



# Roads with underlying tar asphalt - spreading, bioavailability and toxicity of their polycyclic aromatic hydrocarbons<sup>☆</sup>

Jurate Kumpiene<sup>a,\*</sup>, Martin Oscar Larsson<sup>a</sup>, Ivan Carabante<sup>a</sup>, Hans Peter H. Arp<sup>b,c</sup>

<sup>a</sup> Waste Science and Technology, Luleå University of Technology, Luleå, Sweden

<sup>b</sup> Geotechnics and Environment Norwegian Geotechnical Institute, Oslo, Norway

<sup>c</sup> Department of Chemistry, Norwegian University of Science and Technology (NTNU), Trondheim, Norway

## ARTICLE INFO

### Keywords:

Passive samplers  
Toxicity units  
Risk assessment  
Contaminated soil

## ABSTRACT

Some of the older Swedish roads contain road tar underneath a surface layer of bituminous asphalt. This road tar, also known as tar asphalt, contains large amounts of polycyclic aromatic hydrocarbons (PAHs). There is concern about PAHs spreading from the bottom layers of these older roads to the surrounding environment, and that because of this spreading road tar asphalt should not be recycled but rather placed in landfills. However, a risk assessment of PAH spreading below roads has not yet been conducted. The first aim of this study was to assess this potential spreading of PAHs from underlying tar asphalt to the sand beneath, the soil next to the roads, as well as nearby groundwater. The second aim was to measure the bioavailability and estimate the toxicity of PAHs in all relevant media using polyoxymethylene (POM) passive samplers. Four road sections and nearby groundwater in northern Sweden were investigated, including a control road without tar asphalt. PAHs were detected in all analysed solid media at varying concentrations: in asphalt from 2.3 to 4800 mg kg<sup>-1</sup>, in underlying sand from <1.5 to 460 mg kg<sup>-1</sup> and in slope soil from <1.5 to 36 mg kg<sup>-1</sup>. However, the spread of PAHs from the asphalt to roadside soil and groundwater was very limited. Groundwater at most of the road sections contained very low or non-detectable levels of PAHs (<0.08–0.53 µg L<sup>-1</sup>, excluding one site where fuel contamination is hypothesized). The PAHs generally showed low bioavailability. Only asphalt with PAH content >1200 mg kg<sup>-1</sup> exhibited bioavailable concentrations that exceeded threshold concentrations for serious risk. The most PAH contaminated sand and soil samples exhibited low toxicity when considering bioavailability, only in some cases exceeding chronic toxicity threshold concentrations. These results were compared with the Swedish EPA's guideline values for PAH in contaminated soil, which is shown to overpredict toxicity for these sites. Further research on the leaching and transportation processes of PAHs from subsurface tar asphalt is recommended for developing risk analysis approaches.

## 1. Introduction

Most of the Swedish roads have asphalt pavement, and some of the older ones contain tar asphalt, or so-called road tar. Road tar, used as a binder, is produced by heating coal and contains large quantities of polycyclic aromatic hydrocarbons (PAH), which are known carcinogens. Newly manufactured road tar can contain between 15 and 30 weight-% PAHs (Jacobsson and Granvik, 2003). Tar asphalt, which is a mixture of road tar and natural raw materials, may contain over 5000 mg kg<sup>-1</sup> of PAH16, while today's bituminous asphalt coatings usually contain 2–10 mg kg<sup>-1</sup> PAH16 (Jacobsson and Granvik, 2003). According to the

Swedish regulations (Waste Ordinance, SFS, 2011:927), asphalt containing a concentration ≥0.1 wt% of PAH (i.e. ≥1000 mg kg<sup>-1</sup> PAH16) is classified as hazardous waste. This limit might hinder the local recycling of asphalt in older roads, because of increasing concern regarding environmental and human health risks from PAH emissions. In those cases when tar asphalt is removed from use, it is disposed of in landfills. Such management would run counter to the pursuit of a more circular economy by reusing the materials already present in society. The costs of not-recycling tar asphalt are both economic and environmental, as demand for new resources, and their transport, would be substantial. But more importantly, despite the concern of risk from PAH pollution, the

<sup>☆</sup> This paper has been recommended for acceptance by SU SHIUNG LAM.

\* Corresponding author.

E-mail address: [jurate.kumpiene@ltu.se](mailto:jurate.kumpiene@ltu.se) (J. Kumpiene).

<https://doi.org/10.1016/j.envpol.2021.117828>

Received 16 April 2021; Received in revised form 19 July 2021; Accepted 20 July 2021

Available online 22 July 2021

0269-7491/© 2021 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

extent of negative impacts of subsurface tar asphalt on the environment has not yet been clarified. Therefore, it is uncertain if ceasing the recycling of tar asphalt is the best choice. To address this problem, an assessment of the actual risks of tar asphalt is necessary in order to provide scientific data for decision makers to facilitate informed decisions.

A risk from tar asphalt may occur if a hazardous contaminant from the source (e.g. the road) is released, transported to a receptor (human, environment) and causes negative effects to any of the exposed receptors (Swedish EPA, 2009). For such a risk from PAHs spreading from road tar asphalt to occur, they must be bioavailable to exposed organisms in order to cause adverse effects. This means that an estimate of the bioavailable fractions of PAH in asphalt, underlying sand and road banks, and not the total PAH concentration, is essential to assess the real impact of tar asphalt on the environment (Cachada et al., 2014). PAHs that are being strongly sorbed or trapped within the road tar particles can exhibit low bioavailability (Readman et al., 1987; Arp et al., 2009), implying that PAHs would not readily desorb in porewater or exposed organisms. But studies on the bioavailability of PAHs released from roads containing tar asphalt below a bituminous asphalt layer, and subsequent effects on the environment, are lacking.

Coal tar-based sealants containing high levels of PAHs have been extensively applied in US and Canada leading to PAH accumulation in streams and lake sediments through particle runoff (Mahler et al., 2005; Scoggins et al., 2007; Mahler et al., 2012). Previous studies on the environmental impact of tar asphalt in Norway and Sweden show that PAH spreading to the surrounding soil is much more limited, but also occurs mainly due to particle transport rather than through leaching of dissolved PAHs from roads (Norwegian Geotechnical Institute, 1999; Swedish Transport Administration, 2014; Orbicon, 2018).

Traditional risk assessment of PAHs in soil and sediment are not suitable for areas affected by residues from industries, soot, coal and asphalt, because they are based on total PAH concentrations (Readman et al., 1987); whereas more accurate risk assessments can be based on freely-dissolved PAH in porewater expressed as toxicity units, to better account for bioavailability (Arp et al., 2011). It is, however, not so easy to extract porewater from different materials, especially from asphalt. Leaching tests with water and subsequent leachate toxicity tests are not properly adapted to assess the bioavailability of hydrophobic organic compounds, especially of PAHs with a medium and large molecular weight that predominates in asphalt (Brown and Peake, 2006). In addition, ecotoxicity tests performed on leachate are not PAH-specific and may produce toxic effects due to dissolved substances other than PAHs (Enell et al., 2012).

A method has recently been developed to indirectly measure freely-dissolved PAHs in porewater. This method uses passive polyoxymethylene (POM) as an equilibrium passive sampler (EPS) to measure the equilibrium concentration of dissolved PAH in porewater through a batch shake test. This method has been found to better correlate with the uptake of PAHs in the liposomes of living soil organisms than through the use of other, non-EPS methods (Arp et al., 2014). The POM method has been validated on earthworms (*Enchytraeus crypticus*), and benthic amphipods (*Hyalella azteca* and *Leptocheirus plumulosus*) with good results (Arp et al., 2011, 2014).

The aims of this study were i) to assess the potential spread of PAH from underlying tar asphalt to the sand beneath, the soil next to the roads, as well as nearby groundwater; and ii) to measure the bioavailability and estimate the toxicity of PAH in all relevant media using polyoxymethylene (POM) passive samplers. This was assessed in three rebuilt roads in northern Sweden. A road section containing only bituminous asphalt cover was included as a control. The hypothesis of the study is that the leaching of bioavailable PAHs from road tar asphalt under a bituminous asphalt layer is limited, exceeding risk thresholds only within or very close to the road tar asphalt itself.

## 2. Material and methods

### 2.1. Road sections

Four road sections in northern Sweden were selected for this study: 1) Muorjevaara road (E10), 2) Svappavaara road (E10), 3) Kvikkjokk road (805) at Framnäs (Kvikkjokk-F) and 4) Kvikkjokk road (805) between Tjåmotis and Randijaur (Kvikkjokk-TR) (Fig. S1 of the Supplemental Material). Muorjevaara road contained only bituminous asphalt with expected low concentrations of PAHs and was included as a control, tar-asphalt free road.

### 2.2. Sampling

Sampling of asphalt was carried out in September 2018. Installation of groundwater wells and sampling of groundwater and soil was carried out in October 2018. Additional groundwater sampling was carried out in September 2019.

#### 2.2.1. Asphalt and underlying sand

An asphalt drill was used for asphalt sampling. Five cylindrical asphalt samples per road section with diameter 100 mm were drilled through the entire coating depth. The distance between the test points was about 30 m.

Sand under the asphalt layer was sampled by hand (about 500–700 g) from about 0 to 5 cm directly under the asphalt and put in diffusion-proof plastic bags. A hammer was used to release hard-packed particles. Visible asphalt pieces and crumbs were removed manually.

### 2.3. Soil in roadside slopes

Soil sampling in road slopes was carried out in all four road sections. Six samples from each section were taken on both sides of the road (A1-3, and B1-3, Fig. 1, respectively). Samples A1 and B1 were taken 0–1 m from the side of the road (outer edge of asphalt paving) on inner slopes, and Samples A2 and B2 were taken at 1–2 m from the side of the road. Each sample consisted of five subsamples taken according to the envelope principle, i.e. four subsamples were taken in the corners of 1 m<sup>2</sup> plot and the fifth was taken in the middle (Fig. 1). Samples A3 and B3 were taken 2 m from the centre of the ditch lowest point and consisted of 3 subsamples taken lengthwise parallel to the road (Fig. 1). All samples of 200–500 g were taken with a shovel from 0 to 5 cm depth and put in diffusion-proof plastic bags.

#### 2.3.1. Groundwater

Six groundwater wells were installed using a drilling rig at a depth of approximately 3.5 m upstream and downstream the sampling sections of the Muorjevaara and Svappavaara roads, and downstream along both sampling sections of the Kvikkjokk road. Two groundwater wells upstream Kvikkjokk road were already installed during previous projects. The differentiation between the upstream and downstream points was made based on the measured groundwater table depth above the mean sea level. The distance from the road was about 4–8 m. Groundwater was replaced once from the wells before sampling. One litre of each sample was collected in glass vessels with a bailer, stored cold and dark during

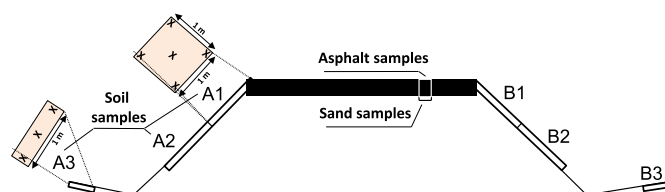


Fig. 1. Points of sampling of asphalt, underlying sand and soil in roadside slopes.

fieldwork and transported as quickly as possible to the laboratory.

#### 2.4. Chemicals and analyses

All sampled materials were sent to the accredited laboratory ALS Scandinavia for PAH analysis. Asphalt samples were crushed and cryomilled. Approximately 10 g of a soil or asphalt sample were extracted with hexane/internal-standard and acetone in glass bottles on a shaking table. Water was added prior to centrifugation and separation of the hexane phase, which was then up-concentrated through solvent reduction and then analysed using gas chromatography-mass spectrometry (GC-MS) by ALS Scandinavia. The PAHs analysed included the low molecular weight PAHs (PAH-L: Naphthalene, Acenaphthylene, Acenaphthene), middle molecular weight PAHs (PAH-M: Fluorene, Phenanthrene, Anthracene, Pyrene, Fluoranthene) and high molecular weight PAHs (PAH-H: Benz [a]anthracene, Chrysene, Benzo [b]fluoranthene, Benzo [k]fluoranthene, Benzo [a]pyrene, Indeno [123cd]pyrene, Dibenz [ah]anthracene, Benzo [ghi]perylene).

Total, organic and inorganic carbon in groundwater samples were analysed using TOC analyzer (TOC-V CSH Shimadzu). Organic matter in soil was measured as loss on ignition at 550 °C (SIS, 1981).

The POM method (Arp et al., 2014) was applied to all solid samples to estimate bioavailable fractions of PAH and to calculate toxicity units in asphalt and soil samples. In short, 76 µm thick POM membranes from CS Hyde (Lake Villa, IL, USA) were purified in acetone:hexane and methanol to remove any impurities. 20 g of crushed solids were placed in 100 ml glass bottles and filled with 87.5 ml of 0.01 M CaCl<sub>2</sub> + 0.015 M NaN<sub>3</sub> (biocidal) solution. POM membranes (4 × 5 cm) were placed in the bottles. The bottles were sealed, put on a shaking table and shaken for 28 days in a dark room. After that, POM were taken out with tweezers, rinsed with ultra-pure water, dried and sent to the accredited laboratory Synlab, Sweden, for extraction and analysis. The extraction of PAH from POM samples was performed using 2 × 20 ml of n-hexane:acetone (1:1) as described in Arp et al. (2014). The concentration of PAHs in the POM, C<sub>POM</sub> (µg kg<sup>-1</sup>) is then used to derive bioavailable, freely-dissolved porewater concentrations, C<sub>pw</sub> (µg L<sup>-1</sup>) using the equilibrium partitioning relationship:

$$C_{PAH,pw} = C_{POM}/K_{POM} \quad (1)$$

Where K<sub>POM</sub> (L kg<sup>-1</sup>) is the PAH specific equilibrium partitioning constant for POM. The K<sub>POM</sub> values were taken from Hawthorne et al. (2011) and are provided in the Supplemental Material (Table S1).

#### 2.5. Toxicity estimation

Results from POM analyses were used to calculate relative bioavailable toxicity units (TU<sub>PAH-16</sub>, Eq. (1)) for the sum of the 16 PAHs:

$$TU_{PAH-16} = \sum_{i=1}^{16} C_{PAH-i,pw} / \text{Screening Value}_{PAH-i} \quad (2)$$

Here, C<sub>PAH-i</sub> is the measured, bioavailable concentration of individual PAHs in the porewater (Eq. (1)) and Screening value<sub>PAH-i</sub> is the corresponding screening values associated with a toxic benchmark concentrations. The calculated logarithmic TU values > 0 indicate a pre-selected risk situation based on the selected toxic benchmark. The following Dutch RIVM benchmarks for (pore) water were used as screening values in the calculations (Verbruggen, 2012):

- (i) MPCeco (maximum permissible concentration, ecosystem), the value indicates the maximum permissible concentration where no risk is considered to occur for the soil ecosystem (similar to the Predicted No Effect Concentration (PNEC) values or values of hazardous concentration to 5 % of tested species). These are the most conservative values. The Swedish EPA's guideline values for

sensitive land use are less strict and were derived to protect 75 % of species, i.e. impact on 25 % of species is accepted;

- (ii) SRC (serious risk concentration), the value is calculated from toxicity data such as the geometric mean of the chronic toxicity EC50 values for terrestrial species, or hazardous concentrations to 50% of tested species. These benchmarks can be compared with the Swedish EPA's guidelines for less sensitive land use which have the same level of protection of soil organisms (i.e. impact on 50 % of species is accepted). More information is given in Supplementary Material (Table S1).

### 3. Results and discussion

#### 3.1. PAH concentrations in asphalt, soil and groundwater

##### 3.1.1. PAHs in asphalt and underlying sand

PAH concentrations in the upper (bituminous), lower (tar), or whole (bituminous or mixed) asphalt layers, and underlying sand are presented in Table 1 and depicted in Fig. 2A, with the thickness and profiles of the asphalt layers of the investigated road sections given in Fig. S2. From Fig. 2A it is evident that the roads with road tar asphalt had substantially higher PAH concentrations than the control road (Muorjevaara), which had just one layer of bituminous asphalt. The three other road sections contained two visible asphalt layers: the lower layer of an old asphalt with a certain amount of road tar (as confirmed by the PAH content), and an upper part of the new, bitumen asphalt pavement with only traces of PAH (Fig. 2A, Table 1 and S2). For the Kvikkjokk road, this division was evident in six out of ten sampling points, but the lower part in two of them (Samples 3.5 and 4.1) was very thin (1.9 cm, and 1 cm respectively), which made it difficult to separate the two layers for analysis. The highest PAH levels (1200–4800 mg kg<sup>-1</sup>) were measured in the old asphalt layer at a depth of 3.1–3.8 cm in both sections of Kvikkjokk road (Table 1, Fig. 2A). In previous studies of this road, PAH concentrations reaching 6000 mg kg<sup>-1</sup> were detected (Orbicon, 2018). Similar products used in other countries have even higher reported concentrations, with PAH28 reaching 10 000 mg kg<sup>-1</sup> in the mixture of a coal tar based pavement binder and aggregates in New Zealand (Ahrens and Depree, 2010), and up to 60 000–66 000 mg kg<sup>-1</sup> PAH16 in coal tar-based sealcoats in Canada (Bowman et al., 2019) and USA (Scoggins et al., 2009). PAH concentrations for the sand and gravel underneath the asphalt layer are presented in Tables 1 and S3, and Fig. 2A. The PAH concentrations here were variable, but generally were substantially larger in roads with tar asphalt than the control road, which had non-detectable levels of PAHs. At the Svappavaara road segment and in two of the samples from Kvikkjokk road (Samples 3.5 and 4.3) this layer contained equal or even higher concentrations of PAH than the above asphalt. The levels in the sand under the asphalt for the other samples from Kvikkjokk road ranged from below the detection limit to 160 mg kg<sup>-1</sup> (Table 1). To account for the high PAH concentrations under the Svappavaara road, which was rebuilt in 2015, a part of the tar-containing asphalt was crushed and used as granulate in the unbound base layer making the underlying sand a mixture of the tar-containing asphalt and natural aggregates. The new asphalt layer of 20–24 cm thickness was laid on either the new base layer or on the old asphalt (0.6–4 cm layer). In summary, the presence of PAHs in underlying sand can be explained largely through mechanical mixing of road tar asphalt during construction, road repair and local particle movement.

##### 3.1.2. PAHs in the soil of the roadside slopes

PAHs were detected in most of the sampling points of the roadside slopes taken at different distances from the roadside, including the soil along the control road (Muorjevaara) (Tables 1 and S4, Fig. 2A). Concentrations along the roads with tar asphalt ranged from <LOD to 36 mg kg<sup>-1</sup> (average 12 ± 14 mg kg<sup>-1</sup>) and on average slightly, but not significantly, larger than the control road, which ranged from <LOD to

**Table 1**

PAH16 in asphalt ( $\text{mg kg}^{-1}$ ), soil under asphalt ( $\text{mg kg}^{-1}$ ), soil in roadside slopes ( $\text{mg kg}^{-1}$ ) and groundwater ( $\mu\text{g L}^{-1}$ ) of the four studied road sections. Sampling points for solid samples are explained in Fig. 1.

Sampling point	Asphalt			Sand under asphalt	Sampling point	Soil	Sampling point	Groundwater	
	Upper	Lower	Whole					2018	2019
<b>Muorjevaara</b>									
1.1			3.2	–	A1	<1.5	upstream	0.53	<0.08
1.2			2.3	<1.5	A2	<1.5	downstream	0.051	<0.08
1.3			4.3	<1.5	A3	8			
1.4			2.9	<1.5	B1	1.8			
1.5			2.8	<1.5	B2	<1.5			
					B3	4.5			
<i>Average</i>			3.1	<					
<i>Std. Deviation</i>			0.7						
<b>Svappavaara</b>									
2.1	11	270		110	A1	16	upstream	3.9	3.2
2.2	3.9	200		140	A2	36	downstream	0.53	<0.08
2.3	3.4	120		150	A3	9			
2.4	5.4	260		460	B1	10			
2.5	2.3	270		270	B2	<1.5			
					B3	<1.5			
<i>Average</i>			5.2	224					
<i>Std. Deviation</i>			3.4	65					
<b>Kvikkjokk-F</b>									
3.1	4.6	1200		2.7	A1	<7.5	upstream	–	<0.12
3.2	25	2000		11	A2	2	downstream	0.025	0.013
3.3			33	<1.5	A3	6.6			
3.4			6.5	<1.5	B1	36			
3.5*			58	160	B2	35			
					B3	<1.5			
<i>Average</i>				33					
<i>Std. Deviation</i>				26					
<b>Kvikkjokk-TR</b>									
4.1*			2.4	<1.5	A1	<1.5	upstream	–	<0.12
4.2			4.4	2.7	A2	12	downstream	<0.23	<0.08
4.3			2.7	4.5	A3	2.8			
4.4	16	4800		4	B1	<1.5			
4.5	12	2200		5.2	B2	35			
					B3	8.2			
<i>Average</i>			3.2	4.1					
<i>Std. Deviation</i>			1.1	1.1					
<i>Hazardous waste**</i>				1000					
<i>Free use**</i>				<70					

\*Two-layer samples analysed as a whole (i.e. as one sample).

\*\*Limit values for PAH16 in asphalt when managing, recycling or re-using asphalt in traffic projects (City of Gothenburg, 2015).

8  $\text{mg kg}^{-1}$  (average  $2.8 \pm 3.0 \text{ mg kg}^{-1}$ ) (Fig. 2A).

No consistent trend could be observed between total PAH concentrations in soil and the distance of the sampling points from the roadside. For some road sections, such as by the Muorjevaara road, the highest PAH concentrations were found furthest from the roadside, while at the other road segments the highest concentrations were observed within 1–2 m from the roadside. However, all data points plotted in the same chart show that elevated levels of both PAH-M and PAH-H mainly occurred in the middle of the road slopes (1–2 m from the roadside) (Fig. 3). Since the top layer of the paving structures does not contain any road tar, it is likely that at least part of the PAH originates from traffic and ends up further down the slopes due to dusting, snow removal and surface runoff. Trench cleaning to remove vegetation on inner slopes may also affect PAH distribution in the slopes. Since Kvikkjokk road has previously been coated with tar asphalt containing high levels of PAH (up to 4800  $\text{kg kg}^{-1}$ , Table 1), some particles may have spread from the road during its earlier use. Medium and high molecular weight PAH have a high affinity for organic matter (Arp et al., 2009), which can lead to PAH remaining in organic matter rich soil over long periods, which tend to be further down the slopes where the amount of organic matter is higher than directly at the roadside. Nevertheless, there was no correlation between the amount of organic matter in roadside soil and

concentration of PAH of any molecular size (correlation coefficients were from  $-0.16$  to  $-0.22$ ). Similar observations were made in studies of PAH spreading from streets in China (Wang et al., 2009; Jiang et al., 2014; Liu et al., 2019). The possible reason can be that interactions between asphalt particles and soil organic matter are very weak and that the PAHs remain strongly bound to asphalt particles rather than getting dissolved and re-sorbed to soil organic matter (Arp et al., 2009). In summary, there is no clear indication that road tar asphalt is the main source of PAHs in roadside soil, as PAHs were found in comparable concentrations in the control road, and PAH concentrations are highly dependent on other sources, as well as on physico-chemical processes in the roadside soil.

### 3.1.3. PAHs in groundwater

Groundwater concentrations are presented in Tables 1, S5 and S6. The levels of PAH in groundwater at Muorjevaara (control) and Kvikkjokk road segments were very low or below the instrument detection limits both in 2018 and 2019. Significantly higher levels of PAH were measured in groundwater taken at Svappavaara road, both upstream and downstream (Table 1). According to an earlier impact assessment of groundwater by PAH4 (sum of benzo(b)fluoranthene, benzo(k)fluoranthene, benzo (ghi)perylene and indene (1,2,3-cd)pyrene), developed



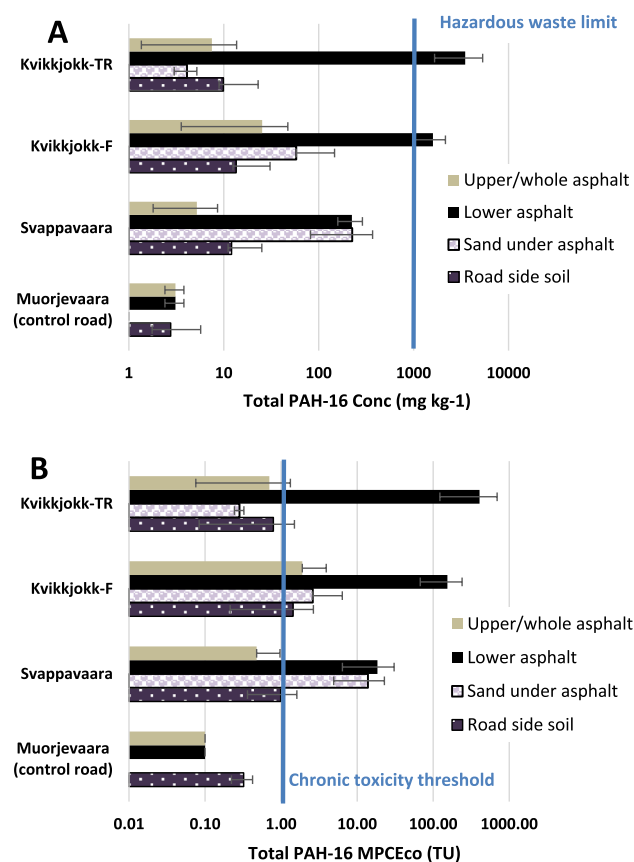


Fig. 2. Comparison of the investigated road sections presenting A) total PAH16 concentrations ( $\text{mg kg}^{-1}$ ) and b) toxicity units (TU) for the sum of bioavailable PAH16 based on the MPCeco threshold by RIVM for chronic ecological toxicity for the upper/whole asphalt, lower (road tar rich) asphalt, sand below asphalt and roadside soils; c) locations of the sampling points.

by the Geological Survey of Sweden (SGU, 2013), groundwater at the Svappavaara road was strongly impacted (based on the SGU Class 4 guideline value  $0.02\text{--}0.1 \mu\text{g L}^{-1}$ ); however, none of the samples contained PAH levels that exceeded recommended guidelines and limits for PAH4 in drinking water of  $0.1 \mu\text{g L}^{-1}$  (Swedish Food Agency, 2001; Swedish Petroleum Institute, 2010) (Table S5). A thin layer of tar asphalt remains in the bottom part of the examined section of Svappavaara road. But it is difficult to determine whether the measured PAH levels in groundwater downstream of the road are an effect of the road itself or other causes, such as emissions from vehicles. Even higher concentrations were measured in the asphalt of the Kvikkjokk road (Table 1), but this did not affect the groundwater in a corresponding way.

The composition of PAH in groundwater upstream of the Svappavaara road differed from that of the downstream sample. The upstream sample contained a significantly higher proportion of low molecular weight PAH than the downstream sample (PAH-L/PAH-H ratio ranged from 12.8 to 49 upstream and 0.4 downstream, Tables S5 and S6). Electrical conductivity was much higher in the upstream samples as well, with  $1.6 \text{ mS cm}^{-1}$  upstream vs  $0.2 \text{ mS cm}^{-1}$  downstream (Table S7). Based on these PAH-ratios, the PAHs found in groundwater upstream of the Svappavaara road most likely had a different origin than the one downstream. Another indication is that fluoranthene accounted for 1–3% of PAH16 upstream and 14 % downstream. The proportion of fluoranthene in the studied asphalt was 18–23 % of PAH16, while the fraction of fluoranthene in vehicle fuel is usually low (Marr et al., 1999; Mi et al., 2000). Naphthalene made up 79 % of PAH16 in 2018 and 90 % in 2019 upstream, while the downstream sample had about 30 times

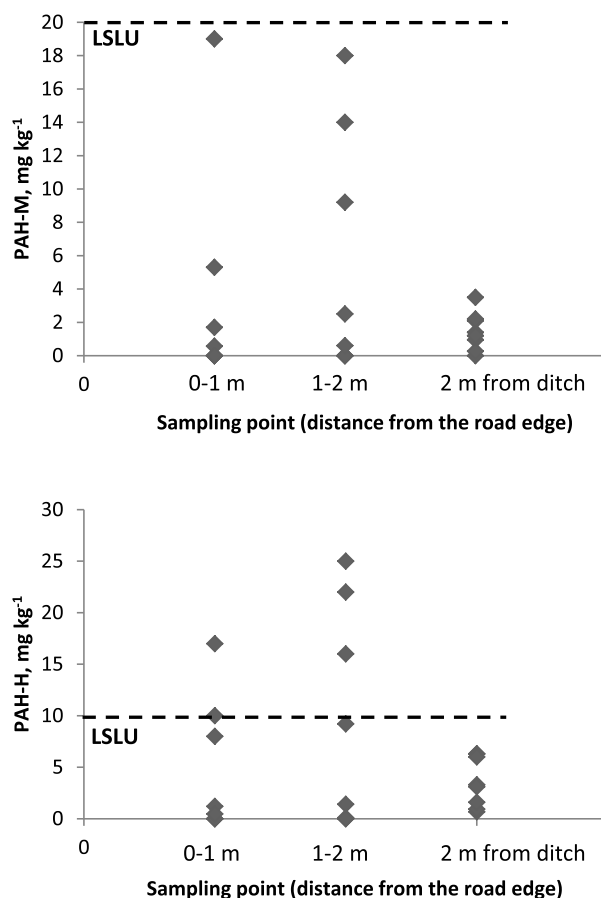


Fig. 3. Relationship between the location of the sampling points (distance from the road edge) and the content of (a) medium molecular weight PAH (PAH-M) and (b) high molecular weight PAH (PAH-H) in roadside soil. Dashed lines indicate the Swedish EPA’s guideline values for PAH in soil with less sensitive land use (LSLU) (Swedish EPA, 2009).

lower concentration of this compound. In general, naphthalene and phenanthrene are the most abundant PAH contaminants found in impacted waters, and both of them are found in high levels in fresh fuels (Colombo et al., 2005a, b; Iturbe et al., 2005). PAH16 in vehicle fuel, especially in petrol, is dominated by naphthalene (97 % of PAH16) (Marr et al., 1999; Mi et al., 2000), therefore the presence of elevated levels of naphthalene in upstream Svappavaara groundwater may point to leaks of petroleum products e.g. from tanks or pipelines in the area.

Naphthalene is relatively soluble (lowest  $K_{oc}$  value among PAH16) and may occur in asphalt leachate in significant quantities compared to the other PAH16 compounds (Brandt and De Groot, 2001). Nevertheless, the total concentration of naphthalene in asphalt was very low. The proportion of naphthalene in those asphalt samples where it was detected ranged from 0.1 to 0.8 % of PAH16. The highest naphthalene concentration in asphalt was measured in sample Kvikkjokk-TR  $4.4 \text{ (} 210 \text{ mg kg}^{-1} \text{ of } 4800 \text{ mg kg}^{-1} \text{ of PAH16)}$ , which was by 3–4 orders of magnitude higher than in any other asphalt sample. Nevertheless, only very low ( $25 \text{ ng L}^{-1}$ ; 2019) and undetectable ( $<13 \text{ ng L}^{-1}$ ; 2019) concentrations of naphthalene in groundwater next to Kvikkjokk-F road strengthen the assumption that leaching of PAH from asphalt was very limited. Therefore, there is no immediate indication that asphalt PAHs are leaching into downstream groundwater; however, this would require vadose zone transport investigations to comprehensively assess this spread.

### 3.2. Diagnostic PAH ratios

There are other sources of PAH in roadside soils other than asphalt, such as vehicle emissions and fuel spills, which can be a substantial source of PAH along roads (e.g. Garcia-Flores et al., 2016; Harrison et al., 1996; Johnsen et al., 2006), therefore assigning all PAH to asphalt can significantly overestimate risks from tar asphalt.

PAH are emitted as a mixture of different congeners and ratios of the molecular concentrations of these congeners can be characteristic of a particular source of emission (Zhang et al., 2008). Diagnostic PAH ratios can be an important tool for identifying sources of contamination, though utilizing such ratios should be done with caution. Relationships between PAH compounds in different media differ from those found in initial sources and correction factors may need to be applied (Riccardi et al., 2008). Lighter PAHs are more water soluble (can be enriched in precipitation water) and the PAH-L/PAH-H ratio is much higher in water than in solid samples (particles) (Li et al., 2010). Therefore, ratios can be affected overtime due to weathering and leaching, generally leading to smaller PAH-L/PAH-H ratios over time (Arp et al., 2011).

Most diagnostic ratios involve pairs of PAHs with the same molar mass and similar physico-chemical properties, so they should undergo similar processes in the environment (Tobiszewski and Namiesnik, 2012). For example, the ratio between benzo(a)pyrene and benzo (ghi) perylene can be used to distinguish traffic-related emissions from non-traffic-related emissions (Katsoyiannis et al., 2007). The benzo(a) anthracene (BaA)/(benzo(a)anthracene + cryene (Cry)) ratio has been used to distinguish between PAH emissions from combustion, car emissions and petrogenic PAH emissions (Yunker et al., 2002; Akyüz and Çabuk, 2010).

In this study, ratios of BaA/(BaA + Cry) and fluoranthene (Flu)/(Flu + pyrene (Pyr)) were investigated only for samples from Svappavaara road as these PAH compounds were detected in all investigated media above instrument detection limits. The Flu/(Flu + Pyr) ratio is one of the most stable and changes significantly less over time. The BaA/(BaA + Cry) ratio varies more because BaA can be broken down faster due to photolysis reactions, which would move this ratio towards lower values over time (Tobiszewski and Namiesnik, 2012).

Fig. 4 shows a clear separation of asphalt samples on the Flu/(Flu + Pyr) axis where bitumen asphalt has higher values than the underlying tar asphalt. Underlying sand and slope soil have similar ratios of these compounds to those of the tar asphalt, but the separation is quite evident on the BaA/(BaA + Cry) axis. Slope soil has the greatest deviation from all asphalt samples and underlying sand (Fig. 4). It seems that PAH in the underlying sand originates from the above asphalt layer. However, the exact PAH source in the roadside slope soil is difficult to identify. Mixed sources are likely to contribute to PAH levels in these soils (asphalt dust,

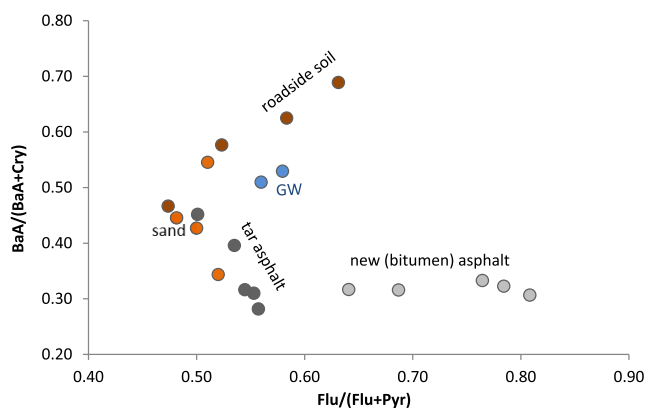


Fig. 4. Diagnostic ratios of PAH compounds at the investigated Svappavaara road section. BaA - benzo(a)anthracene, Cry - chrysene, Flu - fluoranthene, Pyr - Pyrene. GW - groundwater; sand - material layer below the asphalt.

exhaust, tire wear, as well as airborne particles and precipitation) and not just the tar asphalt. Contributions from airborne traffic particles and precipitation have been previously suggested to be quite substantial next to roads (Zhang et al., 2008). If PAH spreading from the road in particulate form was the only PAH source, the ratios between different PAH pairs would be more similar between asphalt and slope soil. Also, the BaA/(BaA + Cry) would likely be smaller due to photolysis, but this was not observed in this study, rather the opposite.

### 3.3. Bioavailability and toxicity of PAH in solid samples

The POM-measured  $C_{pw}$  and derived TU values for asphalt, underlying sand and roadside soil are presented in Tables S8-19. The log TU values were plotted in relation to PAH16 in all asphalt, soil and sand samples in Fig. 2B, along with the Swedish EPA's guideline values for PAH in contaminated soil and sand for comparison in Fig. 5. The results indicate that asphalt samples containing PAH16 below  $12 \text{ mg kg}^{-1}$  did not present a risk to the soil ecosystem, i.e. log TU were below 0 for these soils, according to the RIVM MPCeco model for bioavailable porewater concentrations. Asphalt concentrations between  $12$  and  $270 \text{ mg kg}^{-1}$  exceeded this level where risks can occur (i.e. MPCeco log TU > 0). Only four asphalt samples containing the highest levels of PAH from Kvikkjokk road (PAH16 >  $1200 \text{ mg kg}^{-1}$ , Table 1) indicated serious risk, by exceeding the SRC model threshold for bioavailable porewater concentrations (i.e. SRC log TU > 0).

According to the Swedish EPA's guideline values for PAH in contaminated soil, sand under asphalt in Svappavaara road and in one sample from Kvikkjokk-F road (point 3.5) exceeded the guideline values for PAH-H in contaminated soil with less sensitive land use ( $10 \text{ mg kg}^{-1}$ ), but not according to the RIVM MPCeco values based on the POM-bioavailability method. The same pattern was observed for four soil samples in roadside slopes (Svappavaara 1.3-A2; Kvikkjokk-F 3.3-B1 and B2; Kvikkjokk-TR 4.3-B2).

PAHs originating from pyrogenic solids can be considered as very strongly bound to soil particles (Arp et al., 2009). In this study, as with earlier studies of soil impacted with pyrogenic sources (Arp et al., 2014), there was lower bioavailability and toxicity than expected than based on total concentrations. In this context, lower risk from tar asphalt is expected when considering bioavailability, compared to what the generic

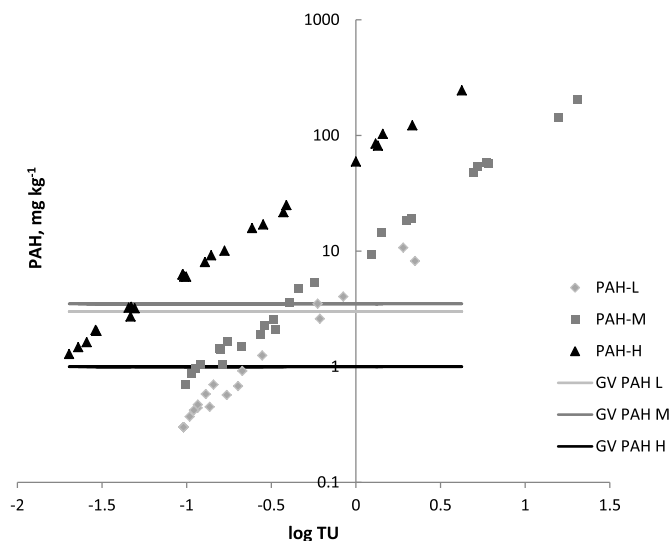


Fig. 5. Concentration of PAH in soil under asphalt and roadside soil ( $\text{mg kg}^{-1}$ ) in relation to log toxicity units (log TU) calculated according to RIVM MPCeco model. Values log TU > 0 indicate potential toxicity. The Swedish EPA generic guideline values (GV) for PAH in contaminated soil with sensitive land use are PAH L =  $3 \text{ mg kg}^{-1}$ , PAH M =  $3.5 \text{ mg kg}^{-1}$ , and for PAH H =  $1 \text{ mg kg}^{-1}$ , respectively.

Swedish risk assessment model based on total concentrations would indicate. This implies that soil samples that exceeded PAH concentration guideline values for soil with less sensitive land use could be assessed as acceptable by considering bioavailability.

Fifteen out of 24 soil samples in roadside slopes, including the control road containing only bituminous asphalt, exceeded the generic guideline values for PAH in soil with sensitive land use either for PAH-M or PAH-H, or both (Table S3). Five of these samples exceeded the guideline values for less sensitive land use. However, based on POM-bioavailability measurements, only four soil samples out of 24 showed toxicity calculated according to RIVM MPCeco model and none of the samples exhibited toxicity according to RIVM SRC. This indicates, again, that the generic guideline values for PAHs in contaminated soil are likely too conservative when applied to tar-asphalt impacted areas, and may overestimate risks related with PAH bioavailability and toxicity in soils along roads.

For PAH-L, the lowest total soil concentration that exceeded bioavailable MPCeco threshold (i.e.  $\log TU > 0$ , Fig. 5) was  $8.2 \text{ mg kg}^{-1}$ . The highest value, which did not exceed this toxic threshold ( $\log TU < 0$ ) was  $4.0 \text{ mg kg}^{-1}$ , i.e. the concentration where no risk is considered to occur for the soil ecosystem (Fig. 5). This means that the lowest concentration at which the studied roadside soil starts exhibiting toxicity is somewhere between  $4.0$  and  $8.2 \text{ mg kg}^{-1}$ . For PAH-M this value is between  $5.3$  and  $9.2 \text{ mg kg}^{-1}$ , while for PAH-H it is between  $25$  and  $60 \text{ mg kg}^{-1}$ . Even if the exact values at which the toxic thresholds are exceeded were not determined, the intervals of possible concentrations exceeding such thresholds are much higher than the generic Swedish guideline model states, particularly for the PAH-H fraction, which was at least 25 times higher.

#### 4. Conclusions

The spread of PAHs from tar asphalt beneath a bituminous asphalt layer to roadside soil and groundwater appeared very limited based on PAH ratios, as well as concentration patterns compared to the control road. Groundwater at most of the road sections contained very low or non-detectable levels of PAHs despite the presence of high PAH concentrations in tar asphalt. According to the diagnostic ratios between different PAH compounds, the origin of PAH in the soils along the roads is of a mixed nature and only a part of the PAH could have originated from the tar asphalt. Non-asphalt PAH sources were the reason that elevated PAH concentrations were detected in soil along the control road containing only bituminous asphalt. However, further modelling of vadose zone transport processes of both dissolved and colloidal PAHs, as well as atmospheric deposition pathways of traffic particles, would be needed to confirm these trends.

PAHs found in the tar asphalt were strongly sorbed and of low bioavailability, according to the POM method, and as found generally for coal tars and other tar residues. Only asphalt with PAH content  $>1200 \text{ mg kg}^{-1}$  exceeded a threshold for serious risk based on the RIVM SRC model (50 % species protection level, chronic toxicity). The other asphalt samples, as well as those of sand and soil, with elevated PAH levels exhibited low bioavailability and estimated toxicity. This implies that soil samples from tar asphalt roads that exceeded the Swedish EPA's guideline values for PAH in contaminated soil with less sensitive land use may actually be much less toxic than the guidelines would expect. The findings of this study generally support the hypothesis that the leaching of bioavailable PAHs from road tar asphalt under a bituminous asphalt layer is limited and only exceeds risk thresholds nearby. Threshold toxicity concentrations, based on bioavailability, were exceeded in the lower layer of asphalt itself, and in many cases the sand directly below the asphalt (though to a significantly lesser extent). In samples of road side soil where MPCeco toxicity limits were exceeded for PAH16, it was not clear that the PAHs originated from the road tar asphalt. Further, there was no clear indication that road tar asphalt was the source of PAHs in the downstream groundwater.

Further risk analysis of tar asphalt could focus on the leaching and transport mechanisms of both dissolved and colloidal PAHs from the surface and subsurface roads to the surrounding environment, to validate these observations. A central point of future research should be to compare the risk and impact of letting the tar asphalt layers be present under the new bituminous asphalt coatings vs the environmental impact of moving these layers to landfills for PAH management and replacement with cleaner asphalt. Such research could be used to develop best management practices for old roads in Sweden and other countries.

#### CRedit roles of authors

Jurate Kumpiene: Funding acquisition, Conceptualization, Investigation, Data curation, Writing - original draft Martin Larsson: Interpretation of data, Writing - review & editing Ivan Carabante: Interpretation of data, Writing - review & editing Hand Peter Arp: Methodology, Resources, Interpretation of data, Writing - review & editing.

#### 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

Asphalt sampling was done in cooperation with the Swedish Transport Administration (Trafikverket). Funding: This work was supported by the Swedish Transport Administration (Registration No. TRV 2017/110306).

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2021.117828>.

#### References

- Ahrens, M.J., Depree, C.V., 2010. A source mixing model to apportion PAHs from coal tar and asphalt binders in street pavements and urban aquatic sediments. *Chemosphere* 81, 1526–1535.
- Akyüz, M., Çabuk, H., 2010. Gas – particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak. *Turkey. Sci. Total Environ.* 408, 5550–5558.
- Arp, H.P.H., Breedveld, G.D., Cornelissen, G., 2009. Estimating the in situ sediment–porewater distribution of PAHs and chlorinated aromatic hydrocarbons in anthropogenic impacted sediments. *Environ. Sci. Technol.* 43, 5576–5585.
- Arp, H.P.H., Azzolina, N.A., Cornelissen, G., Hawthorne, S.B., 2011. Predicting porewater EPA-34 PAH concentrations and toxicity in pyrogenic-impacted sediments using pyrene content. *Environ. Sci. Technol.* 45, 5139–5146.
- Arp, H.P.H., Lundstedt, S., Josefsson, S., Cornelissen, G., Enell, A., Allard, A.S., Berggren Kleja, D., 2014. Native oxy-pahs, n-pacs, and pahs in historically contaminated soils from Sweden, Belgium, and France: their soil-porewater partitioning behavior, bioaccumulation in *Enchytraeus Crypticus*, and bioavailability. *Environ. Sci. Technol.* 48, 11187–11195.
- Bowman, D.T., Jobst, K.J., Helm, P.A., Kleywegt, S., Diamond, M.L., 2019. Characterization of polycyclic aromatic compounds in commercial pavement sealcoat products for enhanced source apportionment. *Environ. Sci. Technol.* 53, 3157–3165.
- Brandt, H.C.A., De Groot, P.C., 2001. Aqueous leaching of polycyclic aromatic hydrocarbons from bitumen and asphalt. *Water Res.* 35, 4200–4207.
- Brown, J., Peake, B., 2006. Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. *Sci. Total Environ.* 359, 145–155.
- Cachada, A., Pereira, R., da Silva, E.F., Duarte, A.C., 2014. The prediction of PAHs bioavailability in soils using chemical methods: state of the art and future challenges. *Sci. Total Environ.* 472, 463–480.
- City of Gothenburg, 2015. Managing Asphalt and Tar Asphalt. Fact sheet Environmental Administration (In Swedish).
- Colombo, J.C., Barreda, A., Bilos, C., Cappelletti, N., Demichelis, S., Lombardi, P., Skorupka, C.N., Suárez, G., 2005a. Oil spill in the Rio de La Plata estuary, Argentina: 1. Biogeochemical assessment of waters, sediments, soils and biota. *Environ. Pollut.* 134, 277–289.

- Colombo, J.C., Barreda, A., Bilos, C., Cappelletti, N., Migoya, M.C., Skorupka, C., 2005b. Oil spill in the Rio de La Plata estuary, Argentina: 2-hydrocarbon disappearance rates in sediments and soils. *Environ. Pollut.* 134, 267–276.
- Enell, A., et al., 2012. Test methods for environmental characterization of reclaimed asphalt, Re-road – End of Life Strategies of Asphalt Pavements. Deliverable 1,6, 7FP project report: [http://re-road.fehrl.org/index.php?m=48&id\\_directory=7325](http://re-road.fehrl.org/index.php?m=48&id_directory=7325).
- Garcia-Flores, E., Wakida, F.T., Rodríguez-Mendivil, D., Espinoza-Gomez, H., 2016. Polycyclic Aromatic Hydrocarbons in Road-Deposited Sediments and Roadside Soil in Tijuana, Mexico. *Soil Sediment. Contam.* 25 <https://doi.org/10.1080/15320383.2016.1113497>, 00–00.
- Harrison, R.M., Smith, D., Luhana, L., 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environ. Sci. Technol.* 30, 825–832.
- Hawthorne, S.B., Jonker, M.T.O., van der Heijden, S.A., Grabanski, C.B., Azzolina, N.A., Miller, D.J., 2011. Measuring picogram per liter concentrations of freely dissolved parent and alkyl PAHs (PAH-34), using passive sampling with polyoxymethylene. *Anal. Chem.* 83, 6754–6761.
- Iturbe, R., Flores, C., Flores, R.M., Torres, L.G., 2005. Subsoil TPH and other petroleum fractions-contamination levels in an oil storage and distribution station in north-central Mexico. *Chemosphere* 61, 1618–1631.
- Jacobsson, T., Granvik, M., 2003. Coal Tar in Asphalt Masses. Progress Report with Advice and Recommendations for Handling, Staging and Recycling. Swedish Association of Local Authorities and the Swedish Road Administration.
- Jiang, Y., Hu, X., Yves, U.J., Zhan, H., Wu, Y., 2014. Status, source and health risk assessment of polycyclic aromatic hydrocarbons in street dust of an industrial city, NW China. *Ecotoxicol. Environ. Saf.* 106, 11–18.
- Johnsen, A.R., Delipthay, J.R., Reichenberg, F., Sørensen, S.J., Andersen, O., Christensen, P., Binderup, M., Jacobsen, C.S., 2006. Biodegradation, bioaccessibility, and genotoxicity of diffuse polycyclic aromatic hydrocarbon (PAH) pollution at a motorway site. *Environ. Sci. Technol.* 40, 3293–3298.
- Katsoyiannis, A., Terzi, E., Cai, Q.-Y., 2007. On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. Is this use appropriate? *Chemosphere* 69, 1337–1339.
- Li, P.-H., Wang, Y., Li, Y.-H., Wang, Z.-F., Zhang, H.-Y., Xu, P.-J., Wang, W.-X., 2010. Characterization of polycyclic aromatic hydrocarbons deposition in PM<sub>2.5</sub> and cloud/fog water at Mount Taishan (China). *Atmos. Environ.* 44, 1996–2003.
- Liu, J., Zhang, J., Zhan, C., Liu, H., Zhang, L., Hu, T., Xing, X., Qu, C., 2019. Polycyclic aromatic hydrocarbons (PAHs) in urban street dust of Huanggang, Central China: status, sources and human health risk assessment. *Aerosol Air Qual. Res.* 19, 221–233.
- Mahler, B.J., Van Metre, P.C., Bashara, T.C., Wilson, J.T., Johns, D.A., 2005. Parking lot sealcoat: an unrecognized source of urban polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* 39, 5560–5566.
- Mahler, B.J., Van Metre, P.C., Crane, J.L., Watts, A.W., Scoggins, M., Williams, E.S., 2012. Coal-tar-based pavement sealcoat and PAHs: implications for the environment, human health, and stormwater management. *Environ. Sci. Technol.* 46, 3039–3045.
- Marr, L.C., Kirchstetter, T.W., Harley, R.A., Miguel, A.H., Herring, S.V., Hammond, S.K., 1999. Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions. *Environ. Sci. Technol.* 33, 3091–3099.
- Mi, H.-H., Lee, W.-J., Chen, C.-B., Yang, H.-H., Wu, S.-J., 2000. Effect of fuel aromatic content on PAH emission from a heavy-duty diesel engine. *Chemosphere* 41, 1783–1790.
- Norwegian Geotechnical Institute, 1999. Environmental Analyzes and Leaching Experiments with Asphalt from Fornebu. NGI reports (in Norwegian)).
- Orbicon, 2018. Environmental Soil Survey of PAH, Road 805, Jokkmokk Municipality. Project number: 171234-2018-01-02 (In Swedish).
- Readman, J.W., Mantoura, R.F.C., Rhead, M.M., 1987. A record of polycyclic aromatic hydrocarbons (PAH) pollution obtained from accreting sediments of the Tamar estuary, U.K.: evidence for non-equilibrium behavior of PAH. *Sci. Total Environ.* 66, 73–94.
- Riccardi, C., Di Filippo, P., Pomata, D., Inconato, F., Di Basilio, M., Papini, M.P., Spicaglia, S., 2008. Characterization and distribution of petroleum hydrocarbons and heavy metals in groundwater from three Italian tank farms. *Sci. Total Environ.* 393, 50–63.
- Scoggins, M., McClintock, N.L., Gosselink, L., 2007. Occurrence of polycyclic aromatic hydrocarbons below coal-tar-sealed parking lots and effects on stream benthic macroinvertebrate communities. *J. North Am. Benthol. Soc.* 26, 694–707.
- Scoggins, M., Ennis, T., Parker, N., Herrington, C.A., 2009. Photographic method for estimating wear of coal tar sealcoat from parking lots. *Environ. Sci. Technol.* 43, 4909–4914.
- SFS, 2011. Waste Ordinance 2011:927. Swedish Constitution Collection, p. 927.
- SGU, 2013. Assessment criteria for groundwater. Swedish Geologic Survey (SGU), Report 2013:01 (in Swedish).
- SIS, 1981. Determination of Dry Matter and Ignition Residue in Water, Sludge and Sediment. SS 028113. Swedish Standard Institute.
- Swedish EPA, 2009. Risk assessment of contaminated sites. A guide from simplified to in-depth risk assessment. Swed. Environ. Protect. Agency (Naturvårdsverket), Rapp. 5977. December 2009 (In Swedish).
- Swedish Food Agency, 2001. The Swedish National Food Agency's regulations on drinking water SLVFS 2001:30 (H 90) (in Swedish).
- Swedish Petroleum Institute, 2010. Remediation of Polluted Petrol Stations and Diesel Plants, Swedish Petroleum Institute's recommendation (in Swedish).
- Swedish Transport Administration, 2014. Environmental Follow-Ups of Recycled Tar Asphalt 2001-2011, Compiled by Anja Enell. Swedish Geotechnical Institute, SGI (in Swedish).
- Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. *Environ. Pollut.* 162, 110–119.
- Verbruggen, E.M.J., 2012. Environmental Risk Limits for Polycyclic Aromatic Hydrocarbons (PAHs): for Direct Aquatic, Benthic, and Terrestrial Toxicity. The Netherlands National Institute for Public Health and the Environment (RIVM), p. 339 report 607711007/2012.
- Wang, D.G., Yang, M., Jia, H.L., Zhou, L., Li, Y.F., 2009. Polycyclic aromatic hydrocarbons in urban street dust and surface soil: comparisons of concentration, profile, and source. *Arch. Environ. Contam. Toxicol.* 56, 173–180.
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* 33, 489–515.
- Zhang, W., Zhang, S., Wan, C., Yue, D., Ye, Y., Wang, X., 2008. Source diagnostics of polycyclic aromatic hydrocarbons in urban road runoff, dust, rain and canopy throughfall. *Environ. Pollut.* 153, 594–596.