



Leaching of PAHs from rubber modified asphalt pavements

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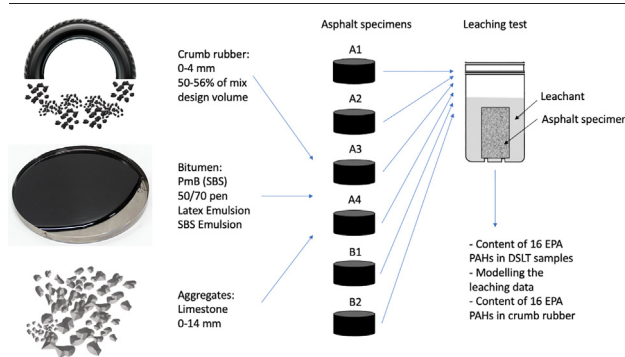
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HIGHLIGHTS

- The first comprehensive study on leaching of 16 EPA PAHs from rubber modified asphalt
- DSLT was carried out on asphalts utilizing SBS, 50/70 pen and latex modified bitumen.
- Content of 16 EPA PAHs in crumb rubber granulates ranged between 0.061 and 8.322 $\mu\text{g/g}$.
- Only benzo[b]fluoranthene, benzo[k]fluoranthene and naphthalene leached $>1 \mu\text{g/m}^2$.
- Leaching of 16 EPA PAHs from rubberised asphalt was a diffusion-controlled process.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study aimed to, for the first time, quantify the total content of 16 priority EPA PAHs in end-of-life tyre derived crumb rubber granulates and various manufactured rubberised asphalt mix designs. After identifying the availability of 16 EPA PAHs, the leaching behaviour of rubberised asphalt specimens, were evaluated using the Dynamic Surface Leaching Test (DSLIT) based on CEN/TS 16637-2:2014 standard. This was prior to modelling the release mechanisms of PAHs by utilizing a mathematical diffusion-controlled leaching model. According to the results, the total content of 16 EPA PAHs in crumb rubber granulates ranged between 0.061 and 8.322 $\mu\text{g/g}$, which were associated with acenaphthene and pyrene, respectively. The total content of PAHs in rubberised asphalt specimens varied between 0.019 and 4.992 $\mu\text{g/g}$ depending on the volume of crumb rubber granulates in the asphalt concrete mix design, and type of binder. Results of the leaching experiments revealed that the highest leached PAHs were benzo[b]fluoranthene, benzo[k]fluoranthene and naphthalene with a 64-days cumulative release per specimen surface area $>1 \mu\text{g/m}^2$. Acenaphthylene, fluoranthene, fluorene and indeno[1,2,3-c,d]pyrene were released in cumulative concentrations between 0.1 and 1 $\mu\text{g/m}^2$. The PAHs with a cumulative release potential below 0.1 $\mu\text{g/m}^2$ during DSLIT were benzo[a]anthracene, benzo[a]pyrene, benzo[ghi]perylene and chrysene. The diffusion coefficients, which were calculated by mathematical modelling of DSLIT data, revealed that the leaching process of 16 EPA PAHs from surface of rubberised asphalt concrete mix designs fitted all the criteria set by the NEN 7345 standard for diffusion-controlled leaching during all stages of leaching experiments.

1. Introduction

Asphalt concrete is known to be one of the most widely used surface paving materials in the world (Su, 2020). The European Asphalt Pavement

Association (EAPA) which represents the manufacturers of asphalt in Europe, has reported the annual total asphalt manufactured in the EU and US. According to the report by EAPA, Europe has annually produced 263.7 to 326.9 million tonnes of hot and warm mix asphalt between 2009 and 2019 (EAPA, 2016). The figures are between 318.1 and 382.0 million tonnes for the US. Asphalt is generally manufactured at a temperature around 150–180 °C, using various types of aggregates and binders

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(Alnadish et al., 2021; Fang et al., 2016). Asphalt binders are generally a product of crude oil manufactured in crude oil refinery facilities (Wang et al., 2020; Qu et al., 2018). Being a product of crude oil means that asphalt binders have complex chemical properties consisting of variety of organic molecules (Yao et al., 2021; Wang et al., 2018). Polycyclic aromatic hydrocarbons (PAHs) are one of the abundant organic compounds in asphalt binders (Muñoz et al., 2021; Xiu et al., 2020). PAHs are classified as widely distributed organic pollutants in the environment through natural processes including forest fires, volcanoes and anthropogenic activities including coal plants and emissions from car exhausts (Patel et al., 2020; Fathollahi and Coupe, 2021a; Lawal, 2017; Kamal et al., 2015; Kong et al., 2012). From hundreds of different PAHs that have been identified in the environment, PAHs with 4–6 aromatic rings are known to be highly toxic and persistent when released into receiving ecosystems (Gupte et al., 2016; IARC, 2007). Sixteen have been designated High Priority Pollutants by the Environmental Protection Agency (EPA), who have identified 16 PAHs as high priority pollutants, including naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHN), anthracene (ANC), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (B[a]A), chrysene (CHY), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), benzo[ghi]perylene (B[ghi]P), indeno[1,2,3-c,d]pyrene (IND), and dibenz[a,h]anthracene (D[ah]A).

There are three main routes through which human body can be exposed to priority PAHs: inhalation, digestion and direct contact (Idani et al., 2020; Nakane, 2012; St. Helen et al., 2012; Kammer et al., 2011). The adverse effect of PAHs on human health is typically dependent on the toxicity of the compound, duration and route of exposure (Sun et al., 2021; Kim et al., 2013). Previous studies have reported various adverse effects from exposure to PAHs on animals and health, including carcinogenicity and teratogenicity (Alhamdow et al., 2020; Chang et al., 2020; Xiong et al., 2021; Abdel-Shafy and Mansour, 2016; Soltani et al., 2015), immunotoxicity (Phelps et al., 2020; Zhang et al., 2020), oxidative stress (Ma et al., 2019; Yuan et al., 2017), neurotoxicity (Perera et al., 2018; Slotkin et al., 2017) and genotoxic effects (Böckers et al., 2020; Wu et al., 2020). Therefore, researchers have been quantifying the occurrence of 16 priority PAHs in various environments including in urban runoff from asphalt pavements to identify their associated sources. Liu et al. (2017) reported traffic volume, land use, distance to highway and roughness of road surfaces as the main factors influencing the release of PAHs from asphalt surfaces. Mahler et al. (2014) reported a median 16 priority PAHs concentration of 328 and 35 µg/L for coal-tar- and asphalt-sealcoated pavements, respectively. Various studies have reported Reclaimed Asphalt Pavements (RAP) as a source of PAHs leaching into urban runoff (Yang et al., 2020; Legret et al., 2005). The use of crumb rubber, which is the recycled tyre rubber, as an additive in hot mix asphalt mixture is a popular sustainable construction method to reduce the extraction of virgin aggregates and prevent the transport of end-of-life tyres into landfills. However, no study is available in the literature on the release of 16 EPA priority PAHs from rubberised asphalt pavements containing crumb rubber granulates.

Leaching tests are standard procedures, in which construction materials including asphalt concrete specimens, are kept in contact with a leachant for a several stages with known duration. During the leaching tests, samples are taken for analytical procedures to quantify the release of organic and inorganic pollutants from the surface of construction materials. The concentrations of released substances during leaching tests are then compared to thresholds set by regulatory bodies including the Water Framework Directive (WFD). Several leaching tests standards have been proposed by the European Commission (EC) for construction materials including CEN/TS 16637-2:2014 and CEN/TS 14405. The Dynamic Surface Leaching Test (DSLTL) based on CEN/TS 16637-2:2014 standard is for determination of the release of “Regulated Dangerous Substances” from construction products into soil, surface water and groundwater. Many studies have used CEN/TS 16637-2:2014 standard quantify the release of organic and inorganic compounds from materials (Bandow et al., 2018; Gupta et al., 2018; Maia et al., 2018; Solouki et al., 2021; Spreadbury et al., 2021).

The purpose of this study was to evaluate the release of 16 EPA PAHs from 6 different rubberised asphalt mix designs manufactured using 50–56% (of total mix design volume) crumb rubber granulates from end-of-life tyres and various binders including warm modified Styrene-Butadiene-Styrene (SBS) bitumen, 50/70 penetration grade neat bitumen, modified bitumen-based latex and modified bitumen-based SBS binders. DSLTL leaching tests based on CEN/TS 16637-2:2014 standard was employed to quantify the leaching of 16 EPA PAHs. The total content of PAHs in crumb rubber granulates and rubberised asphalt specimens were quantified using modified extraction and analytical methodologies. The leaching mechanism of 16 EPA PAHs from rubberised asphalts was further investigated by modelling the release data from DSLTL experiments. The long-term leaching behaviour of rubberised asphalts was estimated by measuring diffusion-controlled coefficients obtained from mathematical modelling of DSLTL.

2. Materials and methods

2.1. Crumb rubber and asphalt specimens

The crumb rubber used in the present study was produced by shredding end-of-life car tyres. Tyres were shredded using an ambient shredding process prior to sieving to <4 mm particle sizes. Sieved crumb rubber granulates were used for manufacturing 6 different rubberised impact-absorbing asphalt pavement mix designs. Rubberised asphalt specimens were manufactured by mixing aggregates and binder using a dry process prior to the addition of crumb rubber granulates. The dry process was used because the rubber is considered an aggregate. Two sets of rubberised asphalt mixture were designed: A-mixes consisting of A1, A2, A3 and A4, were manufactured using 56% (of total mix design volume) crumb rubber content in their mix design. B-mixes consisting of B1 and B2 contained 50% crumb rubber granulates. The reason for choosing 50–56% crumb rubber granulates in the mix designs was to develop an impact-absorbing pavement (IAP) for vulnerable road users (e.g., sidewalks and bike lanes). The aim was to use a known asphalt concrete mix design, in this case, the Hot-Rolled Asphalt (HRA). The crumb rubber granulates partially replaced the limestone aggregates (<14 mm) in the rubberised asphalt mix designs. A total of 4 different binders were utilized in manufacturing process of rubberised asphalts in the present study. Details of binders are as follows:

1. A warm modified Styrene-Butadiene-Styrene (SBS) bitumen.
2. A warm 50/70 penetration grade neat bitumen.
3. A cold modified bitumen-based latex binder.
4. A cold modified bitumen-based SBS binder.

Rubberised asphalt specimens with 150 mm diameter and 40 mm thickness were manufactured for leaching tests using gyratory compaction (EN 12697-31:2019) and static compaction (EN 12697-56:2019) methodologies. Organoleptic assessment of mixtures with bituminous emulsion (EN-12697-55:2019) standard was used to choose the optimum aggregate-bitumen mixing time for manufacturing the rubberised asphalt specimens. This approach guarantees the mix design aggregates to be homogenous and effectively coated by bitumen. The warm rubberised asphalt mixtures were mixed at 160 °C for 30 min prior to 80 cycles of compaction at 80 °C. For cold rubberised mix design specimen manufacturing methodology, aggregates and bitumen were mixed at 23 ± 2 °C for 5 min prior to a static compaction at the same temperature. Table 1 summarises the physical properties of manufactured rubberised asphalts for the leaching tests in the present study.

2.2. Leaching tests

The horizontal dynamic surface leaching test (DSLTL) was performed on the manufactured rubberised specimens according to CEN/TS 16637-2 standard from European Commission Construction Products Regulation (EC-CPR). A set of glass tanks with sealed lids to prevent evaporation of

Table 1
Specifications of manufactured asphalt specimens for leaching tests.

Name	A1	A2	A3	A4	B1	B2
Rubber volume (total mix) [%]	56	56	56	56	50	50
Bitumen type	PmB-SBS	50/70 pen	E-Lat	E-SBS	PmB-SBS	50/70 pen
Bitumen volume (total mix) [%]	15	15	15	15	15	15
Bulk density	1.351	1.292	1.441	1.364	1.533	1.256
Voids content [%]	4	3	5	8	3	6
Indirect tensile strength modulus [MPa]	230	266	148	144	526	209

leachant were prepared for 64-day DSLT tests. The DSLT was carried out in triplicate of specimens for all rubberised asphalt mix designs. According to the CEN/TS 16637-2, the leachant in the present DSLT study was selected to be deionised (DI) water at neutral pH and a conductivity less than 0.5 mS/m. Asphalt specimens were placed in the glass tank filled with DI water. A liquid to surface ratio of 80 was selected for the DSLT studies based on CEN/TS 16637-2 standard. Specimens were placed on small glass beads to avoid direct contact between the asphalt specimen surfaces and the glass tank. A minimum of 20 mm space between asphalt specimens and glass tank walls were maintained throughout the DSLT. The leaching experiments were performed at the room temperature (20–25 °C). 3 glass tanks containing DI water with no asphalt specimens in them were assigned as controls to measure any possible lab environment contamination. The electric conductivity of the samples from control treatments had to be <0.2 mS/m during all stages of DSLT to ensure no external contamination of the experiments. The DSLT consisted of 8 stages during the 64 days from the experimental set-up. At the end of each stage the leachants from glass tanks were sampled for quantification of PAHs content, pH and electric conductivity, prior to the renewal of leachant for the start of next stage. The leachant renewal was done after 0.25, 1, 2.25, 4, 9, 16, 36 days from the start of the DSLT tests, meaning the duration of stages 1 to 8 were 0.25, 0.75, 1.25, 1.75, 5, 7, 20 and 28 days, respectively. The content of 16 EPA priority PAHs in samples taken from all stages of DSLT for 6 different rubberised asphalt specimens was quantified using gas chromatography-mass spectrometry (GC-MS) instrumentation. The cumulative leached compounds from the asphalt specimens after 64 days were calculated for each PAH according to the CEN/TS-16637-2 2014 standards as follows:

$$C_n = \sum_{i=0}^n C_i$$

where C_n (mg/m²) is the cumulative PAH of interest concentration at the stage n of DSLT experiment, C_i is the concentration of the PAH of interest in the leachant at the stage n (quantified during GC-MS-MS analysis) and i is the number of the DSLT stage.

2.3. Extraction of PAHs

Quantifying the total content of PAHs was carried out to evaluate the availability of PAHs of interest to leach into the leachant medium in DSLT experiments. The extraction method by Menichini et al. (2011) was modified and used in the present study to quantify the total content of 16 PAHs in crumb rubber granulates and rubberised asphalt specimens. Crumb rubber has a complex chemical composition, therefore a modified methodology was needed to eliminate coeluting compounds in the chromatograms. To avoid the coeluting compounds, more clean up stages were included in the methodology, recommended by Menichini et al. (2011). 2 g of sieved crumb rubber granulates and crushed rubberised asphalt with grain size <4 mm were weighted separately and placed in tubes prior to spiking with 100 μ L deuterated PAHs (d-PAHs) as internal standards. The matrix was left at room temperature for 12 h to reach equilibrium. The PAH content of the crumb rubber granulates were extracted ultrasonically using 3 sets of extraction stages using 20 mL of dichloromethane followed by a single stage extraction using 20 mL n-hexane prior to the combination of all 4 extracts. The duration of each of 4 extraction stages was 30 min. The combined extracts were then concentrated to half volume

under pressure at 35 °C. A 0.5 mL silica gel comprising of 10% water was used to retain one tenth of the concentrated combined extract. After evaporating the solvent portion of the matrix, the extract was added to a silica gel column comprising of 10% water prior to a prewash stage with 20 mL n-hexane followed by an elution with n-hexane. 1 μ L of n-tetradecane (solution keeper) was added to the solution prior to drying the mix using a nitrogen stream (Turrio-Baldassarri et al., 2003). 500 μ L of ¹³C-BaP solution was added to the dried samples and diluted to 1.5 mL using iso-octane for the GC-MS analysis.

The method performance for the recovery of deuterated standards was evaluated. A recovery rate between 45 and 110% was achieved for d-PAHs with a limit of detection between 0.001 and 0.02 mg/kg. The repeatability of the method (5 replicates) showed standard deviations between 4 and 8% and uncertainties ($k = 2$) ranging between 10 and 46%.

2.4. GC-MS-MS analysis

The extracted PAH samples from crumb rubber granulates and samples from DSLT of rubberised asphalt specimens were analysed by a GC-MS-MS methodology to quantify the total content of 16 priority PAHs. An Agilent 7890 gas chromatogram system (Agilent Technologies, Palo Alto, CA) with Agilent autosampler was used as the GC system in the present study. The capillary injector of the GC system was in splitless mode at a temperature of 250 °C. The capillary injector pulsed splitless at 25 psi for 0.5 min, then split at 50 mL/min for 1 min. A deactivated single gooseneck glass was used as liner in the analysis. The injection volume was set as 1 μ L. Separation was carried out on an Agilent VF-5ms, 30 m \times 0.25 mm \times 0.25 μ m column (Agilent Technologies, Palo Alto, CA) with a flow rate of 1.0 mL/min. Helium was selected as the carrier gas in the methodology. The GC system oven was set to stay constant at 50 °C for 5 min, increasing to 300 °C in 12 °C per minute increments. The oven temperature was kept at 300 °C for 5 min. The eluted PAHs were detected using an Agilent 7010 Triple Quadrupole detector (Agilent Technologies, Palo Alto, CA) in Electron Impact (EI) mode operating in MRM/Scan mode by selected ion monitoring of the molecular ions, using one other fragment as qualifier ion. 3 samples with known concentration of PAHs were analysed after each sequence of analysis for quality control purposes. The detection limit of the methodology for 16 priority PAHs of interest ranged between 0.001 and 0.02 mg/kg.

2.5. Modelling the leaching from rubberised asphalt

In general, there are four paths available for compounds to leach out from building and construction materials: diffusion, surface wash-off, depletion and dissolution. The results from DSLT leaching tests are normally modelled using diffusion models as this would provide 4 main parameters to understand the long-term leaching behaviour of material under investigation in contact with water. In this study, the diffusion modelling procedure proposed by Birgisdóttir et al. (2007) was used. Diffusion is known to control the leaching process from material when the rate of compounds released into the leachant confines reaching the equilibrium concentration. The equation proposed by Crank (1989) was used to model the diffusion-controlled release of PAHs from rubberised asphalt in this study. The Crank equation is as follows:

$$M_{\text{PAHt}} = 2 \times \rho \times C_x \sqrt{\frac{Dx \times t}{\pi}}$$

where M_{PAHt} is the mass of PAH of interest per surface area of the rubberised asphalt diffused into the leachant during stage t of the DSLT, reported in mg/m^2 . ρ is the specific density of the rubberised asphalt specimens used for the DSLT tests reported in kg/m^3 . C_x is the total content of PAH of interest in the asphalt specimen available for leaching, reported in mg/kg . D_x is the diffusion coefficient of diffusion-controlled leaching of PAHs, reported in m^2/s .

The cumulative release of each PAH under investigation in the present study was calculated by summing up the released PAH concentration (result of GC-MS analysis) in all 8 stages of DSLT for each specimen. In order to identify the role of each release mechanism including diffusion, surface wash-off, depletion and dissolution on the leaching behaviour of rubberised asphalt, equation below was used to calculate the cumulative arithmetical release (NEN 7345, 1995):

$$M_i = M_{PAHt} \times \frac{\sqrt{i}}{\sqrt{i} - \sqrt{(i-1)}}$$

where M_i is the cumulative arithmetical release of PAH of interest at stage t of DSLT.

Equations below proposed by NEN 7345 (1995) standard was used to calculate D_x value based on results from DSLT test:

$$DX_i = \pi \times (M_{PAHt})^2 \times \frac{1}{4(\rho \times C_x)^2 (\sqrt{i} - \sqrt{(i-1)})^2}$$

$$D_X = \frac{\sum_{i=0}^n DX_i}{n}$$

where D_{X_i} is the diffusion coefficient at stage i of the DSLT test and is reported in m^2/s . These equations are used when the concentrations measured during GC-MS analysis is higher than detection limit of the instrument for samples taken during all stages of DSLT.

The diffusion coefficient of each PAH in leachant of the DSLT test was calculated using the equation below:

$$D_y = D_x \times \tau \times R_x$$

where τ and R_x are the retardation factor of the rubberised asphalt specimens and PAHs, respectively.

The diffusion coefficient of the PAHs during DSLT experiments can be described as follows:

$$\rho D_x = \rho D_y - \rho \tau - \rho R_x$$

2.6. Materials and reagents

All reagents and solvents used in the present study were of analytical grade. Table 2 summarises the properties and abbreviations of 16 EPA priority PAHs under investigation in the study. The PAHs analytical standards were provided by AccuStandard Inc. (New Haven, US). Analytical grade methanol, ethyl acetate and acetone were provided by Sigma Aldrich (Steinheim, Germany). Dilution of the PAHs standards was prepared in ethyl acetate. Rubberised asphalt specimens were manufactured in Department of Civil, Chemical, Environmental, and Materials Engineering at University of Bologna.

2.7. Statistical analysis

The DSLT experiments were carried out in triplicates for all rubberised asphalt specimens prior to the statistical analysis. SPSS software (Version 21.0, SPSS, Chicago, Illinois) was used to perform statistical analysis on the leaching results from DSLT. A p -value less than 0.05 was assumed as statistically significant in all DSLT data statistical analyses.

Table 2

Details of 16 EPA PAHs under investigation in the present study.

PAH	Abbreviation	MW ^a (g/mol)	Log K _{OW} ^b	CW ^c (mg/L)	No of ring
Acenaphthene	ACE	154.2	3.92	3.47	3
Acenaphthylene	ACY	152.1	4.10	3.93	3
Anthracene	ANC	178.2	4.54	0.0434	3
Benzo[a]anthracene	B[a]A	228.3	5.61	0.014	4
Benzo[a]pyrene	B[a]P	252.3	6.50	0.0038	5
Benzo[b]fluoranthene	B[b]F	252.3	6.60	–	5
Benzo[ghi]perylene	B[ghi]P	276.3	6.50	0.00026	6
Benzo[k]fluoranthene	B[k]F	252.3	6.60	–	5
Chrysene	CHY	228.3	5.91	0.0018	4
Dibenz[a,h]anthracene	D[ah]A	278.4	6.90	0.0005	5
Fluoranthene	FLA	202.3	5.22	0.265	4
Fluorene	FLU	166.2	4.18	0.19	3
Indeno[1,2,3-c,d]pyrene	IND	276.3	7.66	0.062	6
Naphthalene	NAP	128.2	3.36	31	2
Phenanthrene	PHN	178.2	4.57	1.18	3
Pyrene	PYR	202.3	5.18	–	4

^a MW = molecular weight.

^b K_{OW} = octanol-water partitioning coefficient.

^c CW = aqueous solubility.

3. Results and discussion

3.1. Total PAHs content

PAHs extraction methodology described in materials and methods was performed on samples from crumb rubber granulates and crushed rubberised asphalt specimens to quantify their total 16 priority PAHs content. The chromatographic conditions of the GC system were optimized to have a separated chromatogram for 16 PAHs in the study. The results of quantification of total content of PAHs in crumb rubber and different rubberised asphalt mix designs are presented in Table 3. The mean total content of PAHs in the crumb rubber granulates used in the present study ranged between 0.061 and 8.322 $\mu g/g$. The lowest value (0.061 $\mu g/g$) was associated with ACE. PYR (8.322 $\mu g/g$) was the most abundant PAH in the crumb rubber granulates, followed by B[ghi]P (3.535 $\mu g/g$), B[b]F (2.623 $\mu g/g$) and FLA (2.485 $\mu g/g$). PAHs with total concentration between 1 and 2 $\mu g/g$ were B[a]P, B[k]F and B[a]A. CHY (0.612 $\mu g/g$), ANC (0.266 $\mu g/g$), ACY (0.108 $\mu g/g$), ACE (0.061 $\mu g/g$), D[ah]A (0.119 $\mu g/g$), FLU (0.092 $\mu g/g$), IND (0.315 $\mu g/g$) and NAP (0.043 $\mu g/g$) showed total concentrations below 1 $\mu g/g$ in crumb rubber granulates.

The total concentration of selected PAHs in different rubberised asphalt mix designs was quantified following the solvent extraction methodology and GC-MS analysis. The result of the total content analysis of rubberised asphalts under investigation in this study is presented in Table 1. In general, the total content of PAHs in all rubberised asphalt mix designs were

Table 3

16 EPA PAHs content ($\mu g/g$) of the crumb rubber and rubberised asphalt specimens in this study.

PAHs	Crumb rubber	A1	A2	A3	A4	B1	B2
ACE	0.061	0.024	0.030	0.025	0.033	0.020	0.019
ACY	0.108	0.064	0.064	0.034	0.060	0.038	0.064
ANC	0.266	0.135	0.138	0.156	0.135	0.085	0.156
B[a]A	1.358	0.407	0.502	0.434	0.529	0.733	0.407
B[a]P	1.152	0.437	0.656	0.645	0.357	0.529	0.656
B[b]F	2.623	0.944	1.442	0.918	0.839	1.416	1.259
B[ghi]P	3.535	1.696	1.555	1.166	2.121	1.520	1.908
B[k]F	1.282	0.512	0.666	0.628	0.564	0.602	0.499
CHY	0.612	0.299	0.299	0.281	0.348	0.263	0.214
D[ah]A	0.119	0.051	0.079	0.022	0.064	0.029	0.054
FLA	2.485	1.292	1.491	0.745	1.341	1.093	1.118
FLU	0.092	0.041	0.034	0.054	0.037	0.053	0.041
IND	0.315	0.184	0.151	0.150	0.123	0.049	0.105
NAP	0.043	0.013	0.017	0.013	0.020	0.018	0.020
PHN	1.012	0.506	0.506	0.495	0.485	0.354	0.333
PYR	8.322	4.992	4.659	4.076	2.496	3.577	2.662

45–70% lower than the crumb rubber granulates. This observation was understandable due to utilization of 50–56% crumb rubber granulates in asphalt mix designs. This preliminary observation revealed that crumb rubber contributed to the leaching potential of rubberised asphalt. Bitumen is a product derived from petroleum and contains concentrations of different PAHs (Kriech et al., 2002; Su et al., 2019). Previous studies on unrubberised asphalt have reported bitumen as the main contributor to leaching of PAHs into the aqueous solution (Spreadbury et al., 2021; Mahler et al., 2015; Birgisdóttir et al., 2007; Legret et al., 2005; Brandt and De Groot, 2001).

According to Table 3, PYR had the highest concentration in all rubberised asphalt mix designs ranging between 2.496 µg/g and 4.992 µg/g. The lowest concentration of PAHs in rubberised asphalts was associated with ACE ranging between 0.019 and 0.033 µg/g. This observation was consistent with results from extraction of PAHs from crumb rubber granulates where PYR and ACE showed the highest and lowest concentrations, respectively. The A-mix rubberised asphalt specimens showed higher concentrations of PAHs including ACE, CHY, IND, PHN compared to B-mix designs. This may be due to slightly larger volume of crumb rubber granulates in their mix design. B2 specimens had the lowest concentration of ACE (0.019 µg/g), B[a]A (0.407 µg/g), B[k]F (0.499 µg/g), CHY (0.214 µg/g) and PHN (0.333 µg/g). The lower content of mentioned PAHs in B2 specimens may be due to application of 50/70 pen bitumen and lower content of crumb rubber in their mix design.

3.2. Leaching test results

3.2.1. Concentration range of leached PAHs

As described in Materials and methods section, 64-days DSLT experiments were carried out on all rubberised asphalt specimens prior to sampling at different time intervals (0.25, 0.75, 1.25, 1.75, 5, 7, 20 and 28 days), sample preparation and GC–MS analysis to quantify the concentration of leached PAHs in the leachant. Table 4 presents the concentration range of leached 16 priority PAHs during DSLT experiments on rubberised asphalt specimens. The leached concentrations of B[b]F, B[k]F, FLU, NAP and PHN were higher than 100 ng/L and up to 895 ng/L in all stages of DSLT, making them the PAHs with the highest potential to leach out of rubberised asphalt when in contact with water. IND showed a slightly lower range of leached concentrations for specimens (87–189 ng/L), with concentrations higher than 100 ng/L at late stages of DSLT. The range of leached concentrations during DSLT were lower than 100 ng/L for the rest of PAHs under investigation in this study, with the lowest associated with CHY and B[ghi]P. This observation revealed that although crumb rubber and rubberised asphalt specimens had relatively high content of B[ghi]P, its leachability range was amongst the lowest during the DSLT experiments. Previous studies have reported low leaching potential of CHY and B[ghi]P from asphalt specimens (Song et al., 2020; Fernandes et al., 2009;

Table 4

Range of leached concentrations (ng/L) of PAHs from rubberised asphalt specimens during 64-days DSLT.

PAHs	A1	A2	A3	A4	B1	B2
ACE	13–29	9–41	25–34	10–41	15–30	28–36
ACY	64–86	48–65	65–78	53–68	45–81	50–87
ANC	13–26	12–28	22–29	20–25	14–24	17–31
B[a]A	21–33	22–30	19–36	18–40	24–30	21–36
B[a]P	21–25	18–23	19–24	20–25	18–21	19–21
B[b]F	581–623	324–782	363–895	265–591	221–380	270–334
B[ghi]P	9–13	9–18	18–24	16–29	24–32	19–32
B[k]F	119–231	339–416	99–343	182–476	193–397	247–367
CHY	9–14	13–16	4–10	4–14	11–15	6–9
D[ah]A	19–31	11–29	20–26	18–24	16–26	22–29
FLA	39–50	21–45	22–43	32–43	26–33	24–50
FLU	163–354	158–430	254–372	232–422	279–355	254–369
IND	94–189	100–127	119–183	87–109	93–173	97–170
NAP	325–522	296–431	211–324	306–460	373–548	395–471
PHN	130–231	134–239	129–159	173–221	157–233	159–201
PYR	64–78	59–68	71–91	84–91	65–78	61–83

Birgisdóttir et al., 2007). By comparing the leaching behaviour of different rubberised asphalt mix designs it can be noted that B-mix design specimens had lower range of leached concentrations of PAHs compared with A-mix designs. This observation was in line with lower content of the PAHs in B-mix rubberised asphalt mix designs mentioned in Section 3.1.

3.2.2. Cumulative release of PAHs

The concentrations of released PAHs into the leachant during all stages of DSLT (0.25, 0.75, 1.25, 1.75, 5, 7, 20 and 28 days) were quantified for each rubberised asphalt specimen using GC–MS analysis, prior to the calculation of cumulative release of PAHs per surface area of asphalt specimens. The cumulative release of PAHs per surface area of specimens was calculated using the equation mentioned in the Materials and methods section and is presented in Table 5. The 16 PAHs under investigation in the present study could be categorised into 3 groups based on their cumulative release concentrations during DSLT experiments on rubberised asphalt specimens. B[b]F, B[k]F and NAP were the only PAHs in this study to reach cumulative release concentrations per surface area of specimen higher than 1 µg/m². This result may be due to the fact that NAP is relatively more soluble (lowest K_{OC}) in water compared with the PAHs in this study. This observation was in line with previous reported studies on release of PAHs from asphalt concrete (Kumpiene et al., 2021; Song et al., 2020; Väänänen et al., 2006). ACY, FLA, FLU and IND were released in cumulative concentrations between 0.1 and 1 µg/m². The PAHs with a cumulative release potential below 0.1 µg/m² during DSLT included B[a]A, B[a]P, B[ghi]P and CHY. This may be due to their relatively lower solubility in water in comparison with other PAHs (Highest K_{OC} values). Previous studies in the literature have reported B[a]A, B[a]P, B[ghi]P and CHY as lowest released PAHs from asphalt concrete (Bowman et al., 2019; Law et al., 2006). Comparing the cumulative leaching results from different mix designs during 64 days of DSLT revealed that B-mix designs, which had 6% less content of crumb rubber granulates in them, leached lower overall concentrations of PAHs. This observation was consistent with the lower content of PAHs in B-mix design rubberised asphalt specimens. A2 mix designs which were manufactured using 50/70 pen bitumen, showed the lowest release of ACE (0.074 µg/m²), ACY (0.148 µg/m²), ANC (0.051 µg/m²), B[a]A (0.069 µg/m²), B[a]P (0.051 µg/m²), B[ghi]P (0.026 µg/m²), D[ah]A (0.054 µg/m²), FLA (0.085 µg/m²), FLU (0.68 µg/m²), IND (0.237 µg/m²), NAP (0.933 µg/m²), PHN (0.438 µg/m²) and PYR (0.167 µg/m²). The lowest release of 13 out of 16 PAHs from A2 mix design may have two explanations as follows: 1) Lower potential of PAHs release from 50/70 pen bitumen compared to PmB-SBS, E-Lat and E-SBS bitumen; or 2) higher potential of 50/70 pen bitumen in stabilising the PAHs content of the crumb rubber granulates and consequently reducing their release into the leachant during the DSLT experiments. The same trend was observed for B-mix design specimens, where B2 specimens with 50/70 pen bitumen showed lower cumulative release of 13 out of 16 PAHs under investigation (Table 5).

Table 5

Cumulative leached concentrations (µg/m²) of 16 EPA PAHs from rubberised asphalt specimens at the end of 64-days DSLT.

PAHs	A1	A2	A3	A4	B1	B2
ACE	0.055	0.074	0.088	0.078	0.081	0.062
ACY	0.205	0.148	0.180	0.168	0.183	0.162
ANC	0.053	0.051	0.068	0.061	0.071	0.050
B[a]A	0.070	0.069	0.074	0.079	0.077	0.073
B[a]P	0.061	0.05	0.053	0.062	0.059	0.052
B[b]F	1.606	1.410	0.786	1.165	1.733	0.837
B[ghi]P	0.029	0.026	0.075	0.063	0.073	0.056
B[k]F	0.444	1.027	0.804	1.006	0.616	0.830
CHY	0.031	0.039	0.020	0.027	0.017	0.037
D[ah]A	0.071	0.054	0.066	0.054	0.062	0.050
FLA	0.117	0.085	0.097	0.102	0.086	0.080
FLU	0.732	0.685	0.805	0.854	0.898	0.858
IND	0.416	0.237	0.372	0.250	0.392	0.376
NAP	1.101	0.933	1.187	1.063	1.235	0.684
PHN	0.508	0.438	0.490	0.522	0.380	0.555
PYR	0.187	0.167	0.196	0.231	0.221	0.190

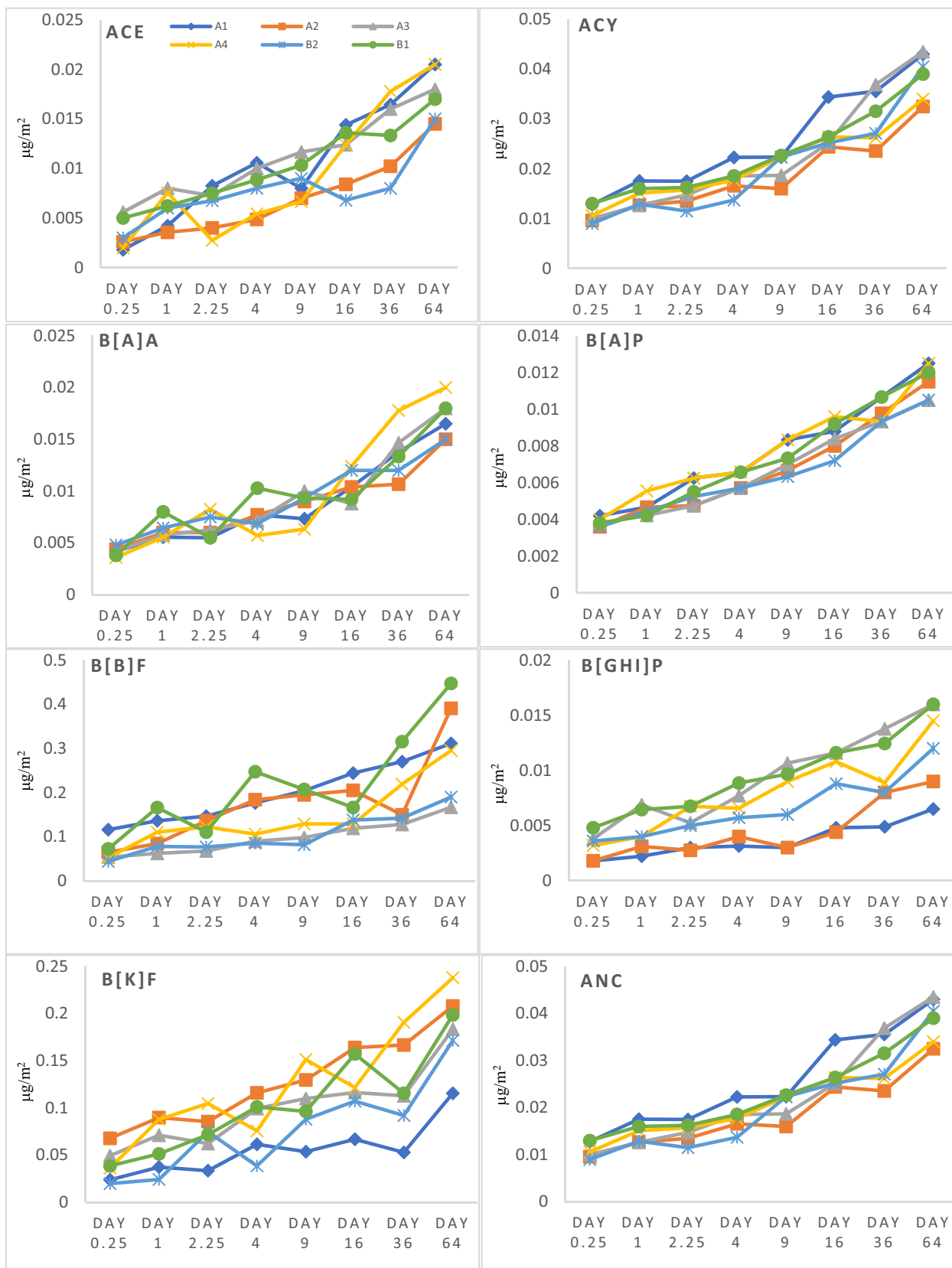


Fig. 1. The leaching profile ($\mu\text{g}/\text{m}^2$) of 16 EPA PAHs during 8 stages of DSLT experiments.

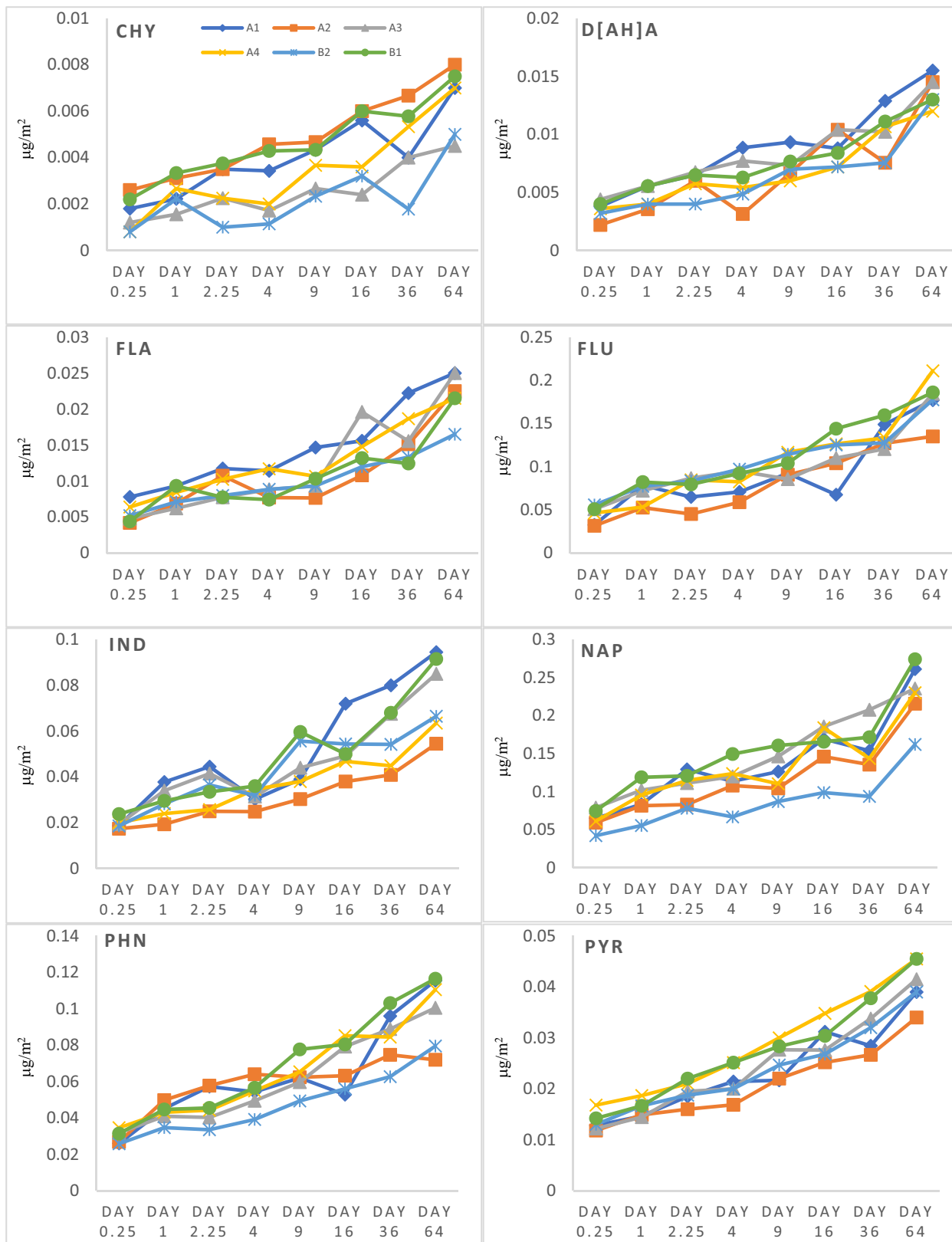


Fig. 1 (continued).

3.2.3. Leaching profile of PAHs

Fig. 1 illustrates the leaching profile of each PAH under investigation in the present study at different stages of DSLT (0.25, 0.75, 1.25, 1.75, 5, 7, 20 and 28 days). The values reported in Fig. 1 are in µg PAH per unit surface of the specimens. In general, the leaching profiles of all PAHs showed that the

release per surface area of all specimens increased during all stages of DSLT with some exceptions of reduced release at some stages (e.g., ACE: A4 specimen, day 2.25). The increase in release of PAHs may be due to longer durations of sampling time intervals at late stages of DSLT which increased the contact time between asphalt specimen surfaces and the leachant.

Consequently, higher concentrations of PAHs in rubberised asphalt were released. The leaching profile of ACE illustrates that the released concentrations from unit surface of A2 and B2 specimens were generally lower than other mix design specimens. As described in Section 3.2.2, this may be due to lower content of PAHs in 50/70 pen bitumen or its role in reducing PAHs release from crumb rubber content. The same pattern was observed for ANC, B[k]F, D[ah]A, NAP and PYR. By comparing the slope of lines during different stages of DSLT, it was observed that at earlier stages of experiments, the increase of release had a lower rate (gentle slope) for all PAHs. However, a sharp slope and increase in release per surface area of specimens was observed at last stage of most PAHs release profiles. This may be due to 2 main factors: 1) the long contact time (28 days) between specimens and leachant; 2) role of increased pH of the leachant on mobility and release of PAHs from surface of asphalt specimens (Fathollahi and Coupe, 2021b).

According to the leaching profile of PAHs from rubberised asphalts, the lowest released concentrations per surface area of specimens were associated with ACE (0.001–0.020 $\mu\text{g}/\text{m}^2$), ANC (0.002–0.015 $\mu\text{g}/\text{m}^2$), B[a]A (0.003–0.021 $\mu\text{g}/\text{m}^2$), B[a]P (0.003–0.012 $\mu\text{g}/\text{m}^2$), B[ghi]P (0.001–0.016 $\mu\text{g}/\text{m}^2$) and CHY (0.001–0.007 $\mu\text{g}/\text{m}^2$). This observation was consistent with cumulative released concentrations from specimens presented in Table 5. However, the highest release concentrations per surface area were for B[b]F (0.053–0.447 $\mu\text{g}/\text{m}^2$), B[k]F (0.019–0.208 $\mu\text{g}/\text{m}^2$) and NAP (0.042–0.274 $\mu\text{g}/\text{m}^2$) which led to the highest cumulative released during 64-day DSLT experiments.

3.3. Modelling the leaching of PAHs

The results from all stages of DSLT tests (Fig. 1) and cumulative release per surface area (Table 4) of all asphalt mix design specimens were modelled using diffusion leaching models elaborated in the Materials and methods section. Effective diffusion coefficient (ρD_x), diffusion coefficient in water (ρD_y), physical retention factor ($\rho\tau$), chemical retention factor (ρR_x) were calculated for all PAHs release profiles during the DSLT experiments and are presented in Table Supporting Information (SI) 1. The regression analysis of the released PAHs per surface area of samples (Fig. 1) revealed that all 16 PAHs under investigation had a slope ranging between 0.39 and 0.63 for mix designs A1, A3, A4 and B1 which fitted within the slope value ranges associated with diffusion-controlled leaching (NEN 7345). However, for mix designs A2 and B2 the slope values ranged between 0.30 and 0.58 which did not fit the diffusion-controlled leaching model for last stage of DSLT experiments (between day 36 and 64). This observation was in line with reports from previous studies (Birgisdóttir et al., 2007; Brandt and De Groot, 2001).

According to Table SII, the value of effective diffusion coefficient (ρD_x) ranges between 16.7 and 22.04 for different mix designs of rubberised asphalt. According to the ρD_x equation, the effective diffusion coefficient is divided into ρD_y , $\rho\tau$ and ρR_x . The values of ρD_y (ACE) ranged between 11.54 and 13.94 for 6 different mix designs in this study. This observation revealed that the tendency of ACE to be released from specimen surface into the leachant was not significantly different for A- or B-mix designs. Moreover, the value of ρD_y was not significantly different for 16 PAHs which indicated that their diffusion coefficient in water did not significantly vary. The physical retardation values ($\rho\tau$) ranged between 3.51 and 6.54 for different PAHs and asphalt mix designs. The statistically significant variety in $\rho\tau$ value showed that the physical retardation of the asphalt specimens in contact with water was dependent on the asphalt constituents and amount of released PAHs. Finally, the value of ρD_x was very similar for all mix designs of specimens, indicating the fact that the specimen mix designs did not have any correlation with the type of PAH leached out into the leachant during the DSLT experiments (Birgisdóttir et al., 2007). Overall, the diffusion coefficients from modelling the DSLT data revealed that the leaching process of 16 priority PAHs from surface of A1, A3, A4 and B1 rubberised asphalts fitted all the criteria set by NEN 7345 standard for diffusion-controlled leaching during all stages of DSLT. However, late stages of DSLT for A2 and B2 mix design specimens partly fitted in criteria

of diffusion-controlled leaching. This observation was in line with A2 and B2 specimens releasing lower concentrations of PAHs compared to specimens with similar content of crumb rubber granulates in their mix design.

4. Conclusion

In this study the availability of 16 priority PAHs in crumb rubber granulates and rubberised asphalts were evaluated prior to performing the DSLT leaching tests to, for the first time, quantify and model the leaching behaviour of manufactured asphalts specimens containing crumb rubber granulates. The total concentration of 16 EPA PAHs in the crumb rubber derived from end-of-life tyres was as follows: ACE (0.061 $\mu\text{g}/\text{g}$), ACY (0.108 $\mu\text{g}/\text{g}$), ANC (0.266 $\mu\text{g}/\text{g}$), B[a]A (1.358 $\mu\text{g}/\text{g}$), B[a]P (1.152 $\mu\text{g}/\text{g}$), B[b]F (2.623 $\mu\text{g}/\text{g}$), B[ghi]P (3.535 $\mu\text{g}/\text{g}$), B[k]F (1.282 $\mu\text{g}/\text{g}$), CHY (0.612 $\mu\text{g}/\text{g}$), D[ah]A (0.119 $\mu\text{g}/\text{g}$), FLA (2.485 $\mu\text{g}/\text{g}$), FLU (0.092 $\mu\text{g}/\text{g}$), IND (0.315 $\mu\text{g}/\text{g}$), NAP (0.043 $\mu\text{g}/\text{g}$), PHN (1.012 $\mu\text{g}/\text{g}$) and PYR (8.322 $\mu\text{g}/\text{g}$). The total content of PAHs in rubberised asphalt specimens were lower than crumb rubber granulates and varied between 0.019 and 4.992 $\mu\text{g}/\text{g}$ depending on the volume of crumb rubber granulates in the asphalt concrete mix design and type of binder. This observation was due to 50–56% volume of crumb rubber granulates in the asphalt concrete mix designs.

Results of the leaching experiments revealed that the highest leached PAHs during DSLT tests of rubberised asphalts were B[b]F, B[k]F and NAP with a 64-days cumulative release per specimen surface area of 1.733, 1.027, 1.235 $\mu\text{g}/\text{m}^2$, respectively. ACE, FLA, FLU and IND were released in cumulative concentrations between 0.1 and 1 $\mu\text{g}/\text{m}^2$. The PAHs with a cumulative release potential below 0.1 $\mu\text{g}/\text{m}^2$ during DSLT were B[a]A, B[a]P, B[g,h,i]P and CHY. The mathematical modelling of leaching tests results indicated that the release of 16 EPA PAHs from the surface of A1, A3, A4 and B1 rubberised asphalt specimens had a diffusion-controlled nature during all stages of leaching experiments.

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Alireza Fathollahi: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing. **Christina Makoundou:** Investigation, Writing – review & editing. **Stephen J. Coupe:** Conceptualization, Methodology, Validation, Writing – review & editing. **Cesare Sangiorgi:** Validation, 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.

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