PAH accessibility in particulate matter from road-impacted environments

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Abstract

Snowmelt, surface run-off or stormwater releases in urban environments can result in significant discharges of particulate matter-bound polycyclic aromatic hydrocarbons (PAHs) into aquatic environments. Recently, more specific activities such as road tunnel washing have been identified as contributing to contaminant load to surface waters. However, knowledge of PAH accessibility in particulate matter (PM) of urban origin that may ultimately be released into urban surface waters is limited. In the present study, we evaluated the accessibility of PAHs associated with seven distinct (suspended) particulate matter samples collected from different urban sources. Laboratory-based infinite sink extractions with silicone rubber (SR) as extractor phase demonstrated a similar pattern of PAH accessibility for most PM samples. Substantially higher accessible fractions were observed for the less hydrophobic PAHs (between 40 and 80 % of total concentrations) compared with those measured for the most hydrophobic PAHs (< 5 % of total concentrations). When focusing on PAHs bound to PM from tunnel wash waters, first-order desorption rates for PAHs with $\log K_{ow} > 5.5$ were found in line with those commonly found for slowly or very slowly desorbing sediment-associated contaminants. PAHs with $\log K_{ow} < 5.5$ were found at higher desorbing rates. The addition of detergents did not influence the extractability of lighter PAHs but increased desorption rates for the heavier PAHs, potentially contributing to increasing the toxicity of tunnel wash waters when surfactants are used. Implications of total and accessible PAH concentrations measured in our urban PM samples are discussed in a context of management of PAH and PM emission to the surrounding aquatic environment. Although only fully assessing

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PAHs in this work, further study should consider other contaminants such as OPAHs, which were also detected in all PM samples.

Graphical abstract

INTRODUCTION

Urban aquatic environments often represent a sink for particulate matter (PM), dirt and dust, or eroded surface particulate originating from roads and other paved and constructed areas. The sorption of hydrophobic organic contaminants to this PM can strongly affect their fate, distribution and ecotoxicological risk in the aquatic environment[1–3]. Urban run-off has been identified as an important source of polycyclic aromatic hydrocarbons (PAHs) to the aquatic environment[4]. The type of organic matter (OM) present in soils, sediment, or run-off waters from urban areas affects the extent of sorption of compounds such as PAHs, and ultimately their availability for transfer to the water column or into organisms. Exceptionally strong (ad)sorption to combustion-derived carbonaceous materials such as black carbon, soot or kerogen is responsible for organic carbon-water distribution coefficients significantly higher than those predicted from equilibrium partitioning between amorphous regions of OM and water[2]. Implications of this phenomenon are lower than expected and variable sediment-to-biota bioaccumulation factors, and limited potential for microbial biodegradation[2]. PAHs emitted together with this OM have been shown to be strongly bound, resulting in low pore water concentrations in sediments, a low proportion of chemicals in sediment available for partitioning, and slow to very slow desorption rates[5–7]. The risk posed by PM-associated contaminants in urban environments can be better assessed by estimating freely dissolved concentrations using passive sampling[8–11], estimating the accessible concentration of contaminants[12], or estimating contaminant desorption rates[13].

Direct release through surface run-off and sewer and storm water networks following heavy rainfall represents an important pathway for this urban PM to the aquatic environment (e.g. rivers, lakes, or coastal areas)[14]. However in recent years, other more specific activities have been identified as potentially significant sources of PAHs to the urban aquatic environment. PM accumulated in snow over a long period of time during winter can be released during snowmelt into peak events[15]. In Oslo (Norway), trials of a snow-melting plant built on a

barge using seawater to melt and process excess snow removed from urban areas are under way. Typical seasonal processing of hundreds of thousands of cubic meters of snow has the potential to discharge urban PM into fjord waters. Despite the ability of the plant to remove a significant proportion of suspended particulate matter (SPM) through sedimentation tanks and filters, the PM content of the effluent waters can still reach hundreds of milligrams per liter. Another sporadic yet significant source of PM-associated contaminants that has received increased attention in recent years is tunnel washing[16]. PM concentrations up to 23 g L^{-1} have been measured in wash waters from tunnels in Norway while PAH concentrations as high as 49 μg L^{-1} have been measured previously in tunnel wash waters[17]. Large volumes of water are used (*ca* 60 – 100 L water per meter in a two tube tunnel (two-lanes/tube) and depending on traffic density, tunnels may require washing up to 12 times a year. Tunnel wash waters containing detergents are commonly discharged into storm water retention basins. However, the majority of the Norwegian tunnels (~1000) do not have any treatment of the tunnel wash water, and are directly discharged into the local environment.

Data on PAH availability or accessibility in actual urban particulate matter that may reach aquatic environments remain scarce. Therefore, the present study aimed to assess the accessibility of PAHs present in seven road-impacted PM samples that would likely be discharged into the aquatic environment. These samples included (i) SPM from tunnel wash waters from two different tunnels in Norway, (ii) PM samples collected from mobile road sweepers collecting settled dust from the road prior to tunnel washing, (iii) SPM from the effluent waters of a snow-melting barge, (iv) SPM from the River Alna, an urban river in Oslo, and (v) marine sediments collected in the vicinity of the outlet pipe where tunnel wash water and seepage water from the Oslofjord sub-sea tunnel are discharged. The primary objective was to evaluate the rapidly desorbable or accessible concentration of PAHs in these PM samples using SR passive samplers. A secondary objective was to evaluate the effect of the detergent used for tunnel wash on PAH desorption from tunnel wash water SPM samples. During processing, several samples analyzed for oxygenated PAHs (OPAHs). Finally, implications of observed PAH accessibility are discussed for these particulate sources of contamination for the surrounding aquatic environments.

MATERIAL AND METHODS

Solvent and standards

An Elgastat Maxima HPLC deionization option 3 ultrapure water system was used to obtain ultrapure water. HPLC-grade dichloromethane and pentane were from Rathburn. HPLC-grade methanol was from Riedel-de-Haen, and HPLC-grade cyclohexane was from J.T. Baker. Sodium azide was obtained from Sigma-Aldrich. Standards for PAHs and their deuterated homologues from Chiron were of analytical-grade with purities of >99 % for PAHs and >99.5 % for deuterated PAHs. A full list of PAHs studied here and their respective $\log K_{ow}$ values can be found in Table SI-3. For OPAHs, standards with purity of 97% or higher were obtained from CDN Isotopes (Pointe-Claire, Quebec, Canada), Chiron (Trondheim, Norway) and Sigma-Aldrich, (St. Louis, MO).

Silicone rubber

AlteSil™ SR sheets purchased from Altec Products Ltd were initially Soxhlet extracted with ethyl acetate for 24 hours to remove oligomers and other impurities. Sheets of silicone rubber were then left to dry before being cut into pieces (mean of 4.67 g, RSD of 1.8 %, n = 81). A final clean of these passive samplers was undertaken by soaking in methanol for two consecutive periods of 24 hours. The samplers were then left to dry before storage in a clean glass jar until use. Five samplers were kept as preparation blanks.

Particulate matter sample collection

Seven urban PM samples collected from various road-impacted environments in and around Oslo (Norway) were evaluated in this study (Table 1 and further detail in SI). Samples were taken at different times of the year, but all will be expected to be impacted through traffic, road-associated and urban activities, and may ultimately reach the aquatic environment. The (S)PM samples include those from tunnel washing (Nordby and Granfoss tunnels), from mobile road sweepers (also from Nordby and Granfoss tunnels), from the Alna River, a snow-melting plant in Oslo, and a marine sediment sample from the Oslofjord. All samples were placed in clean glass jars and frozen at −20 °C upon collection.

Laboratory batch experiments

Non-exhaustive extractions were set-up to quantify the rapidly desorbing (or accessible) concentration of PAHs in the different PM samples. Depending on the material (coarse or fine), 3–16 g wet weight of PM was placed in 50 mL centrifuge tubes (previously cleaned in the furnace at 550 °C), and capped with aluminium-lined lids. Higher samples masses were used for the coarser materials because of the lower organic carbon contents. Samples were thawed and homogenized prior to sub-sampling, and ultrapure water (40 mL) was added to each tube. To limit PAH biodegradation during the test, sodium azide (NaN_3) was added as biocide (final concentration of 100 g L^{-1}). The volume of the SR was selected to ensure the extraction was not limited by the capacity of the passive sampler[18]. Centrifuge tubes were placed on an orbital shaker at 150 rpm (19–22 °C), and tubes were manually rotated daily. After two weeks, passive samplers were removed from solution with clean tweezers, rinsed with ultrapure water and wiped with a clean tissue before being placed in clean glass jars for solvent extraction. Visual inspection showed that minimal amounts of particles were left on the surface of the silicone samplers following retrieval from the centrifuge tubes. New clean passive samplers were placed in the centrifuge tubes for two additional weeks since four weeks were expected to be sufficient to measure the accessible PAH concentration in these PM samples[18]. Passive samplers from each centrifuge extraction tube were pooled for analysis. For selected assays, this manipulation was repeated with a third SR sampler and samplers analysed separately to evaluate how exhaustive the extraction procedure was. Extractions were prepared in triplicate for fine PM samples, while five replicates were used for the coarser PM samples.

For tunnel wash water samples (samples TUN1 and TUN2), extractions were performed as above, and also undertaken in the presence of different concentrations of detergent. The detergent TK 601 (Teknisk Kjemisk Produksjon AS, Norway), a commonly used detergent for tunnel washing was added at concentration levels of 0.5, 3 and 6 % (L/L). The detergent

is composed of 1–4 % trisodium nitrilotriacetate, 1–5 % 2(2-butoxy ethoxy) ethanol, 1–5 % ethoxylated C_{12}-C_{14} alcohols, and 1–5 % ethoxylated C_9-C_{11} alcohols.

SR and particulate matter extraction

Passive samplers were extracted and analysed for PAHs. Passive samplers were cleaned in the laboratory by rinsing with ultrapure water and then dried using a clean paper tissue before soaking overnight in pentane (150 mL). Surrogate standards for PAHs (d_8-naphthalene, d_{10}-biphenyl, d_8-acenaphthylene, d_8-dibenzothiophene, d_{10}-pyrene, d_{12}-benz[a]anthracene and d_{12}-perylene) were added during the first extraction step. This step was repeated with fresh pentane for another 12 hours. Extracts were combined and reduced under a stream of nitrogen and diluted by 50 % with dichloromethane for further clean-up by gel permeation chromatography with dichloromethane as mobile phase[19]. Extracts were further reduced to 50–100 μL before PAH analysis by GC/MS. SR samplers spiked with known amounts of PAHs were used to check recoveries for our extraction procedure. The first pentane extraction allowed the recovery on average of 96 % of PAHs (93–97 %) while the second extraction allowed the recovery of 4 % on average of PAHs (2.8–4.7 %). The third extraction resulted in proportion of PAHs recovered in the range 0.12–0.63 % indicating that the pentane-based PAH extraction was quantitative. Spiked SR samplers (180–270 ng $sampler^{-1}$ of individual PAHs) analysed with every batch of SR analysis were used to evaluate Interbatch variability in extraction and analysis of PAHs from SR. The median of absolute deviations for individual PAHs between the measured concentrations in the spiked sample and the mean values from all measurements undertaken from this batch of spiked samplers was 9.1 % (range of 1.3–30 %).

Results of our participation to the Quasimeme DE-13 passive sampler intercomparison exercise for which a total of 21 labs reported data showed our measurements are robust (Z-scores for PAH concentrations measured in field-exposed silicone rubber passive sampler were ~0 for 4 compounds, < 1 for 6 compounds, < 2 for 2 substances and < 3 for one compound).

For the measurement of total PAH concentrations in PM samples, an extraction of 1–2 g PM was undertaken with dichloromethane (20 mL) in an ultrasonic bath (Branson 5510, Frequency: 40 kHz) for 120 min. Surrogate standards for PAHs (d_8-naphthalene, d_{10}-biphenyl, d_8-acenaphthylene, d_8-dibenzothiophene, d_{10}-pyrene, d_{12}-benz[a]anthracene and d_{12}-perylene) were added during the first extraction step. This step was repeated with fresh dichloromethane (20 mL) for 60 min. Extracts were combined and traces of water removed with Na_2SO_4. Extracts were further reduced and cleaned-up by gel permeation chromatography. Extracts were reduced using nitrogen before GC/MS analysis. A certified reference material, SRM-1944 (NIST) was analysed together with the samples. The median of deviations between measured concentrations and certified values for all PAHs of interest was 15 % (range of 0 to 61 %).

GC/MS analysis

Analysis was on a Agilent 7890A gas chromatograph (GC) linked to an Agilent 5975c inert XL EI/CI mass spectrometer (MS) operated in single ion monitoring mode (SIM) with

electron impact ionisation (70 keV). Separation was on a DB-5MS column (30 m, 0.25 mm i.d. and 0.25 μm film thickness, Agilent JW Scientific) following a pulsed splitless injection (1 μL injection, pulse pressure 20 psi for 1.2 min, injector temperature of 300 °C). The helium carrier gas flow was set to 1.2 mL min^{-1}. The GC oven temperature programme started with a step at 60 °C (held for 2 min) before an increase to 250 °C (at the rate 7 °C min^{-1}), followed by an increase to 310 °C (at the rate of 15 °C min^{-1}) with this temperature held for 5 min. Temperatures for the ion source, quadrupole and transfer line were set to 230, 150 and 280 °C, respectively. The relative response of surrogate standards and 7-point calibration curves were used for the quantification. A deviation of the qualifier/quantifier ion response under 20 % was used for identification. Limits of detection for SR sampler extracts and for particulate matter samples were 5 ng sampler^{-1} and 2 ng g^{-1} dry weight PM (except for naphthalene wih a value of 10 ng g^{-1}).

Supporting parameters

Grain size distribution was obtained using laser granulometry (Figure SI-1). Rock-Eval analysis was conducted to estimate the total organic carbon (TOC) content of the PM samples and to provide further information on the nature of the organic carbon (Table SI-2).

RESULTS AND DISCUSSION

Total PAH concentrations

Total PAH concentrations varied by up to three orders of magnitude between the different particulate samples (Tables 1 and SI-3). The sum of 16 US EPA PAHs ranged from 0.67 μg g^{-1} for a mobile road sweeper sample to a maximum of 26 μg g^{-1} for the River Alna SPM. PAH concentrations in Samples TUN1 and TUN2 (SPM from tunnel wash waters) were very similar despite being from different tunnels where key factors such as traffic, driving speed, type of vehicle or time interval since last wash may affect PAH content of the PM. As described in SI, the only major difference between the two tunnels is the cleaning frequency of the Granfoss tunnel twice as high as that of the Nordby tunnel. PAH concentrations in PM samples from the two mobile road sweepers were also comparable, but a factor of 5–10 below those found for TUN1 and TUN2. This is not surprising since sweeper samples were coarser (Figure SI-1) and had correspondingly lower TOC content (Table SI-2). When total PAH concentrations are normalized to TOC content, no major differences between tunnel washing samples can be seen (Table SI-4). Incidentally, TOC-normalized concentrations in SPM from the snow-melting plant are also comparable to tunnel wash samples. PAH concentrations for the Alna River SPM remain higher than those from tunnel washing. On a TOC-normalized basis, Oslofjord sediments are generally present at the highest PAH concentrations, particularly for the lighter PAHs. However this may be the result of the low and uncertain organic carbon content of that sediment sample.

PAH levels measured in SPM from tunnel wash waters in our study are of similar order of magnitude as concentrations reported previously[20–22]. Indeed, Oda et al. (2001)[21] found concentrations of individual PAHs in the range of 0.14–1.1 μg g^{-1} for road soil sampled inside a tunnel with 30 000 cars/day usage. However, they measured higher PAH concentrations (0.2–6.9 μg g^{-1}) in tunnel dust collected from the guard rail, most as a result

of sampling of finer (soot) particles with higher concentrations. PAH concentrations in fine road dust (< 2 μm) measured by Rogge et al. (1993)[20] were slightly higher (0.16–9.4 μg g^{-1}). PAH concentrations in the Alna River SPM sample (25.7 μg g^{-1}) are relatively high when compared with PAH concentrations measured in SPM from rivers with strong urban influence[23–25]. Fluoranthene and pyrene concentrations in the Alna River SPM (5 and 4.1 μg g^{-1}, respectively) were one order of magnitude higher than the average of concentrations found by Zhou et al. (2008)[25] in SPM in rivers in the United Kingdom. Stout et al. (2004)[23] reported that PAH concentrations in 96 % of 280 bed sediment samples from urban-influenced environments were below 20 μg g^{-1}. The specific release of snow-associated PM during snowmelt could be responsible for the high PAH concentrations measured bound to the Alna River SPM.

PAH diagnostic ratios

Diagnostic ratios of PAHs can be used to trace the possible source of PAH contamination[26–28]. Selected diagnostic ratios are plotted on Figure SI-2 and represent some of the most commonly used PAH diagnostic ratios. First, it is interesting to note that most of these ratios are able to separate samples RIV and SED (Alna River SPM and Oslofjord bottom sediments) from the other PM samples. All four samples from the tunnel washing (from tunnel wash waters and road sweepers) are generally grouped together for most PAH diagnostic ratios (Table SI-2). This is perhaps not surprising since PAH contamination in tunnel and snowmelter samples may be less weathered than for the river SPM and fjord sediments. While traffic intensity is low for the Oslofjord tunnel (that impact the fjord sediment sample), the proportion of heavy vehicles and is high compared with the other two tunnels and this could affect PAHs profiles.

The fluoranthene/(fluoranthene+pyrene) ratios (FL/(FL+PYR)) between 0.33 and 0.38 are slightly lower than expected for road dust and samples from road tunnels[27]. However, this ratio may be lower if PAH input also included sources such as used engine oil or diesel oil, diesel combustion which show FL/(FL+PYR) ratio 0.30–0.39[27]. The low indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene+benzo[ghi]perylene) ratios (IP/(IP+BghiP)) for tunnel samples TUN1, TUN2, SWE1 and SWE2 (0.15–0.20) could be indicative of gasoline combustion and are lower than those found previously for tunnel samples[27]. Ratios of benz[a]anthracene/(benzo[a]anthracene+chrysene) (BaA/(BaA+CHRY)) > 0.35 may be representative of vehicular emission[28]. Tunnel samples showed ratios in the range 0.33–0.35 (Figure SI-2). Sample SED shows a much lower BaA/(BaA+CHRY) ratio indicating a possible petrogenic source of contamination, possibly related to bitumen in asphalt or car tires. The benzo[a]pyrene/benzo[ghi]perylene ratios (BaP/BghiP) for tunnel samples (0.16–0.38) would be indicative of non-traffic related sources according to Katsoyiannis et al. (2007)[29]. Ratios of anthracene over phenanthrene (ANT/(ANT+PHE)) below 0.1 for tunnel samples and SNW (from the snowmeltingfacility) are indicative of traffic-related PAH emissions[26]. A benzo[a]pyrene/(benzo[a]pyrene+benzo[e]pyene) ratio (BaP/(BaP+BeP)) of 0.5 is expected for freshly emitted particles while ratios lower than 0.5 would be indicative of ageing as a result of preferential photolysis of BaP[28]. A ratio slightly closer to 0.5 can be seen for the SPM from the Alna River indicating input of freshly emitted particles. For all other PM samples, ratios are much lower than 0.5. These diagnostic ratios generally show

that PAHs present in these PM samples do not originate from single emission sources, but instead are the result of multiple traffic and road-related sources. Diagnostic ratios appear to efficiently group and distinguish tunnel PM samples from other samples.

PAH accessibility

Non-exhaustive extractions were conducted using SR. All passive sampler-PM exposures, except for the Oslofjord sediment, resulted in PAH concentrations well above quantification limits. We expected that extraction conditions resulted in sufficient capacity of the passive samplers to extract over 90 % (see Supporting information) of the accessible fraction of PAHs able to desorb within the experimental time frame[18]. In addition, depletive conditions were assured by exchanging passive samplers after two weeks. For Sample TUN1, SR samplers were used in three consecutive exposures and were analysed separately. The largest amounts of individual PAHs with $logK_{ow} < 5.5$ were extracted during the first SR exposure (on average 63 %) with decreasing amounts absorbed over the second (23 %) and third exposures (14 %). For more hydrophobic PAHs, this was not the case. On average, the first to last extractions of more hydrophobic PAHs (log $K_{ow} > 5.5$) were 20, 45, 35 %, respectively.

The proportion of PAH extracted with SR from PM presented in Table SI-5 and shown graphically on Figure 1 were calculated as the ratio of the PAH mass extracted by SR per gram of PM (dry weight) ove the total PAH concentration in PM measured by exhaustive extraction. These ranged from a few percent for the highest molecular weight PAHs (e.g. benzo[ghi]perylene) to values approaching 80 % for acenaphthene and fluorene in TUN1. Notably, most PM samples (TUN1, TUN2, SWE1, SWE2, RIV and SNW) show a similar PAH extractability. For sample SED, the Oslofjord bottom sediments, passive sampler extractions demonstrated a very low PAH accessibility (see Table SI-5). Relative standard deviations (% RSD) of the accessible concentration measurements ranged from 1.7 to 72 % across PAHs and PM samples (n = 3 or 5). The average of RSDs calculated for each PAH for each PM sample were 38, 13, 20, 10, 14, 18 and 15 % for TUN1, TUN2, SWE1, SWE2, and SNW, respectively. For acenaphthene and fluorene, the fraction extracted is between 50 and 80 % of the total concentrations for most PM samples. The accessible concentration of dibenzothiophene, phenanthrene, and anthracene amounts to approximately half of the total PM concentrations. For fluoranthene, the extractable fraction can vary from 22 % for SPM from the Alna River to 64 % for particles from Nordby tunnel wash water. The extractable fraction for benz[a]anthracene and pyrene is between 16 and 50 %. Finally for higher molecular weight PAHs, the accessible concentration reduced to below 15 % of the total PM concentrations. No more than 5 % of benzo[ghi]perylene could be extracted from any of the samples. Overall these results generally indicate a substantial accessibility of lower molecular weight PAHs in most of these road-impacted PM. The desorbable concentration appears generally lower for naphthalene and acenaphthylene than for other PAHs with $logK_{ow} > 5.5$. The rapidly desorbing fraction of these volatile substances may have been reduced as a result of particle ageing, volatilization following particle emission or desorption into water following their release into washwaters. With increasing compound's hydrophobicity, the extractable concentration of PAHs decreases, reaching values below 15 % of the total concentration for the most hydrophobic PAHs ($logK_{ow} > 6.0$). Smedes et

al. (2012)[18] found accessible concentrations of PAHs in sediment a factor of 2 to 10 lower than total PAH concentrations, in agreement with our results. Our results are also in agreement with the strong PAH sorption observed in soot-water systems[30, 31]. Jonker and Koelmans (2001)[30] found organic carbon-water distribution coefficients ($logK_{oc}$) in the range of 6.24–8.89 for PAHs in traffic soot. They also estimated that the fraction of PAHs unavailable for partitioning/equilibrium distribution in this traffic soot-water system ranged from 50 % for phenanthrene to 85 % for benzo[ghi]perylene. This is consistent with our results. For the low MW PAHs, data from successive extractions of sample TUN1 indicate that the desorbing fraction generally becomes exhausted. In these conditions, the fraction obtained with two successive sampler extractions provides acceptable estimates (86 % on average for the lower MW PAHs of the three consecutive extractions) of the fraction of these particle-bound compounds that is available for partitioning. Since such depletion is not observed for the higher MW PAHs, it is possible that in TUN1, the operationally-defined rapidly desorbing fraction is small and the measurement we undertake here is mostly of PAHs in the slowly or very slowly desorbing fraction[13, 31, 32]. According to Poot et al. (2014)[6], the percentage of refractory carbon in sample TUN1 would tend to support this.

We must mention procedural artefacts that can influence our results. First, continuous-flow centrifugation (CFC) may not allow the sampling of the finest particles in suspension (e.g. < 1 μm). SPM samples from tunnel wash waters or from the snow-melting floating plant may not include the entire finest fraction of suspended particles. It is also possible that a PAH loss from the rapidly desorbing fraction occurs during sampling with CFC. When comparing PAH accessibility in samples from tunnel wash waters with those from mobile road sweepers, only minor differences in accessibility can be observed. Significantly more accessible naphthalene and acenaphthylene (and acenaphthene for Sample SWE2) is seen in Samples SWE1 and SWE2 from mobile road sweepers compared with respective samples from tunnel washwaters. The lower accessibility in tunnel washwater PM samples may be due to near instantaneous PAH desorption following the release of particles into washwaters.

Influence of tunnel wash detergent on PAH extractability

TUN1 and TUN2 were also subjected to non-exhaustive extraction in the presence of a detergent (TK 601) often used during tunnel wash operations in Norway. Accessible concentrations of PAHs obtained in the presence of TK 601 (volume ratios of 0.005, 0.03 and 0.06) relative to those measured without detergent are presented in Figure 2 (and in Tables SI-6 and SI-7). A ratio above 1 indicates an increase in PAH extractability with use of detergent. We calculated relative percent differences (RPD) based on duplicate measurements of accessible PAH concentrations in presence of detergent. These RPDs were low and in the range of 0.2–35 % (median of 6.6) and 1.6–38 % (median of 15 %) for samples TUN1 and TUN2, respectively across the three detergent concentrations (Tables SI-6 and SI-7). For TUN1, the dispersion of the data appears significantly lower for the extractions in the presence of detergent (Table SI-6). For TUN2, data dispersion in absence or presence of detergent is similar. The use of detergent does not seem to influence the extractability of lighter PAHs (i.e. from naphthalene to pyrene), with ratios between 0.60 and 1.18 (and an average of 1.0 and 0.96 for TUN1 and TUN2, respectively for PAHs with $logK_{ow} < 5.5$). For the more hydrophobic PAHs, the addition of detergent resulted in

increased extractability. This increase was more pronounced for the more hydrophobic PAHs, reaching an increase of a factor of 8 for benzo[ghi]perylene for TUN1 when using 3 % of TK 601. However, no clear pattern of relative increase in PAH extractability can be seen for the different detergent concentrations. For TUN1, the 3 % concentrations appeared to provide the maximum enhancement in extractability. For sample TUN2, the two higher detergent concentration levels (3 and 6 %) resulted in similar PAH extractability, but clearly higher than those obtained with 0.5 % detergent.

It is generally well-known that the addition of surfactants to soil and sediment slurries can promote the desorption of hydrophobic contaminants such as PAHs from soils and sediments[33, 34]. Allan et al. (2007)[33] showed that hydropropyl-β-cyclodextrin (HPCD) addition to contaminated soil slurries was able to enhance the fraction of PAHs available to degrading bacteria in these soils. These conclusions were supported by a study by Zhu and Aitken (2010)[34] who used other types of surfactants. Such enhancements were observed for all PAHs (except for naphthalene) in their study. We only see an enhancement for the higher MW PAHs. The contaminant mobilization effect of TK 601 does not appear to be significant for the lighter PAHs. Cuypers et al. (2002)[35] demonstrated that the use of TritonX-100 surfactant for the extraction of PAHs from two sediments did not result in appreciably different residual sediment concentrations for three-ring PAHs, from those obtained through either Tenax® extraction, HPCD or through biodegradation. TritonX-100 was, however, able to enhance the extractability of 4–6 ring PAHs considerably. This is in agreement with our data. More recently, tests involving the use of an infinite absorptive sink (e.g. SR) and a mobilizing agent (cyclodextrin or digestive fluids) have been proposed for the measurement of bioaccessibility and applied to PAH in wood or fuel soot[36, 37]. The detergent in our study or mobilizing agent likely enhances the solubility of the most hydrophobic PAHs in water and facilitates the transfer into the silicone. It is also possible that the detergent has an impact on the physico-chemical characteristics of the PM samples, enabling a PAH fraction to desorb that would otherwise not be available for partitioning into water.

The results from extractions with addition of detergent have some procedural implications. The addition of detergent tends to increase the release of the more hydrophobic PAHs. At the same time it does not influence low molecular weight PAH amounts absorbed by SR samplers. These results confirm that the volume of SR used in this experiment was sufficient to achieve depletive conditions. The low accessibility of more hydrophobic PAHs in these PM samples is not an artefact of the extraction test using SR.

Apparent first-order PAH desorption rates

For TUN1, passive samplers from the first, second and third exposures were extracted separately. It is therefore possible to calculate apparent first-order PAH desorption rates (k_d) for the 6 week-long assays conducted without and with 6 % detergent. Apparent desorption curves with first-order kinetics were generally good with R^2 in the range 0.69 to 1.00 (with the mean of R^2 across all substances and treatments > 0.90). Examples of desorption curves with and without the presence of detergent (6 %) are presented in Figure SI-3 for selected PAHs across a range of $\log K_{ow}$ values. Mean $\log k_d$ (n = 2 and 3 for experiment with and without detergent) are reported in Table SI-8 and presented in Figure 3. As expected, k_d

values appear to decrease with increase PAH molecular weight or hydrophobicity[38]. The logarithm of desorption rates (h^{-1}) ranged from –2.47 for fluorene to –4.4 for benzo[ghi]perylene. Desorption rates for the more hydrophobic PAHs correspond generally well with literature values of slow to very slow desorption rates of PAHs from sediments or from industrial sites[6, 39]. For naphthalene and acenaphthylene, desorption rates were lower than expected (Table SI-8). This could indicate, as mentioned previously, earlier losses of these volatile substances from the rapidly desorbing pool of the PM due to ageing. PAH desorption curves obtained using Tenax® extractions[13, 32, 40] can generally be modelled through an initial rapid desorption stage followed by periods with slow and very slow desorption rates with the rapidly desorbing stage expected to be complete after 30 hours[40]. This means the desorption rates we report may be a mixture of rapid and slow desorption rates. At the same time, Jonker et al. (2005)[32] found that the rapidly-desorbing fraction of PAHs in traffic or oil soot were extremely low. This is supported by the high refractory carbon content of the tunnel wash SPM (Table SI-2). Barnier et al. (2014)[39] also found small rapidly-desorbing fractions for PAHs in industrial soils. In addition, the size of the slowly desorbing fraction relative to the rapidly desorbing fraction tends to increase with increasing compound's hydrophobicity[13]. This implies that the effect of the mixture of desorption rates will tend to have less effect on the more hydrophobic PAHs. Poot et al. (2014)[6] demonstrated that the size of the very slowly-desorbing PAH fraction in European riverbed sediments increases with increasing amount of residual carbon as measured by Rock-Eval. The proportion of Rock-Eval-measured RC in TUN1 was in the range of values by Poot et al. (2014)[6], indicating that much of the PAHs are likely present in the slowly to very slowly-desorbing pool of contaminants.

Adding the detergent at a 6 % concentration level did not appear to result in increased desorption rates for the least hydrophobic PAHs (see Table SI-8). For more hydrophobic PAHs (from benz[a]anthracene to benzo[ghi]perylene), desorption rates in the presence of detergent are consistently higher than those obtained with water only. Bueno-Montes et al. (2011)[41] also found that adding the surfactant Brij 35 to already-bioremediated soil suspensions was able to increase the fraction of desorbing PAHs.

Implications

Different procedures exist for the measurement of contaminant availability and accessibility in soils and sediments. These include the estimation of freely dissolved concentrations, of contaminant desorption rates, or the estimation of an accessible fraction/concentration[9, 12, 18, 40]. It becomes apparent from our data that the optimal extraction time for the estimation of an accessible concentration is somewhat operational. It is likely to vary with sediment characteristics and the way the extraction is conducted. In our case, a four to six-week long extraction of tunnel wash water SPM appears to result in the extraction of a proportion of the more hydrophobic PAHs in the slowly-desorbing fraction that cannot be considered directly available for partitioning. The rapidly-desorbing concentration for these substances is likely to be very low and this is supported by the high % RC measured by Rock-Eval[6].

We evaluated the accessibility of PAHs in a range of urban particulate matter that may ultimately find their way into the aquatic environment. Despite the varied sources and methods for obtaining these PM samples, similar trends in accessible concentrations of PAHs could be observed, and this information can be helpful to those in charge of urban water management. A large proportion of less hydrophobic PAHs is likely capable of desorption when such PM is released into urban aquatic environments. For the more hydrophobic compounds, only a very small proportion will be available for partitioning into the dissolved phase. According to our k_d estimates, months, if not years will be needed for desorption of 99 % of sorbed higher MW PAHs. The use of detergent during tunnel washing may affect the accessibility of the more hydrophobic particle-bound PAHs particularly when wash waters are transferred to retention ponds where the detergent-containing waters are kept for periods of weeks before discharge into the environment.

One interesting question that we may be able to answer is whether particle emission into rivers through stormwater discharge or snowmelt has the potential to increase freely dissolved concentrations in urban rivers. We have undertaken some rudimentary modelling to evaluate to what extent PAH accessibility measured in PM in the present study can affect freely dissolved concentrations when this PM is emitted to rivers (see supporting information). Modelling based on accessible concentrations shows that PM release resulting in a SPM content in the Alna River of 45–480 mg L^{-1} (actual range measured in 2003, Table SI-9) has the potential to increase freely dissolved concentrations by a factor of 10–1000. While this assumes that the accessible concentration measured here can desorb near instantaneously, it may not be the case since most of the desorbing hydrophobic PAHs are likely in the slowly or very slowly desorbing fraction[6]. Similar modelling based instead on desorption rates measured here (for tunnel wash PM) and a PM residence time of 10 hours in the river demonstrates that lower fluctuations in freely dissolved concentrations of the more hydrophobic PAHs may be expected upon release of this PM into the river Alna. For a relatively short urban river such as the Alna (16 km long), the release of urban PM into the river may not be a crucial driver of the freely dissolved concentration of PAHs. For such a transfer of PAHs to be possible, a higher activity of PAHs on the particulate matter than in water is needed to ensure PAH desorption can occur. In our experiment, we assume the driving force for desorption was maximal while under environmental conditions it will not be. More accurate in situ measurements and modelling is required to evaluate this.

However, this work has only considered several PAHs. Many more substances including other polycyclic aromatic substances (e.g. OPAHs) are present in urban PM are likely to find their way into water[42, 43]. Preliminary analyses of OPAHs in PM material from this study show seven different OPAHs (Table SI-10), with at least 5 OPAHs present in each sample. Anthraquinone was typically seen at or near the highest concentrations (41–191 ng g^{-1} dw), which is consistent with other OPAH data in river water[44] and urban stream sediments[45]. Further work should therefore aim to evaluate the release of these chemicals in urban aquatic environments. Since the organic carbon in most of the PM samples evaluated here consisted of a substantial amount of refractory carbon as measured with Rock-Eval, the emission of this PM into rivers will provide an additional sorption phase with strong sorption capacity, particularly for planar substances[3]. This may ultimately act to reduce freely dissolved concentrations of contaminants in waters to which this PM is emitted.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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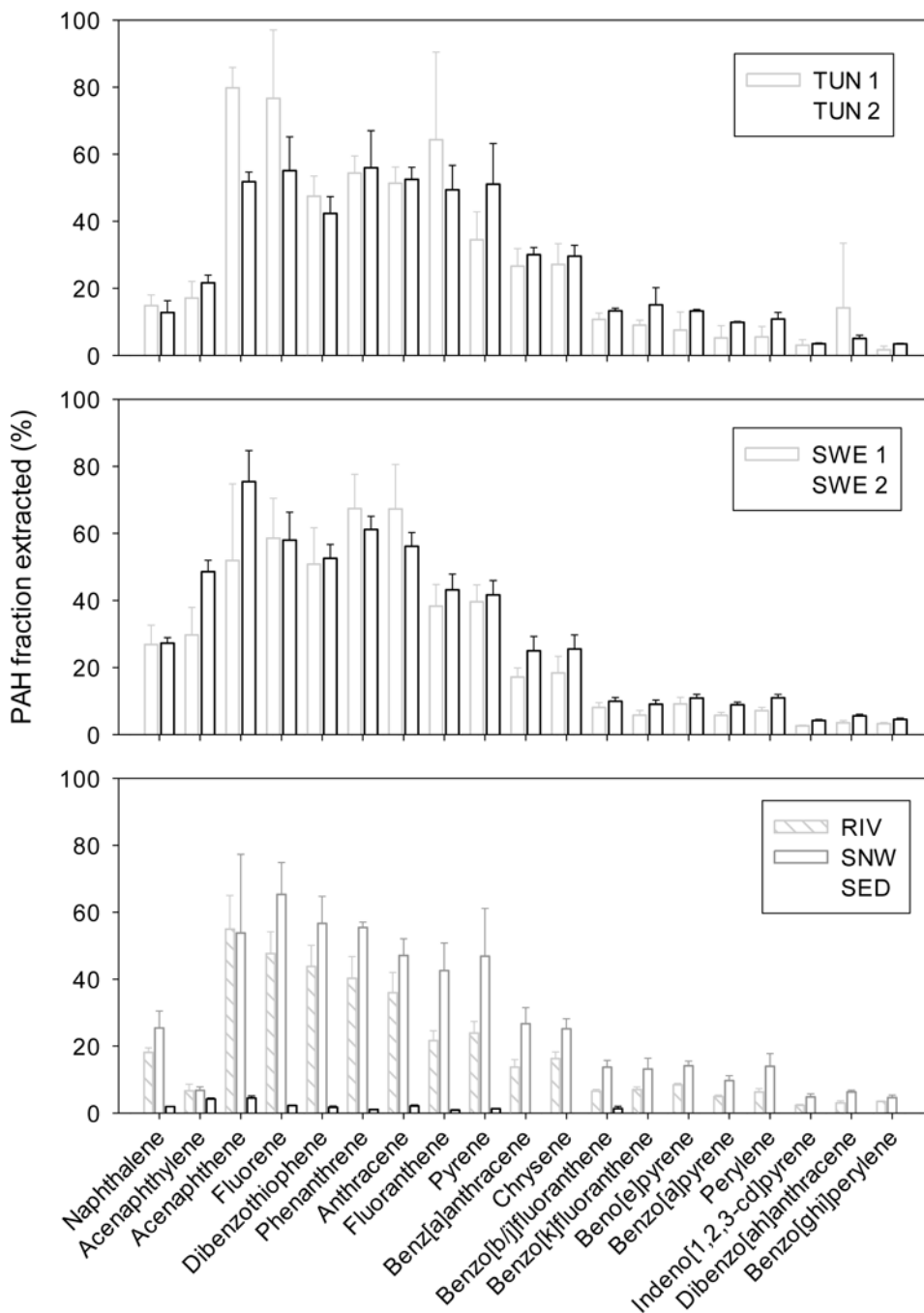
Figure 1.
Fraction of PAHs extracted with two consecutive SR extractions from seven PM samples from various road-impacted aquatic environments (including for TUN1). Note that for Sample SED (Oslofjord sediment), masses absorbed into silicone for PAHs with $\log K_{ow} > 5.5$ that were below LOQ are not shown. For fluoranthene, only data from duplicate extractions are used.
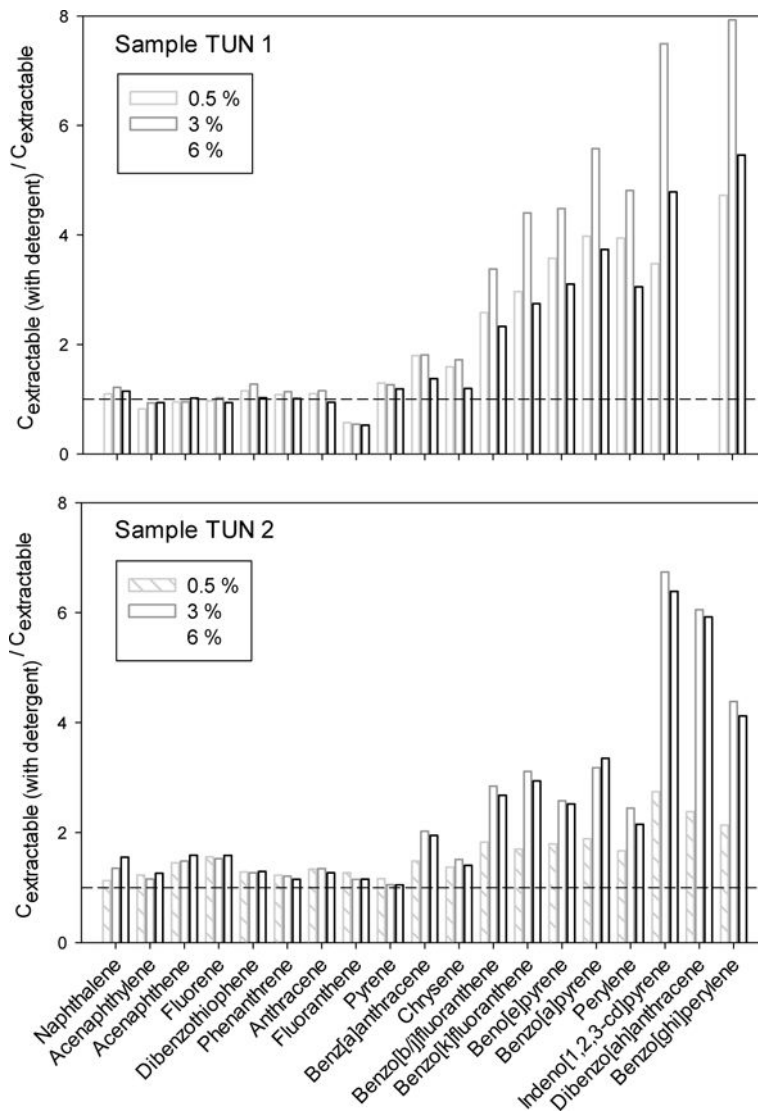
Figure 2.
Accessible PAH concentration estimated using SR in the presence of 0.5, 3 and 6 % (v/v) of detergent relative to extractions without detergent
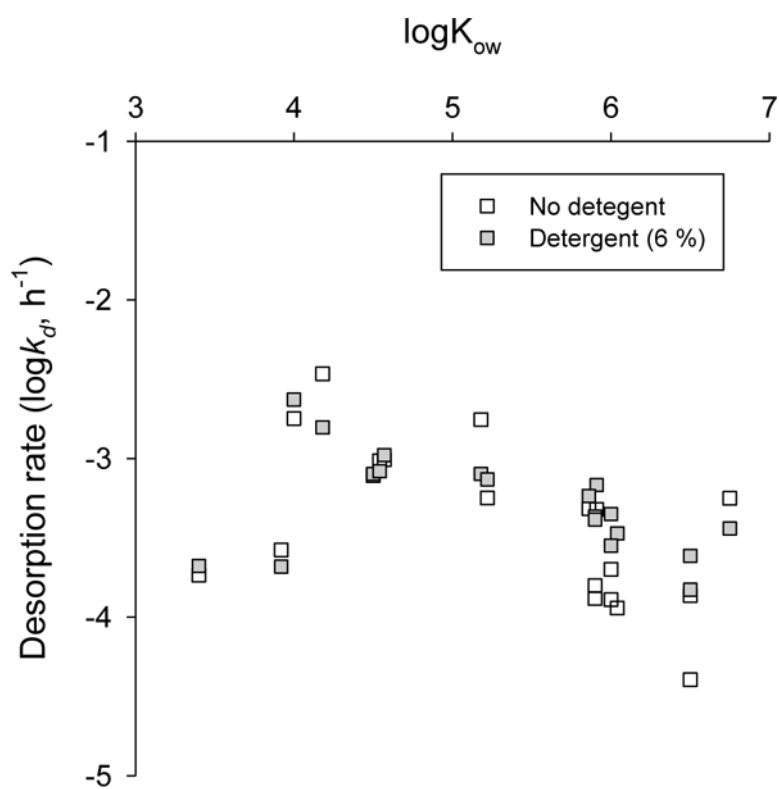
Figure 3.
Logarithm of PAH desorption rates for tunnel wash PM, TUN1 (h^{-1}) in the presence and absence of detergent

Table 1

Description of the seven particulate matter samples obtained from in and around Oslo (Norway)

Sample ID	TUN1	TUN2	SWE1	SWE2	SPM	SNOW	SED
Sample type	SPM from tunnel wash waters		PM from mobile road sweepers		River SPM	SPM from effluent	Bottom sediment
Location	Nordby tunnel	Granfoss tunnel	Nordby tunnel	Granfoss tunnel	Alna River	Snow-melting plant	Oslo fjord
Sampling procedure	CFC[a]	CFC[a]	Grab	Grab	Sediment trap	CFC[a]	Grab
TOC[b] (%)	9.4	8.4	1.3	1.0	4.7	8.6	0.20[d]
RC[c] (%)	3.8	3.1	0.78	0.37	3.0	4.0	0.19[d]
ΣPAHs[e] (μg g^{-1} dw)	6.7	5.6	0.81	0.67	26	6.0	2.3

[a] CFC: continuous- flow centrifugation;

[b] total organic carbon content measured with Rock-Eval;

[c] Refractory carbon content measured with Rock-Eval;

[d] unreliable results due to low TOC value of the sediment;

[e] Sum of 16 US EPA PAHs