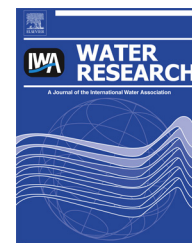


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Sorption and degradation of petroleum hydrocarbons, polycyclic aromatic hydrocarbons, alkylphenols, bisphenol A and phthalates in landfill leachate using sand, activated carbon and peat filters

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ABSTRACT

Landfill leachates are repeatedly found contaminated with organic pollutants, such as alkylphenols (APs), phthalates and polycyclic aromatic hydrocarbons (PAHs) at levels exceeding water quality standards. It has been shown that these pollutants may be present in the colloidal and truly dissolved phase in contaminated water, making particle separation an inefficient removal method. The aim of this study was to investigate sorption and degradation of petroleum hydrocarbons (PHCs), selected APs, bisphenol A (BPA), phthalates and PAHs from landfill leachate using sand, granulated activated carbon (GAC) and peat moss filters. A pilot plant was installed at an inactive landfill with mixed industrial and household waste and samples were collected before and after each filter during two years.

Leachate pre-treated in oil separator and sedimentation pond failed to meet water quality standards in most samples and little improvement was seen after the sand filter. These techniques are based on particle removal, whereas the analysed pollutants are found, to varying degrees, bound to colloids or dissolved. However, even highly hydrophobic compounds expected to be particle-bound, such as the PHCs and high-molecular weight PAHs, were poorly removed in the sand filter. The APs and BPA were completely removed by the GAC filter, while mass balance calculations indicate that 50–80% of the investigated phenols were removed in the peat filter. Results suggest possible AP degradation in peat filters. No evidence of phthalate degradation in the landfill, pond or the filters was found. The PHCs were completely removed in 50% and 35% of the measured occasions in the GAC and peat filters, respectively. The opposite trend was seen for removal of PAHs in GAC (50%) and peat (63%). Oxygenated PAHs with high toxicity were found in the leachates but not in the pond sediment. These compounds are likely formed in the pond water, which is alarming because sedimentation ponds are commonly used treatment techniques. The oxy-PAHs were effectively removed in the GAC, and especially

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the peat filter. It was hypothesized that dissolved compounds would adsorb equally well to the peat and GAC filters. This was not completely supported as the GAC filter was in general more efficient than peat.

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1. Introduction

Removal of petroleum hydrocarbons (PHCs), selected alkylphenols (APs), bisphenol A (BPA), phthalates and polycyclic aromatic hydrocarbons (PAHs) and their degradation products oxygenated PAHs (oxy-PAHs) from landfill leachates are of high importance to meet the demands in the European Water Framework Directive. Alkylphenols – including 4-nonylphenol (4-NP), 4-t-octylphenol (4-t-OP) and 4-t-butylphenol (4-t-BP) – bisphenol A (BPA), phthalates and PAHs have previously been reported in wastewater (Aparicio et al., 2007; Sanchez-Avila et al., 2009; Ballesteros et al., 2006), urban snow (Bjorklund et al., 2011; Fries and Püttmann, 2004; Reinosdotter et al., 2006), runoff (Bjorklund et al., 2009; Bressy et al., 2012; Clara et al., 2010; Strömvall et al., 2007) and landfill leachate (He et al., 2009; Kalmykova et al., 2013; Slack et al., 2005). In Sweden, landfill leachate is often treated in nearby wastewater treatment plants (WWTP). However, in pursuit of the national proposition suggesting that 40% of the phosphorous in sludge should be recycled on arable land by 2018, many WWTPs are undergoing agricultural-quality certification of sludge, which demands disconnection of landfill sites from the WWTP (Swedish Water, 2013). The scientific challenge is to develop local treatment technologies with high efficiency to remove organic pollutants (OPs), organic matter, metals and nitrogen compounds occurring in complex mixtures in landfill leachate (Ocampo-Perez et al., 2012; Plosz et al., 2010; Renou et al., 2008; Rocha et al., 2013; Wu et al., 2011).

Recently, OPs were shown to be present in dissolved and colloidal forms in stormwater and landfill leachate (Kalmykova et al., 2013). Alkylphenols, BPA, phthalates and PAHs, including the most hydrophobic compounds, were detected in a majority of filtered samples (<0.7 µm, 12 sampling sites) and frequently in the colloidal phase. The study also showed that calculated K_{OW} values of specific organic pollutants were lower than theoretical values and dissolved organic carbon (DOC) colloids were suggested carriers of pollutants in the colloidal phase. These findings suggest that the mobility and consequently toxicity and associated risks of the compounds are potentially higher than previously believed. Hence, efficient treatment methods for stormwater and landfill leachates targeting OPs should be developed to prevent their transport to surface waters.

The landfill in the current study was among the sites where high concentrations of OPs were previously measured and frequently found in the dissolved and colloid-bound phases (Kalmykova et al., 2013). This explains why the current leachate treatment, which is among the most commonly used for landfill leachate and stormwater, consisting of an oil separator and a sedimentation pond, is not effective. We

assume that adsorption filters will be suitable treatment for dissolved and colloidal OPs in leachate and stormwater, as they have been proven successful in previous research on organic contaminants in wastewater (Liu et al., 2011; Ray et al., 2006; Tsai et al., 2006).

The criteria for selecting filter material for this study included: adsorbent affinity for the targeted pollutants; adsorption capacity; and hydraulic properties. Organic-based filters often show an affinity for hydrophobic OPs, along with the possibility of biological degradation if a microbial community is established. Studied pollutants differ in their polarity from the least polar PAH to polar APs; therefore adsorbents with both polar and nonpolar surfaces are suitable. For this study, granulated activated carbon (GAC) and *Sphagnum* peat moss were selected. In addition, a sand filter was studied as an inorganic example and because of its frequent application in leachate and stormwater treatment. Activated carbon is a widely available material that has been used for water treatment already in the 19th century (Department of The Army 2001). It is produced by heating of coal, peat or wood at temperatures between 400 and 600 °C in the absence of oxygen. Using waste materials such as coconut shells as raw material reduces the GAC price and potentially provides an environmental benefit. In addition, GAC can be regenerated or reactivated several times and re-used in the filters. Due to its large surface area and non-polar surface, GAC is efficient for adsorption of non-polar pollutants (Bansal and Goyal, 2005). However, in the presence of carbon-oxygen surface groups, polar compounds and metal cations can also be adsorbed. *Sphagnum* peat is a low-cost adsorbent, widely available, biodegradable and a natural, renewable resource. The oxygen-containing functional groups in peat, such as carboxyl, hydroxyl, and carbonyl groups, provide adsorption sites for metals and polar compounds while the nonpolar parts such as waxes and methyl groups adsorb hydrophobic organic molecules (Kalmykova et al., 2008). Earlier studies have shown extensive adsorption capacity of peat for heavy metals (Brown et al., 2000; Kalmykova et al., 2008), oils (Cohen et al., 1991), pesticides (Smith et al., 1978), phosphorous and nitrogen (Brown et al., 2000).

The aim of this study is to investigate the removal and degradation of PHCs, selected APs, BPA, phthalates, PAHs and oxy-PAHs from landfill leachate by a sand, GAC and peat moss filters in an *in-situ* pilot treatment plant. The hypotheses are that:

1. Conventional treatment techniques, such as oil separators and sedimentation ponds, are not efficient in removing colloidal and dissolved OPs. To meet water quality standards, adsorption filters should be used to further reduce the concentrations of OPs in landfill leachate;

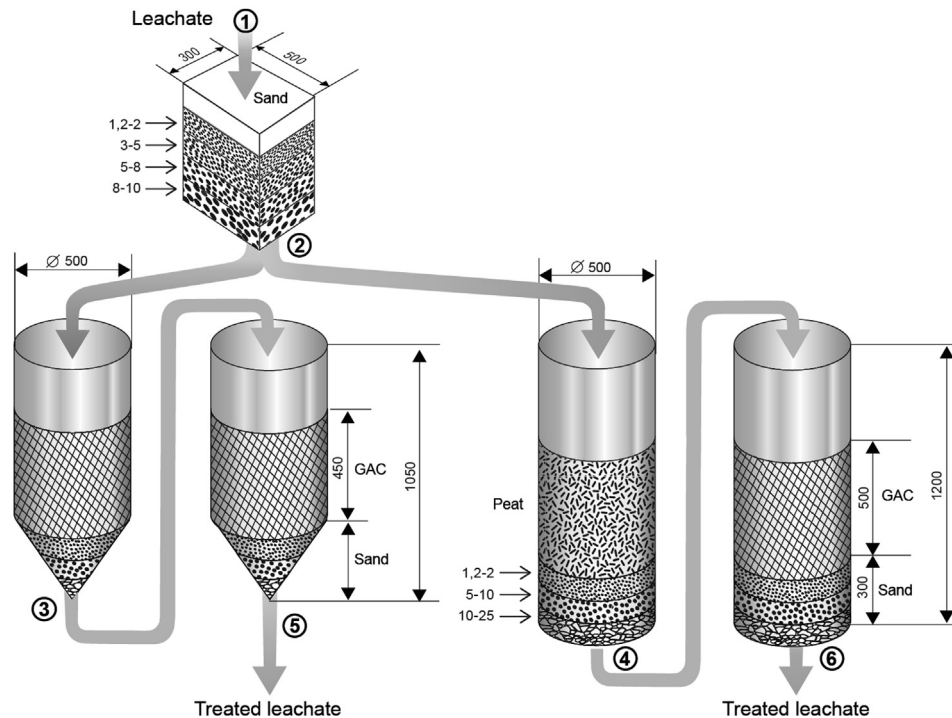


Fig. 1 – Pilot plant facility with sand, GAC and peat filters and the leachate sampling points 1–6 (all dimensions are in [mm]).

- Highly hydrophobic compounds, such as high molecular weight (HMW) phthalates and PAHs, and to some extent APs, are attached to particles hence effectively removed by all the tested filters;
- The compounds previously detected in the truly dissolved phase, e.g. 4-t-BP, 4-t-pentylphenol and naphthalene, will adsorb well in both the peat and GAC filters, while those found in the colloidal phase, such as low molecular weight (LMW) PAHs and BPA, will be removed by the GAC filter through co-sorption with humic colloids, but not by the peat or sand filters.

2. Material and methods

2.1. Study site

Leachate from the Brudaremossen landfill in Gothenburg, Sweden was chosen for this study for two reasons: i) it has been shown to contain all the compounds in question and in considerable concentrations (Kalmykova et al., 2013); ii) it is situated in a forest-and-lakes area with possible emission routes to surface and ground waters, the lakes are also used for drinking water supply. The landfill was in use 1936–1976 and contains a mixture of household and industrial waste with high organic content. A previous study of the landfill showed moderate metal and APs leachate concentrations, whereas concentrations of 4-t-BP, di(2-ethylhexyl) phthalate (DEHP) and PAHs were higher than in other studied landfills (Kalmykova et al., 2013). The Brudaremossen leachate has to be disconnected from the WWTP by 2015.

2.2. The plant

The pilot plant was installed on-site at the Brudaremossen landfill, close to the leachate sedimentation pond. The plant was kept inside a container (i.e. without sunlight) at ambient temperature and consisted of two series of sorption columns: 1) two columns with GAC and; 2) a *Sphagnum* peat moss column followed by a GAC column (Fig. 1). A sand filter was installed to protect the sorption filters from high concentrations of iron precipitates and to remove large particles present in the pond water. The leachate was pumped from the sedimentation pond outlet, at the point from where it is conveyed to the WWTP, to the sand filter (sampling point 1, Fig. 1), which was backwashed once a week. From the sand filter, leachate flowed by gravity at a constant 1.4 L/min rate into the parallel GAC and peat column systems as the sand filter was raised 2 m above. Stainless steel columns and copper pipes were used. The volume of the GAC and peat columns when filled was 78.5 L and 102.1 L, respectively. The contact time was 20 and 30 min in the carbon and peat columns with corresponding hydraulic loading rates of 12.8 m/h and 9 m/h, respectively. The columns were kept saturated at all times, with a water mirror above the adsorbent.

2.3. Adsorbents

The *Sphagnum* peat was obtained from a horticultural firm in Sweden. Properties are as follows: a decomposition degree of H 5 to 6 (von Post scale), packing density 357 kg/m³, particle size 2.0–5.6 mm, organic content 80%. The Filtrasorb 400 ChemvironCarbon GAC has a density of 450 kg/m³, particle size 0.8–1.2 mm, surface area 1050 m²/g by N₂ BET, and

Table 1 – Phenol, phthalate and PAH concentration ranges and medians ($\mu\text{g/L}$) at the sand inlet and outlet (sampling points 1 and 2, respectively, Fig. 1), number of samples (n) and samples with concentrations above the detection limit ($> \text{d.l.}$), compared with European water quality standards. Data for individual samples are found in the Table S1.

Compound		Sand filter inlet	$n (> \text{d.l.})$	Sand filter outlet	$n (> \text{d.l.})$	Water quality standards and guidelines
		(sampling point 1, Fig. 1)		(sampling point 2, Fig. 1)		
		Range (median)		Range (median)		AA/MAC ^a
4-Nonylphenol	4-NP	0.41–0.67 (0.48)	5 (5)	0.11–0.87 (0.46)	12 (12)	0.3/2.0
Nonylphenol monoethoxylate	NP1EO	<0.10	5 (0)	<0.10–0.17 (<0.10)	12 (1)	– ^b
4-tert-Octylphenol	4-t-OP	0.28–0.49 (0.43)	5 (5)	0.21–0.5 (0.40)	12 (12)	0.1/NA ^c
Octylphenol monoethoxylate	OP1EO	<0.10–0.05 (<0.10)	5 (2)	<0.001–0.04 (0.02)	12 (7)	–
4-tert-Butylphenol	4-t-BP	0.34–4.5 (1.1)	5 (5)	<0.001–6.2 (0.02)	12 (7)	–
4-tert-Pentylphenol	4-t-PP	0.14–0.54 (0.36)	5 (5)	0.06–0.7 (0.02)	12 (12)	–
Bisphenol A	BPA	<0.10–0.03 (<0.10)	5 (2)	<0.001–9.3 (0.03)	12 (10)	–
Dimethyl phthalate	DMP	<0.10	5 (0)	<0.10	12 (0)	–
Diethyl phthalate	DEP	<0.05	5 (0)	<0.005–0.11 (<0.005)	12 (2)	–/–
Di-n-butyl phthalate	DnBP	<0.05	5 (0)	<0.005–0.15 (<0.005)	12 (1)	–
Butyl benzyl phthalate	BBP	<0.05	5 (0)	<0.005	12 (0)	–
Di-(2-ethylhexyl) phthalate	DEHP	<0.05–0.18	5 (1)	<0.005–58 (0.12)	12 (7)	1.3/NA
Di-n-octyl phthalate	DnOP	<0.05	5 (0)	<0.005–5.6 (<0.005)	12 (1)	–
Diisononyl phthalate	DINP	<0.05	5 (0)	<0.005	12 (0)	–
Diisodecyl phthalate	DIDP	<0.05	5 (0)	<0.005–0.21 (<0.005)	12 (2)	–
Naphthalene	NAP	<0.01	4 (0)	<0.01–31 (<0.01)	12 (1)	2.4/NA
Acenaphthylene	ACY	<0.01–0.03 (<0.10)	4 (1)	<0.01–56 (<0.01)	12 (2)	–
Acenaphthene	ACE	<0.01	4 (0)	<0.01–101 (<0.01)	12 (1)	–
Fluoranthene	FL	<0.01–0.12 (<0.10)	4 (1)	<0.01–102 (<0.01)	12 (3)	0.1/1
Phenanthrene	PHE	<0.01–0.04 (<0.10)	4 (1)	<0.01–18 (<0.01)	12 (1)	–
Anthracene	ANT	<0.01–0.04 (0.02)	4 (3)	<0.01–41 (<0.01)	12 (2)	0.1/0.4
Fluorene	FLU	<0.01–0.14 (<0.10)	4 (1)	<0.01–64 (<0.01)	12 (2)	0.1/1
Pyrene	PYR	0.04–0.13 (0.10)	4 (4)	<0.01–85 (<0.01)	12 (12)	–
Benzo[a]anthracene	BaA	<0.01–0.06 (<0.10)	4 (1)	<0.01	12 (0)	–
Chrysene	CHY	<0.01–0.06 (<0.10)	4 (1)	<0.01	12 (0)	–
Benzo[b,k]fluoranthene	BbKF	<0.01–0.03 (0.01)	4 (2)	<0.01–34 (<0.01)	12 (1)	0.03/NA
Benzo[a]pyrene	BaP	<0.01–0.06 (<0.10)	4 (1)	<0.01	12 (0)	0.05/0.1
Benzo[g,h,i]perylene	BPY	<0.01–0.06 (<0.10)	4 (1)	<0.01	12 (0)	$\Sigma = 0.002/\text{NA}$
Indeno[1,2,3-cd]pyrene	INP	<0.01	5 (0)	<0.01	12 (0)	–
Dibenzo[a,h]anthracene	DBA	<0.01	5 (0)	<0.01	12 (0)	–

^a AA = annual average and MAC = maximum allowable concentration for inland surface waters (Environmental quality standards in the field of water policy, 2008).

^b Not available.

^c Not applicable.

organic content 86%. To begin with, sand and pebble (Rådsand, Fig. 1) were filled at the bottom of the columns in three homogeneous layers of size ranges: 10–25 mm (density 1440 kg/m³), 5–10 mm (density 1440 kg/m³) and 1.2–2 mm (density 1400 kg/m³). The peat and GAC adsorbents were soaked in water overnight. The resulting slurry was continuously mixed and introduced to the column in small portions under bottom-up water flow, which ensured a homogeneous adsorbent medium. Before start-up of the plant, the columns were conditioned for one week by a clean water rinse to obtain a stable compaction. A metal grid was placed above the peat material to prevent material loss during backwash. This was not necessary for the GAC columns as the material is heavy.

2.4. Sampling and chemical analysis

The plant was run for two consecutive years between April–November (2011) and June–November (2012) and stopped, but left water-filled, during the winter season.

Samples were collected from the inlet (sampling point 2, Fig. 1) and the outlet (sampling points 3–6, Fig. 1) of each of the four columns once a week for analysis of PHCs and metals, and once a month for analysis of PAHs, phenols and phthalates. General water quality parameters including TOC/DOC, pH, dissolved Fe, conductivity, oxygen and alkalinity were measured in the weekly samples. The leachate was collected as grab samples in solvent-rinsed stainless steel buckets from which 1 L samples were separated into dark solvent rinsed glass bottles, kept at +4 °C and directly sent to the commercial laboratories for chemical analysis of OPs. Water samples were also collected weekly in the sedimentation pond (sampling point 1, Fig. 1). Two sediment samples were collected from the pond, and filter material from all four sorption columns were collected by core sampling after cessation of the facility and draining of the columns. From the first GAC and peat columns, mixed samples of the upper 10 cm of the core were collected for analysis of the OP occurrence and indication of OP degradation in the columns. From all filters' cores, mixed samples

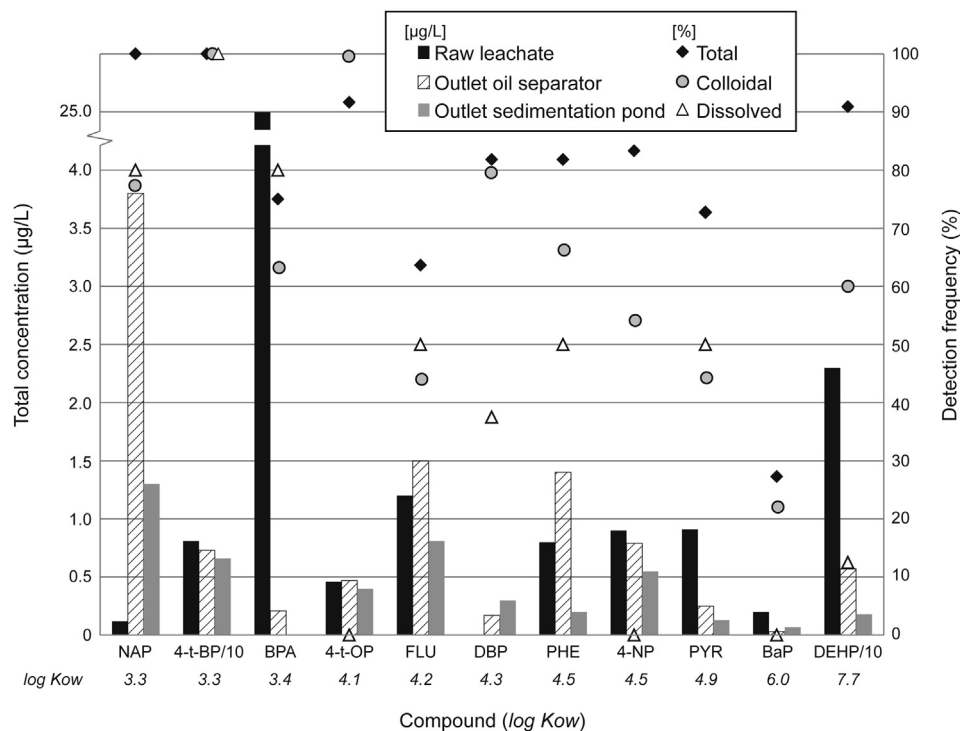


Fig. 2 – Total concentrations (left y-axis, $\mu\text{g/L}$, bars) of selected phenols, PAHs and phthalates in leachate before and after each treatment step of the current full-scale facility at the Brudaremossen landfill, and detection frequencies (right y-axis, %, points) of each compound in the total, colloidal and dissolved phases (data from Kalmykova et al., 2013). The numbers below the x-axis denote the hydrophobicity as $\log K_{ow}$. The 4-t-BP and DEHP concentrations are scaled down to fit the graph.

of the upper and lower 2 cm were dried and the organic content and dry density were determined and compared with the original material packed in the columns.

Included in the study are 16 specific PAHs, nine oxy-PAHs, BPA, 4-t-octyl- and 4-nonylphenols and their ethoxylates, 4-t-butyl- and 4-t-pentylphenol, eight phthalates and phthalate monoesters (Table 1, S1). Water samples were analysed by the commercial laboratory GALAB, Germany. Samples for analysis of phenols, PAHs and phthalates were weighted, internal standards were added and the samples liquid–liquid extracted (LLE) three times with dichloromethane. The extracts were concentrated by rotary evaporation followed by drying through Na_2SO_4 , evaporated to 1.0 ml by N_2 and analysed by GC-MSD. For phthalate monoester analysis, samples were acidified and internal standard added; extracted with organic solvent; evaporated; derivatized using MSTFA followed by GC-MSD (EI) analysis in SIM mode. All pollutants in sediment and column materials and oxy-PAHs in water were analysed by commercial laboratory ALS, Sweden. The following extraction and analytical methods were used for solids: dry substance analysed according to SS028113/1 or DIN 38414-S22; PAHs were solvent extracted using acetone:hexane:cyclohexane (1:2:2) and analysed by GC-MS; oil index and alkane fractions (C_{10} – C_{40}) were solvent extracted with acetone/hexane, florisil clean-up according to CSN EN 14039 and analysed by GC-FID; OPs/OPEOs and NPs/NPEOs were analysed using GC-MS, phthalates were solvent extracted with *n*-hexane on homogenised samples, then analysed using GC-MS; oxy-PAHs both

in solids and water were analysed by GC-MS. Total organic carbon, DOC were measured by TOC-V CPH (Shimadzu, Japan) following the method SS-EN 1484, UV adsorption by UV-1800 (Shimadzu, Japan). Iron was analysed on samples filtered through $0.45 \mu\text{m}$ cellulose-acetate filters using the HACH method 8008. Conductivity, pH and oxygen were measured with electrodes connected to a Multiliner P4 universal meter.

2.5. Mass balance calculations

To estimate mass balances of pollutants in water, it was assumed that measured concentrations (sampled monthly) were valid for the days preceding the sampling, up to the previous sampling occasion. The cumulative time between sample occasions was multiplied by the average flow rate and the measured concentration to get the pollutant mass. Mass balances were calculated for pollutants with at least six inlet concentrations above detection limit. An exception was made for the sand filter where five values were used for calculations.

3. Results and discussion

3.1. Organic pollutants in the landfill leachate

Water characteristics such as pH, temperature (C_o), oxygen content (mg/L), redox potential (mV), conductivity ($\mu\text{S/cm}$),

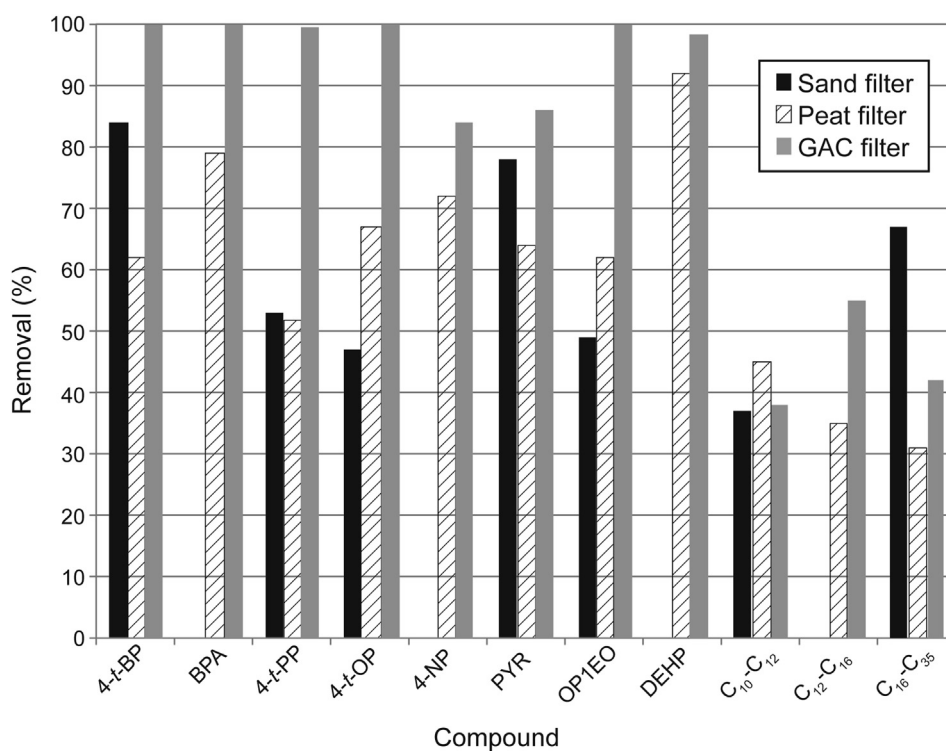


Fig. 3 – Removal (% of inlet mass) of compounds using sand, peat and GAC filters. Compound hydrophobicity (K_{ow}) increases to the right on the x-axis. For the sand filter, negative removal was estimated for BPA, 4-NP and C₁₂–C₁₆ while for DEHP no estimation was made due to too few samples above detection limit.

colour (pt Co) and concentrations of TOC/DOC at all sampling points 1–6, see Table S1.

Fig. 2 shows that the pollutant concentrations are in the same order of magnitude before and after the current treatment steps at the landfill (oil separator and sedimentation pond), which indicates inefficient treatment (data from Kalmykova et al., 2013). The pollutants were frequently detected in the dissolved phase, suggesting that colloid-facilitated transport or transport of truly dissolved OPs causes the inefficient removal by the oil separator and the sedimentation pond.

In the sand filter inlet (Table 1) 4-NP, 4-t-PP, 4-t-BP, 4-t-OP and PYR were detected in all samples, and in concentrations one order of magnitude higher than concentrations reported for leachates from Japan, except for 4-t-OP, but similar to reported data for Swedish landfills (Asakura et al., 2004; Herbert et al., 2006; Kurata et al., 2008; Öman and Junestedt, 2008, see Table S2 for details). Concentrations of other analysed APs and all the phthalates were generally lower than elsewhere reported concentrations. The median PHC concentration (oil index = 84 µg/L) and the dominating fraction C₁₆–C₃₅ found in the leachate (Table S1) are comparable to data from a previous Swedish screening of PHCs in leachate (Junestedt et al., 2003).

3.2. Overall improvement of water quality

The sand filter was inefficient in improving the water quality to meet the environmental quality standards (Table 1). The outlet concentrations repeatedly exceeded the European

environmental quality standards for OPs ($n = 12$ exceeding annual average, AA), NPs ($n = 10$ exceeding AA) and DEHP ($n = 2$ exceeding AA) in surface waters. The European water quality standards for PAHs were exceeded in all samples where the substances were detected (Table 1). In contrast, the GAC and peat filters effectively removed the pollutants far below the thresholds and often below the detection limit.

Mass balance calculations of compounds in the filters reveal that considerable removal of pollutants is taking place in the organic filters, especially in the GAC filter (Fig. 3, data for other compounds were too few to calculate mass balances). It should be noted, that the purpose of the mass balance calculation is a relative comparison of different materials and indication of their efficiency for groups of pollutants. Recognizing the uncertainty of calculation due to few values, the mass balance results should not be used for projecting treatment facilities. The removal of 4-t-BP, BPA, 4-t-PP, 4-t-OP and OP1EO by the GAC filter has the highest certainty in the estimation because inlet values were consistently above and outlet values below the detection limit.

The hypothesis was that the HMW compounds, such as DEHP, PYR and higher alkanes, would be removed well in all filters as these compounds are found attached to particles. Indeed, PYR removal is high in all the filters which suggests it being particle-bound (Fig. 3). In addition, DEHP is the only compound for which the peat filter shows as good removal efficiency as the GAC filter. The sand filter reduced the concentrations of higher alkanes considerably, which suggests them being present in the particulate phase. However, peat

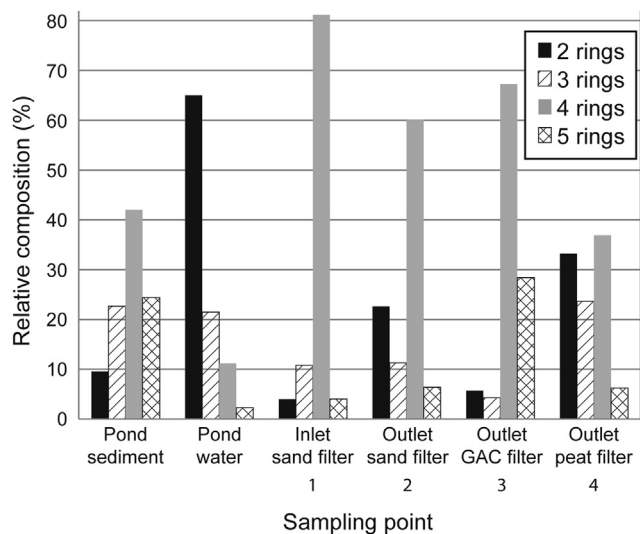


Fig. 4 – The relative composition (%) of 2- to 5-ring PAHs in pond sediment and leachate before and after the different filters (sampling points 1–4 according to Fig. 1).

and GAC showed lower efficiency for these pollutants. Moderate removal of 4-t-PP and 4-t-OP and no removal of BPA and 4-NP in the sand filter offer support to previous findings of their considerable presence in the dissolved phase (Kalmykova et al., 2013). However, 4-t-BP was efficiently removed by the sand filter, despite it being previously found in the dissolved phase. The incoming high particle, DOC and Fe concentrations may have caused it to be particulate-bound. It was also hypothesized that the compounds frequently detected in the truly dissolved phase, e.g. 4-t-BP and 4-t-PP, would adsorb well to both peat and GAC, while those found in the colloidal phase, e.g. LMW PAHs and BPA, would be better removed by the GAC filter through co-sorption with humic

colloids. However, 4-t-BP and 4-t-PP were removed to a higher degree in GAC than peat and almost 80% of the BPA was removed in the peat filter (Fig. 3). The results suggest that the pollutants exist in both truly dissolved form and attached to colloids, see Fig. 2 for guidance on pollutant partitioning. The GAC filter will adsorb both dissolved and colloidal compounds, whereas the humic colloids and thereto attached pollutants are not adsorbed by the peat filter. Hence, the GAC filter shows slightly higher removal efficiencies for these compounds.

The PAHs were completely removed in 50% and 63% of the measured occasions in the GAC and peat filter, respectively. Removal of PYR in the filters was dependent on the inlet concentration, as it was completely removed when the concentration was in the same range as other PAHs, but was only reduced by 30–70% when the initial concentration was 50–70% higher than other PAHs. The number of samples with moderate PYR concentrations was however too limited to statistically prove this relationship. Pyrene was effectively removed also by the sand filter. However, the relative composition of other PAHs before and after the sand filter was similar, which is an indication of PAHs passing through the sand filter without being retained or degraded (Fig. 4).

3.3. Petroleum hydrocarbons

About one hundred water samples, collected before and after the filters, and two sediment samples were analysed for concentrations of PHCs (Table S1). In eluates from all filters, the C_{16} – C_{35} alkane fraction was found in the highest concentrations, whereas the C_{35} – C_{40} fraction was more rarely detected (Fig. 5). Neither the composition nor the concentrations of PHCs were highly affected by the particle removal process in the sand filter. The PHCs were effectively sorbed and completely removed in 50% and 35% of the measured occasions in the GAC and peat filters, respectively.

When the sand filter was saturated with iron particles and in need of back wash, it was bypassed and leachate with high

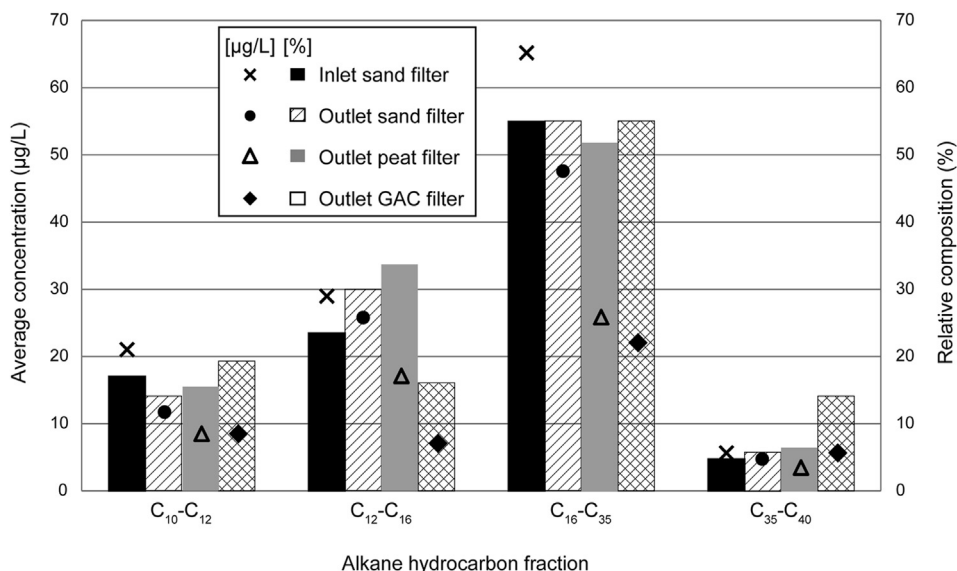


Fig. 5 – The average concentration (µg/L, left y-axis) and relative percent composition (right y-axis) of alkanes before and after different filters.

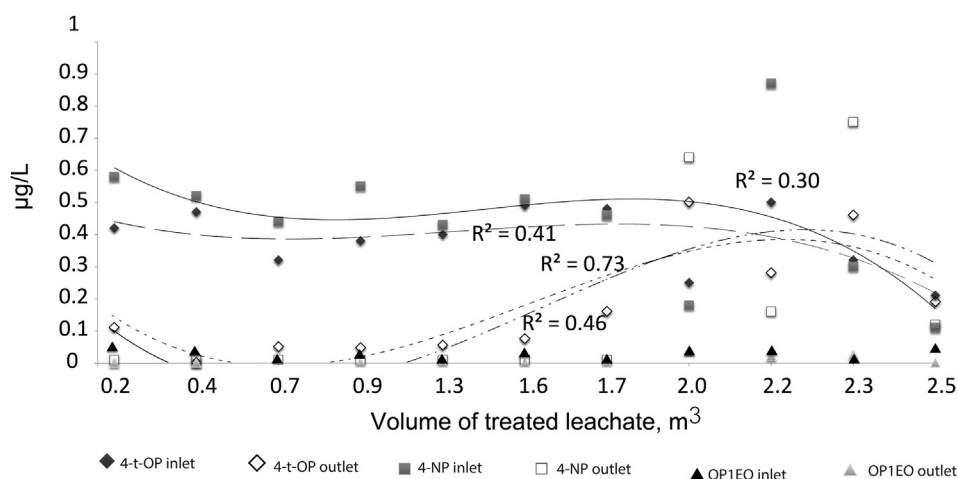


Fig. 6 – Alkylphenol and alkylphenol ethoxylate concentrations (ng/L) in the peat filter outlet.

particle, TOC/DOC and dissolved Fe concentrations was directly conveyed to the GAC and peat filters. Under these conditions, the PHCs were less effectively adsorbed and leached out from the GAC, and especially the peat filter. As suggested by the strong correlation ($r = 0.7$) between the inlet and outlet concentrations, and by the unchanged percentage composition of the alkane hydrocarbons $C_{10}\text{--}C_{12}:C_{12}\text{--}C_{16}:C_{16}\text{--}C_{35}:C_{35}\text{--}C_{40}$ in the inlet 14:30:55:6 and at the outlet 15:33:52:7 (Fig. 5), the PHCs were transported through the peat filter without being adsorbed. Colloid-facilitated transport of PHCs through the peat filter, probably by DOC compounds, is likely since $C_{12}\text{--}C_{16}$, $C_{16}\text{--}C_{35}$ inlet and outlet concentrations correlate with DOC ($r = 0.58\text{--}0.74$, $n_{>.d.l.} = 8\text{--}18$). The peat surface cannot adsorb humic compounds due to the similar negative surface charge; humic and fulvic acids are degradation products of peat and constantly emitted at trace concentrations from the peat filters (Kalmykova et al., 2010).

The PHC composition in the GAC filter eluate 19:16:55:14 was different compared to the inlet 14:30:55:6. The shorter chain $C_{10}\text{--}C_{12}$ PHCs, which are more water-soluble, were found in higher amounts in the outlet than the inlet, indicating desorption, in contrast to colloidal transport from the peat filter. The PHCs elute from the filter column in the order as if the GAC material was saturated. It is hypothesized that the GAC is temporarily saturated with Fe and DOC, hence the most water-soluble LMW PHCs leave the filter matrix first. Activated carbon has previously been shown to efficiently adsorb humic and fulvic acids and is used for this purpose in drinking water treatment (Kalderis et al., 2008). However, this is also a weakness of the GAC filter, as high TOC/DOC concentrations saturate the filter and previously adsorbed pollutants may eventually leach. The GAC filter showed no sign of full saturation during this study as outlet concentrations of neither TOC/DOC nor PHCs increased by the end of the study.

Petroleum hydrocarbon degradation in the environment involves both physical processes, such as adsorption, dispersion, diffusion in pores, volatilisation, chemical oxidation and reduction, and anaerobic and aerobic biological processes (Yang et al., 2013). Initially, different oxygenated

hydrocarbons are produced (Mao et al., 2009). No signs of PHC degradation were detected in the leachates; if degradation had occurred, the more LMW and water soluble $C_{10}\text{--}C_{12}$ fraction would have decreased significantly. In a degradation study of PHCs in soil, the *n*-alkanes were found to be even more resistant to degradation than PAHs with up to three aromatic rings (Mao et al., 2009).

In the pond sediments (Table S4) the mean PHCs concentrations were 5400 $\mu\text{g/g}$ for $C_{16}\text{--}C_{35}$ > 740 $\mu\text{g/g}$ for $C_{12}\text{--}C_{16}$ > 510 $\mu\text{g/g}$ for $C_{35}\text{--}C_{40}$ > 69 $\mu\text{g/g}$ $C_{10}\text{--}C_{12}$. The relative composition of $C_{10}\text{--}C_{12}:C_{12}\text{--}C_{16}:C_{16}\text{--}C_{35}:C_{35}\text{--}C_{40}$ was 1:11:81:8 as compared to 17:23:55:5 in the sand filter inlet. The low content of $C_{10}\text{--}C_{16}$ in the sediment compared to the leachates may be explained by a combination of volatilization, partition/water-solubility and degradation.

3.4. Alkylphenols and alkylphenol ethoxylates

Among the alkylphenol ethoxylates (APEOs), 4-*t*-octylphenolmonoethoxylate (OP1EO) was frequently detected before and after the sand filter, while 4-*t*-octylphenoldiethoxylate (OP2EO) and nonylphenol monoethoxylate (NP1EO) only once. Alkylphenol ethoxylates were not detected in the outlet of the GAC filter while OP1EO was detected twice in the outlet of the peat filter towards the end of the study (Fig. 6).

Alkylphenols were completely removed by the GAC filter, except for one sampling occasion. In contrast, the peat filter was shown to be less effective for removal of APs. In particular, 4-*t*-BP was as a rule detected in the peat filter outlet. Bisphenol A, 4-NP, 4-*t*-OP and 4-*t*-PP were generally removed during the first year of the study, but leached during the second year (Fig. 6). The leaching may be due to filter saturation or APEO degradation as outlet concentrations of both 4-NP and 4-*t*-OP increased gradually along with their inlet concentrations decreasing (Fig. 6). Alkylphenol polyethoxylates are degraded through the loss of ethoxylate groups under both aerobic and anaerobic conditions (Mayer et al., 2007). Anaerobic conditions appear to favour degradation of the polyethoxylates into alkylphenols, e.g. iso-NP, 4-*t*-OP, whereas aerobic conditions favour the formation of carboxylated

ethoxylates (ECB, 2002). However, mass balance calculations of 4-NP and 4-t-OP do not reveal any excess of the compounds in the outlet. Therefore it cannot be concluded that degraded APEOs are the source to 4-NP and 4-t-OP in the outlet and saturation of the filter may have occurred.

In general, the removal efficiency in the peat filter decreases in the following order: BPA > NP > OP > 4-BP > 4-PP, which is the order of an increasing occurrence in the colloidal phase, previously shown in Kalmykova et al. (2013). The nature of the colloids is likely to be organic, i.e. humic and fulvic acids, because the pollutants are completely (apart from 4-NP) removed by the GAC filter along with the DOC. In addition, concentrations of all of the measured APs and APEOs increased ($r = 0.50–0.85$, $n > \text{d.l.} = 6–10$) with increasing inlet and outlet DOC concentrations in the sand and peat filters, which confirms their colloid-facilitated transport through these filters.

Among the studied pollutants, only the APs exhibited probable relationships with water characteristics other than DOC in the sand and the peat filter. A comparable analysis was not possible for the GAC filter as few values were above the detection limit in the outlet. Higher 4-NP and 4-t-OP concentrations were measured at higher pH (varied in the range 6.5–8.1) in the outlet of the sand filter ($r = 0.61–0.73$, $n_{>\text{d.l.}} = 10$). This could be explained by the phenols' higher water-solubility at higher pH depending on the negative charges caused by loss of hydrogen; NPs $\text{pK}_a \sim 5$ and OPs $\text{pK}_a \sim 10$. The 4-t-OP may be attached to humic and fulvic acids, which are not attracted to the negative sand surface, hence transported out of the filter. The NPs are more likely partly soluble in water than attached to humic and fulvic acids at the prevailing pH. On the contrary, lower 4-NP, 4-t-OP and 4-t-PP concentrations were measured in the outlet of the peat filter at higher pH ($r = 0.54–0.73$, $n_{>\text{d.l.}} = 10$). This may be explained by sterically hindrance of the phenols, but also the other organic pollutants, at a decreased pH in the peat matrix. At higher pH values, the peat macro-molecules open up, because of the repellent forces of the negatively charges in the molecules, acting as traps for larger molecules. The results in this study confirm this theory as the more HMW organic pollutants appear to be more effectively sorbed in the peat column than in the GAC. The simultaneous increase of the colour value and the AP concentrations in the peat filter outlet may be an indication of colloid-facilitated transport as colloidal iron and humus content are measured by colour indication ($r = 0.60–0.79$, $n_{>\text{d.l.}} = 6–10$).

3.5. Phthalates

Phthalates were only sporadically detected at the sand filter inlet and at the outlet of all filters, see Table S1. Most concentrations were $<0.5 \mu\text{g/L}$, except for a few samples with higher concentrations of DEHP, DINP and DnOP, maximum 58, 8.5, and $5.6 \mu\text{g/L}$, respectively. The detection frequency was highest for DEHP at all sampling locations, whereas other analysed phthalates were rarely or never detected (Table 1). Notably, DINP was detected in several leachate samples. This phthalate was not in use during the active period of the landfill, but have been used increasingly since the 1990s as a replacement for DEHP (Statistics for Chemicals, 2013). It is

suspected that a plastic source, e.g. bag for transporting the filter materials, is giving rise to the DINP contamination of the samples.

The peat filter showed slightly higher removal of phthalates than the GAC filter throughout the study. This trend may be due to the compounds' biodegradation in peat (Peterson and Staples, 2003). However, as the detection frequencies of phthalates were so low, no general conclusion on the filters' removal efficiency can be drawn.

It has been shown that phthalates biodegrade to a large extent to monoesters and phthalic acid in landfills under both aerobic and anaerobic conditions, while abiotic degradation is considered negligible (Jonsson et al., 2003b). Using landfill simulation reactors, Jonsson et al. (2003a) found monoesters and phthalic acid at concentrations that occasionally exceeded the phthalate diester concentrations by several orders of magnitude in the leachate. In the current study, the presence of mono-2-ethylhexyl phthalate, mono-ethyl phthalate and mono-*n*-butyl phthalate (degradation products of DEHP, DEP and DBP, respectively) was studied in a selection of samples. All monoesters were below the detection limit (100 ng/L) in all samples. However, it should be noted that the samples were not preserved by freezing as suggested for the long-term storage of samples used specifically for monoester analysis, and further degradation, for example to phthalic acid, may have occurred during sample storage.

3.6. Polycyclic aromatic hydrocarbons and oxygenated PAHs

More than 60 leachate samples and two sediment samples were analysed for the concentrations of 16 specific PAHs (Table S1). The relative composition of 2- to 5-ring PAHs before and after the filters (Fig. 4) shows that the majority of the PAHs leaching from the GAC filter are HMW, indicating that the GAC filter is not efficient in sorbing HMW organic pollutants. On the contrary, the more LMW PAHs were dominant in the peat filter leachate. If these more water soluble PAHs leave the peat column, it may be an indication of filter saturation. This is supported by theoretical considerations; according to the distribution and partition theory, the LMW PAHs should be released first if the filter material it saturated. The leaching pattern of the PAHs from the GAC and the peat column could not be explained by colloidal transport because then there should have been a higher colloidal transport of the HMWs in the GAC than in the peat.

The peat column is rich in humic acids, which may enhance the PAH degradation rate (Smith et al., 2009). However, no signs of PAH degradation could be found in the peat column because if degradation had occurred, the most volatile PAHs would degrade first, causing a decrease in HMW/LMW PAH ratio (Jonsson et al., 2007; Mao et al., 2009). In the GAC column, the LMW PAHs were effectively removed. However, this is more likely due to GAC's excellent ability to adsorb volatile hydrocarbons than degradation of the PAHs.

The main degradation route for PAHs in soil and water is microbial degradation (Baboshin and Golovleva, 2012; Bamforth and Singleton, 2005). Photochemical degradation is also an important degradation route in air (Keyte et al., 2013), water (Shemer and Linden, 2007) and surface soil (Xu et al.,

2013). In this study, nine oxy-PAHs with high toxicity were analysed in more than 40 samples at 14 occasions (Table S3). Oxygenated PAHs were detected in four sand-filter inlet samples, and in seven sand-filter eluates, while they were below the detection limit in all the seven GAC and peat-filter eluates. None of the oxy-PAHs were identified in the pond sediment samples (Table S4), indicating that these compounds, with relatively high water-solubility, are transported in the water phase from the sedimentation pond. The compounds are likely formed under the prevailing aerobic and sunlight conditions with high nitrogen (Jacobs et al., 2008) and iron oxide concentrations (Jonsson et al., 2007) in the sedimentation pond. The hydroxyl radical (HO^\bullet) could degrade the PAHs and may be generated by photochemical reactions in the pond water, which includes photolysis of nitrate, nitrite, photo-Fenton chemistry, ligand-to-metal charge-transfer reactions or direct photolysis of coloured dissolved organic matter (Jacobs et al., 2008; Vaughan and Blough, 1998). In the oxidation processes, a wide variety of PAH transformation products are formed, including oxygenated and hydroxylated PAHs, as well as ring-cleavage products such as aldehydes and carboxylic acids (Bamforth and Singleton, 2005; Lundstedt et al., 2007). Of these, the oxy-PAHs are of highest interest to study because they are persistent, highly toxic to both human and the environment, and are more water soluble than their corresponding PAHs (Lundstedt et al., 2007). Oxygenated PAHs have shown a widespread occurrence in the environment but has previously not been analysed in landfill leachates.

The oxy-PAHs detected in sedimentation pond outlet water and sand-filter eluate samples (Table S3) included fluoren-9-one, a degradation product of 9H-fluorene; anthracene-9,10-dione degraded from anthracene; 2-methylanthracene-9,10-dione, a product of methyl anthracene; and 4H-cyclopenta[def]phenanthrene-4-one from pyrene. The calculated ratios of oxy-PAH₉/PAH₁₆ in untreated leachate are similar to ratios reported for groundwater samples (see Table S3). The lower ratio of the oxy-PAHs after the sand filter indicates that they are not formed during sunlight exposure and aeration in the pilot facility, but more likely in the sedimentation pond as suggested above; otherwise the oxy-PAH concentrations should have been slightly higher after the sand filter than in the pond water.

3.7. Organic pollutants in the filter materials

A majority of the about 50 compounds analysed in the filter materials were detected (Table S4). Total PHCs were found at the highest concentrations of all the analysed compound groups in both GAC and peat; the C₁₆–C₃₅ alkanes was the dominating fraction and the highest total PHC concentration of 300 mg/kgDS was found in peat (Table S4). The PHC composition in the peat filter is comparable to the composition in the pond sediment, indicating that the peat filter may also act as a trap for iron particles.

The GAC contained 12 mg/kgDS of total PAHs (Table S4), which is 24 times higher than in the peat and in the same order as concentrations in the pond sediment. The HMW phthalate DEHP was 12 mg/kgDS in peat, which is seven times higher than in the GAC column. The trend seen for PAHs and DEHP is also seen for PHCs; the more volatile and water soluble

pollutants are effectively sorbed by GAC and the more HMW pollutants are more effectively sorbed by peat. Oxygenated PAHs were not detected in the pond sediment or in the GAC, but were detected in surprisingly high concentrations in the peat. The detected oxy-PAHs in peat are the same as found in pond outlet, i.e. fluoren-9-one, anthracene-9,10-dione, 2-methyl anthracene-9,10-dione and 4H-cyclopenta[def]phenanthrene-4-one. These results indicate that the water soluble and highly toxic oxy-PAHs may be effectively sorbed in the peat column but not in the GAC. For 4-t-OP and its mono-, di- and tri-ethoxylates, GAC contained twice as high concentrations as peat, but for 4-NP and its mono-, di- and tri-ethoxylates the concentrations were similar in both filters.

3.8. Degradation and compaction of the filter materials

From the measurements of organic content (LOI) and dry density of the GAC and peat, before and after use in the columns, some small sign of degradation of the peat and carbon was identified. Peat's LOI value showed very little change, whereas GAC from first filter showed increase in LOI value. This is because GAC from first filter was covered with precipitated iron oxides/hydroxides which protected the GAC from combustion during the LOI determination, resulting in lower values of organic content than expected. The Fe precipitation will cause problems when regenerating GAC filters used in full-scale.

After the 2-year study, the GAC and peat filters showed compaction of around 10% and 20%, respectively, measured by the subsidence of the filter materials' surfaces of the total column length including sand.

4. Conclusions

There is evidence that conventional leachate treatment methods such as oil separators and sedimentation ponds are not effective in removing OPs, as detected pollutant concentrations were generally in the same order of magnitude before and after these treatment options (hypothesis 1). It is likely that OPs are transported through the facility as truly dissolved and/or colloid-bound. Therefore, a different or complementary treatment system efficient for dissolved and colloidal pollutants has to be found. Removal of PHCs, 16 specific PAHs, oxy-PAHs, BPA, 4-t-OP and 4-NP and their ethoxylates, 4-t-BP and 4-t-PP, eight phthalates and monoesters was studied in sand, GAC and peat filters. The main findings are the following:

The removal efficiency of the sand filter is not satisfactory to meet water quality standards. However, sand filter is a necessary pre-treatment of precipitated iron as saturation of the filter material led to lower removal efficiencies for PAHs and PHCs in both peat and GAC filters.

Hypothesis 2 (equal removal of particle-bound pollutants in all tested filters) appear to be only partly true for the most hydrophobic compounds; PYR and DEHP are removed to a similar degree by all filters, whereas the removal efficiency of the higher alkanes is lower for the peat and GAC filters. In general, PHCs were the most difficult compounds to remove, possibly because of colloid-facilitated transport from the peat filter and desorption from the GAC filter.

Compounds previously detected in the truly dissolved and colloidal phases (DEHP, 4-t-PP, BPA and 4-NP among others) are effectively removed by peat and GAC filters, but not by sand (hypothesis 3). In general, GAC was the most effective filter for all the pollutants except C₁₀–C₁₂ and C₁₆–C₃₅. This may be explained by the capacity of GAC to remove both colloidal and truly dissolved pollutants, whereas peat is not efficient in adsorbing humic colloids and thereto attached compounds.

Among the monitored water characteristics, including temperature, oxygen content, redox potential, conductivity etc., only DOC concentrations and to some extent pH were found to have an impact on filter performance.

Occurrence of oxy-PAHs in pond water, but not in sediment, suggests that these compounds are formed in the pond. The oxy-PAHs are effectively removed by both the GAC, and especially the peat filter.

Alkylphenol degradation in peat filters was suggested. No evidence of phthalate degradation in the landfill, pond or the filters was found.

From the filter material results, it can be concluded that a combination of filters with different materials is the best solution for leachate treatment; first an automatic back-washing sand filter for removal of larger particles, then a peat filter for removal of the more high-molecular PHCs, DEHP, oxy-PAHs, and also for trapping smaller particles escaped from the sand, before a final step where the most volatile PHCs and PAHs are sorbed in the GAC filter.

The studied filters are a promising solution for reduction of particulate, dissolved and colloidal OPs, either completely or sufficiently to meet the water quality standards. It is recommended to supplement oil separators and sedimentation ponds with filters in order to prevent further transport of dissolved OPs from landfills.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2014.03.011>.

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