effect of organic matter on adsorption, high contents of organic matter may be disadvantageous for the overall bioretention functionality e.g. due to the risk for nutrient leaching (Hurley et al., 2017).

As already illustrated in the box plots (Figs. 2–5), a strong correlation was also found between depth and concentrations, mainly for the PAH and PCB group. For PAHs the trends are stronger for PAH-H and PAH-M while PAH-L, which was less frequently detected, is close to the center of the plot. A general trend is that the higher occurrence and concentration

which can be seen for PCBs that are stretched out from PCB 153 down to PCB 28 but also for the alkylphenol NP and the phthalate DEHP. Age and area ratio have some impact in the weaker second component, mainly connected to PCBs. In general, one would assume that age should have a considerable impact on pollutant concentrations in bioretention due to accumulation over time. One reason that this was not corroborated clearly by the PCA is that the evaluated sites all around 10 years old (Table 1), i.e. age had a relatively little variation. If newly-built sites and/or considerably older sites had been included in the study, age would likely have had a clearer impact. The land use did not have a clear impact either. Also here, one reason might be that the variability and number of sites with the different land uses was too small to identify potential impacts. On the other hand, all land uses (urban, road, industry, fuel station) included numerous potential pollutant sources for OMP. From the score plot one can see that different sites have a tendency of clustering with correlation to certain pollutant groups, especially site 6 which is correlated to PCBs.

In the PCA shown in Fig. 6, site 1 was excluded due to the exceptionally high PAH concentrations at that site which indicate that an extraordinary incident had happened there. That site was included in the PCA shown in supplementary Fig. 3.1, where it becomes clear that the site is a statistical outlier (score plot) and correlated to PAHs (loading plot). That specific site affects the results of the PCA, e.g. residential land use is strongly correlated to PAHs since site 1 was located in a residential area.

The Kendall's-tau (τ) correlation test showed significant ($P < 0.01$) correlations between all of the 18 pollutants detected in a high enough proportion of samples for correlations to be tested (see Table S3.1 in Supplementary data). All correlations were strong ($\tau > 0.27$), though stronger correlations were observed within a given pollutant family (i.e. for PAH with PAH and PCB with PCB, τ ranges from 0.61 to 0.90) than between the pollutant families (i.e. for PAH with PCB, PAH with DEHP and PCB with DEHP, τ ranges from 0.27 to 0.53). This finding corroborates the general observation of the PCA (see also loading plot in Fig. 6) where most PCBs, PAHs and

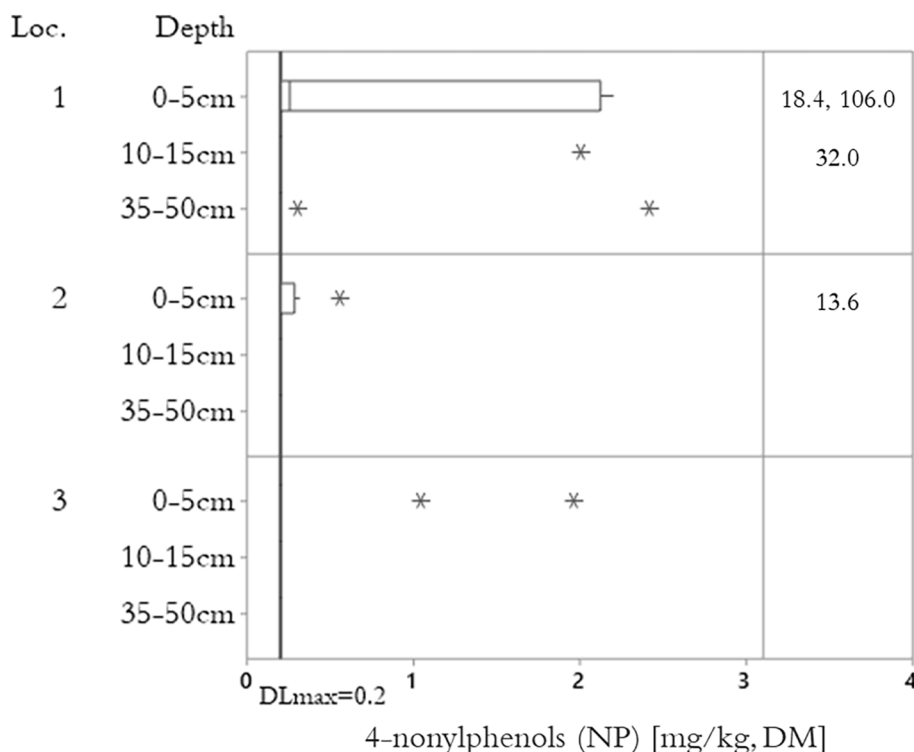


Fig. 5. Boxplot of the alkylphenol 4-nonylphenols (NP). Outliers of greater magnitude are indicated as numbers to the right for easier visualization of boxplots due to the scale.

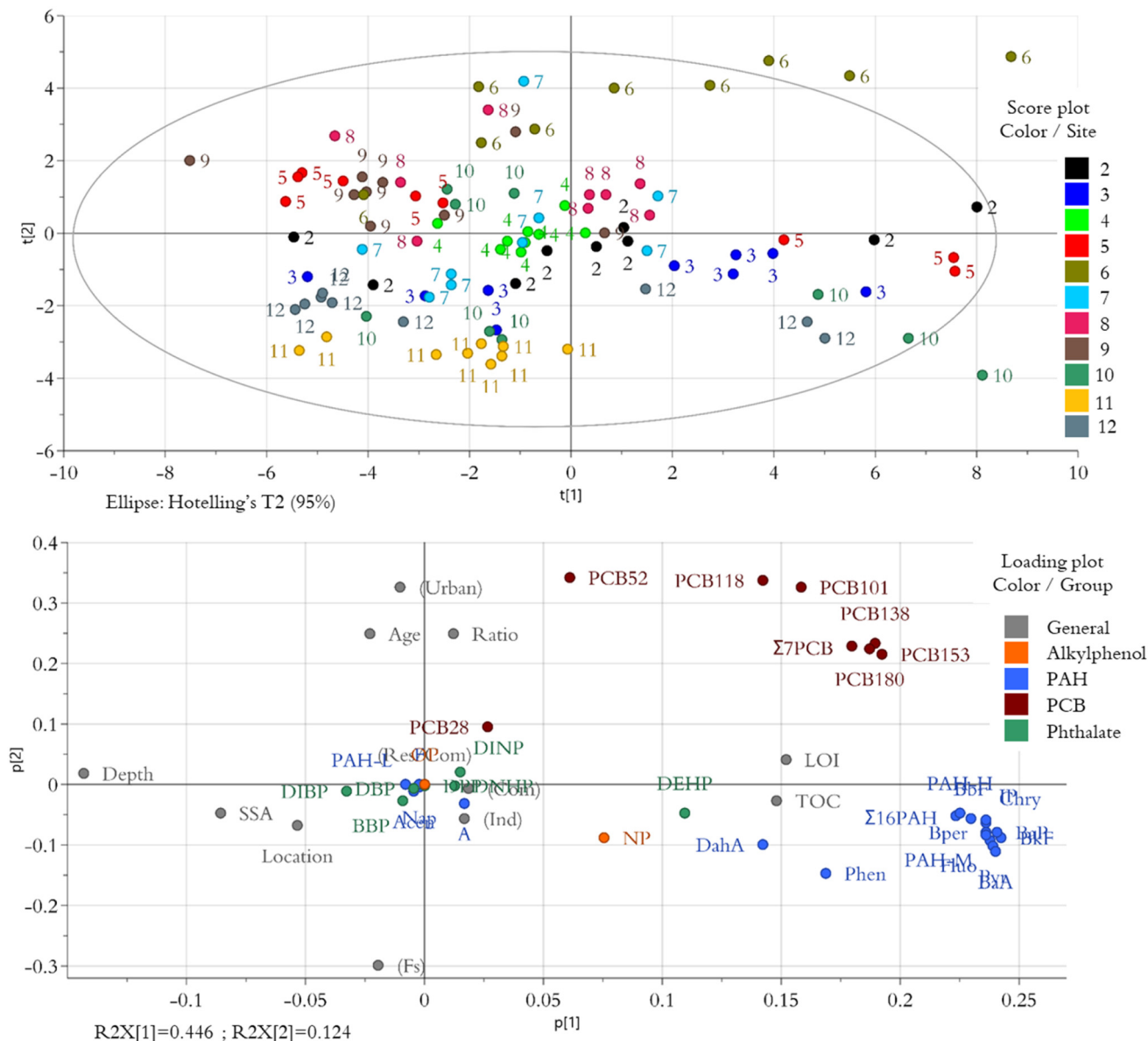


Fig. 6. Score plot (upper) and loading plots (lower) for components 1 and 2. The score plot is colored by site number and the loading plot is colored after the four pollutant groups (alkylphenols, PAHs, PCBs and phthalates) and general parameters. The general parameters include Depth, Specific Surface Area (SSA), Location, Loss On Ignition (LOI), Total Organic Carbon (TOC), Age, Ratio (Filter Area/Catchment Area) and the Land Use parameters Commercial (Com), Industrial (Ind), Down town urban (Urban) and fuel stations (FS). The $R^2X_{cum} = 0.90$ (Cumulative X-variation modelled after all seven components) and $Q2(cum) = 0.41$ (Cumulative overall cross-validated R^2X). $R^2X(p1) = 0.446$ and $R^2X(p2) = 0.124$. The model where UV scaled and log transformed (auto transformed on skewed variables). For a PCA including site 1 see Supplementary Fig. 3.1.

DEHP (i.e. the contaminants included in the Kendall's tau-test) are grouped in the same section of the plot, but with specifically strong grouping within the PCB and PAH group.

3.6. Contaminant patterns

The occurrence and concentration patterns of organic contaminants in bioretention filter material are the result of a number of processes, including their emission and mobilization from a given catchment, their retention in the bioretention facility (which depends on their hydrophobicity and solubility), and fate processes occurring in the filter media (biodegradation, volatilization) that may limit their accumulation over time. Hydrophobic compounds are expected to be more readily retained in the filter media than hydrophilic compounds. The

compounds studied cover a range from very hydrophobic ($\log Kow > 6$, 5-to-7-ring PAHs, heavy PCBs e.g. PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180 and phthalates e.g. DNOP, DEHP, DCP, DIDP, DINP and DNHP) to moderately hydrophobic ($4 < \log Kow < 6$, 3-to-4-ring PAHs, PCB 28 and PCB 52, phthalates DPP, DIBP, DBP, DNPP and BBP and alkylphenols) and less hydrophobic ($\log Kow < 4$, 2-ring PAHs and phthalates e.g. DMP and DEP).

In the present study, PAH-H and PAH-M were more abundant than PAH-L. Previous studies suggested that high concentrations of PAH-H in runoff could indicate sources such as fossil fuels typically found in high density urban areas (Zgheib et al., 2011a). Studies of organic pollutants in Gothenburg, Sweden also indicated that PAH-H and PAH-M occur in higher concentrations than PAH-L in road and traffic-related runoff (Järnskog et al., 2021; Markiewicz et al., 2017), although they vary over time. The five

PAHs found in the highest concentrations herein (i.e., Fluo, Pyr, Phen, Chry and BbF) were the same as a previous study of 16 PAHs accumulated in the soil of stormwater infiltration facilities (Tedoldi et al., 2017). Heavy PAH molecules are expected to be better retained in filter media since they are more hydrophobic compared to lighter PAHs, they are less soluble, more strongly particle-bound, less biodegradable, and less volatile (Crane, 2014; David et al., 2015; Flanagan et al., 2018; MacKay, 2006a).

Like PAHs, PCBs are highly hydrophobic and often found attached to particles in stormwater (Hwang and Foster, 2008) and are thus effectively treated by bioretention facilities (Gilbreath et al., 2019). PCB concentrations in the bioretention filter media generally followed the order PCB 153 > PCB 138 > PCB 180 > PCB 118 ≈ PCB 101 > PCB 52 > PCB 28. This is similar to the trends observed for particulate concentrations in stormwater in Paris, France by Zgheib et al. (2011a), with the exception of PCB 28, which was much less abundant in the present study. While it is possible that sources of PCBs in the USA and Europe may be different, it may also be explained by the fact that PCB 28 was the least chlorinated of the PCBs in both studies. As the hydrophobicity of PCBs increases with increased chlorination, more chlorinated PCBs tend to be more effectively retained in bioretention facilities than less chlorinated PCBs (David et al., 2015). More chlorinated PCBs are also less biodegradable and less volatile (Mackay, 2006b), making them more susceptible to accumulate within the filter media over time.

While phthalates have been commonly detected in studies of both stormwater (Björklund et al., 2009; Gasperi et al., 2014; Zgheib et al., 2011b) and stormwater pond sediments (Crane, 2019; Flanagan et al., 2021), they were less commonly found in samples of filter material. This may be explained by a decrease in the industrial production and use of phthalates over time (Bergé et al., 2013). According to the PCA no clear trend of phthalate concentration by land use were observed. In addition, due to their more variable hydrophobicity, phthalates are less often found in particulate form in stormwater and are thus less effectively treated in bioretention facilities compared to PAHs (Flanagan et al., 2018). Further, phthalates are more biodegradable than most PAHs and PCBs (Mackay, 2006b), which may decrease their likelihood to accumulate in bioretention facilities over time. DEHP was by far the most frequently detected phthalate in this study. A substance flow analysis of phthalates in an urban catchment showed that DEHP, along with DIDP and DINP, are often present at environmentally relevant concentrations in stormwater (Björklund, 2010). DIDP and DINP were never (i.e., 0 %) and very rarely (6 %) detected in the present study, respectively, likely due to much higher detection limits than those for DEHP (2.5 mg/kg vs. 0.05 mg/kg). Besides its widespread industrial use, the properties of DEHP (i.e., higher hydrophobicity, lower volatility, and lower biodegradability) favor its accumulation in soil as compared with lighter congeners.

Alkylphenols were only rarely detected in the filter media, despite growing evidence illustrating their presence in stormwater (Björklund et al., 2009; Gasperi et al., 2014; Zgheib et al., 2011b). Like phthalates, alkylphenols are less effectively treated in bioretention facilities than PAHs (Flanagan et al., 2018) and are relatively biodegradable as compared with heavy PAHs and PCBs (MacKay, 2006a), which may limit their accumulation in filter media. Nonylphenol was more frequently detected (18 % of samples), and at higher concentrations, than octylphenol (1 % of samples). A major reason for this difference is that nonylphenol ethoxylates have greater industrial use than octylphenol ethoxylates (Bergé et al., 2012). Data from this study adds to previous observations which show concentrations of 4-tert-octylphenol relative to NP in stormwater sediments to be lower in the USA than in Europe (Crane, 2019; Flanagan et al., 2021), possibly reflecting different legislation concerning their use in industrially-produced materials.

Biodegradation, occurring essentially during longer dry periods, is likely to be a major fate process for organic pollutants in biofilters systems that influences the observed contaminant patterns. Indeed, Zhang et al. (2014) performed in-situ column tests on a biofilter system and defined adsorption and biodegradation to be one of the most important treatment processes for organic micropollutants (such as PAHs, phthalates and

phenols). However, the present study, which focused on the occurrence and concentrations of pollutants in filter material, does not allow biodegradation to be quantified, both due to the lack of information on the pollutant loads associated with runoff entering and exiting each system and due to the significant uncertainties associated with calculations of pollutant mass accumulated in the filter media of such systems (Flanagan et al., 2019).

3.7. Intra-site variability

The general behavior between the studied groups of pollutants (PAHs, PCBs, phthalates and alkylphenols) is similar in that occurrence frequencies and concentrations are generally higher in the top layers of the filters and decrease rapidly with increased depth from the surface. PAHs and PCBs in stormwater are often associated with suspended solids, (LeFevre et al., 2015; Marsalek et al., 1997; Hwang and Foster, 2008) and are similar to other particle-bound pollutants which are primarily removed in the surface layers through sedimentation and filtration of particles (Blecken et al., 2009b). Alkylphenols and phthalates may have more variable speciation in stormwater, making them more mobile in bioretention facilities (Flanagan et al., 2018), and in turn result in lower concentrations of these pollutants near the surface. In contrast, these compounds have been shown to accumulate in filter media below the surface in a 1-yr-old biofiltration facility, likely due to emissions from construction materials (Flanagan et al., 2019). However, there is no evidence of subsurface accumulation in the present study, which may indicate that such emissions did not occur in the studied facilities or that the emitted contaminants degraded over the 7–13 years of operation since the construction of the facilities studied in this research.

There was an observed trend, albeit not statistically significant, of concentrations and occurrence frequencies being higher close to the inlets and decreasing with increased distance from the inlets. This trend was most obvious in the top layer and less marked than the trend with depth variation. The variation of occurrence and concentration with increased distance from the inlet could be explained as a combination of the effect of pollutants being mainly particle-bound and the long-term effects of filter hydrology and many smaller rainfall events causing a higher pollutant load closer to the inlets (Al-Ameri et al., 2018) and, therefore, also higher pollutant accumulation.

3.8. Inter-site variability

There was a large variation in concentrations between the materials analysed from different sites. This may be the result of different catchment characteristics, the ratio of catchment area to filter area, and land use that contribute different pollutant types and loads (Cao et al., 2019; Crane, 2019). However, the PCA did not show a clear impact of land use and catchment/biofilter ratio on pollutant concentrations. Given the few sites within each land use, variations within each land use group may have contributed to that result.

When considering local and site-specific characteristics, very high concentrations of PAHs at all depths and locations were observed at one site (site 1, Table 1) compared to all other sites. The median concentration of PAH16 in the samples from the outlier site was 410 mg/kg, 273-fold larger than the median PAH16 concentration for the other 11 sites (1.5 mg/kg). Similarly, the difference between site 1 and the other sites was extreme for PAH-M (250 mg/kg compared to 0.57 mg/kg), PAH-H (150 mg/kg compared to 1.3 mg/kg), and PAH-L (4 mg/kg compared to 0.15 mg/kg). These concentrations of PAHs (for example, 186 mg/kg fluoranthene, 138 mg/kg of pyrene and 127 mg/kg of phenanthrene) are very high for samples from a bioretention facility (DiBlasi et al., 2009; Tedoldi et al., 2017), and are also in the range of what would be considered highly PAH-polluted soil. However, no clear explanation was found for the high concentrations at that specific site. In general, the catchment area did not obviously vary from other catchments included in this study. According to the bioretention operator (City of Columbus), possible reasons could be a major car accident

that occurred in this area, repaving a stretch of the road or illicit discharge of motor oil.

3.9. Practical implications

Observed PAH-H, PAH-M and PAH-L concentrations were compared with the Swedish guidelines for pollutant concentrations related to soil classification (Swedish EPA, 2009). In that comparison, PAH-H show the greatest exceedance of “soil for sensitive land use” (KM) as compared with PAH-M and PAH-L. It can be seen in Fig. 2 that the PAH-H concentrations are frequently above the limits for KM ($KM_{PAH-H} = 1 \text{ mg/kg}$) and also sometimes above limits for soil classified as “soil for less sensitive land use” (MKM; $MKM_{PAH-H} = 10 \text{ mg/kg}$). Concentrations above the relevant MKM level are classified as hazardous waste (FA) and need certified transportation and disposal at licensed landfill sites. However, concentrations above MKM were mostly present in the upper layer (with a depth 0–5 cm) except for few outliers, where the concentrations were above MKM in the 10–15 cm deep layer, close to the inlet.

Most organic pollutants were generally found in the upper 5 cm of the filter material. This has critical implications for bioretention operators. Removing only the top layer of media periodically may be all that is necessary to ensure that the entire filter media does not saturate and result in discharge of OMPs. Similar guidance has been suggested concerning heavy metals and PAHs (e.g. Al-Ameri et al., 2018; Blecken et al., 2011; Tedoldi et al., 2017). The top media layer is likely to retain the most pollutants and should be managed and prioritized accordingly. Also, the majority of sediment is trapped in that top layer and thus removing it will likely also restore the infiltration capacity of the filter in the event its saturated hydraulic conductivity has decreased due to clogging. According to (Al-Ameri et al., 2018) clogging is more likely to be the limiting factor for bioretention's long term functionality than contamination with high concentrations of pollutants (Al-Ameri et al., 2018) and his study confirms that this could be the case. If the whole filter media needs to be replaced, then it is reasonable to consider managing the filter material close to the surface (which may have to be treated as dangerous waste) differently from material farther below the surface.

Given that most evaluated contaminants in this and other studies (e.g. DiBlasi et al., 2009) were retained in the surface layer of the filters (top 0–10 cm), one could argue that a relatively shallow design filter depth (around 10–20 cm) would be sufficient to ensure pollutant removal. However, other organic micropollutants need to be investigated. While this study mainly focused on particle-bound organic pollutants, studies show that dissolved pollutants (e.g. metals, nutrients) can migrate further down in the system or require a deeper filter depth for sufficient treatment. For instance, Davis et al. (2006) suggested filter depths of 60–80 cm for sufficient removal of nitrogen species and phosphorus. Another relevant factor concerning filter depth is vegetation. Commonly, roots require greater filter depths than 10–20 cm. In summary, the filter depth is not only determined by the removal of particulate or easily adsorbed pollutants, but also other factors.

3.10. Further studies

Further work regarding the long-term function and maintenance needs of bioretention systems is required to better understand the accumulation and distribution of OMPs and other pollutants, both particle-bound and dissolved, in these facilities. Studies which can include a wider age variation than that in the present study could reveal more information on the pollutant accumulation trends which can be expected over the lifetime of these systems, although this likely differs largely depending on site-specific parameters. The impact of different filter materials (e.g., varying particle size distribution, varying composition, use of amendments) should be further explored. Given varying national/regional regulations, use of building materials etc., further studies should also include samples from other countries to capture the geographic variability in these pollutants as well as geographical ambient variations such as temperature, humidity and variation in precipitation hydrographs.

Results from field studies are always to some extent site-specific and cannot readily be translated to other geographic locations. Finally, the biodegradation of organic pollutants can involve the formation of potentially-toxic degradation products, which should be a subject of future research.

4. Conclusions

The OMPs included in this study (16 PAHs, 7 PCBs, 13 phthalates and 2 alkylphenols) were commonly found in the filter material of the twelve bioretention facilities across Michigan and Ohio (USA) aged 7–13 years. In total, 32 of the 38 analytes were detected in at least one of the filter material samples while six substances (five phthalates and one PAH) were never detected. The most frequently detected pollutants in the study were PAHs and PCBs, while phthalates and alkylphenols were less frequently detected. Very large variations between the different bioretention sites were observed, most likely due to differences in pollutant sources. In general, the concentrations of most studied OMPs were highest in the upper 5 cm of the filter material and decreased with increased depth in the filter. Further, the highest concentrations tended to be found near the inlet of the facilities and decreased as sample locations increased in distance from the inlet. The overall trend of decreasing concentrations with depth and distance from the inlet are similar for all four studied groups of OMPs (PAHs, PCBs, phthalates, and alkylphenols). Since the results in this study of the behaviors of particle-bound OMPs show similarities in pathways and accumulation with other studies of particle bound pollutants, such as metals, there are likely similarities in long term performance and maintenance needs. Regularly replacing only the top layer of the filter may be all that is necessary to ensure that the entire filter function can be restored, as similarly suggested earlier for metal accumulation and clogging. Safe disposal of polluted filter material must be ensured and, thus, OMP concentrations should be analysed to allow an environmental assessment of the material.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.157372>.

CRediT authorship contribution statement

Robert Furén: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Writing – original draft. **Kelsey Flanagan:** Methodology, Formal analysis, Resources, Data curation, Writing – review & editing. **Ryan J. Winston:** Conceptualization, Methodology, Investigation, Resources, Writing – review & editing, Supervision. **R. Andrew Tirpak:** Methodology, Investigation, Resources, Writing – review & editing. **Jay D. Dorsey:** Methodology, Investigation, Resources, Writing – review & editing. **Maria Viklander:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Godecke-Tobias Blecken:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The financial support for this work was provided by VINNOVA (Swedish Governmental Agency for Innovation Systems, Grant No. 2016-05176, DRIZZLE Centre for Stormwater Management) and SBUF (The Development Fund of the Swedish Construction Industry, Grant No. 13623).

We thank Peter Rosander and Kerstin Nordqvist at LTU for their help with the laboratory work and discussion on the data.

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