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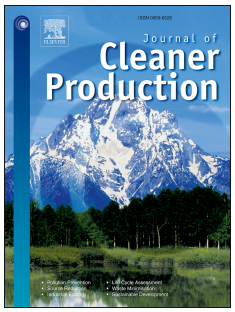

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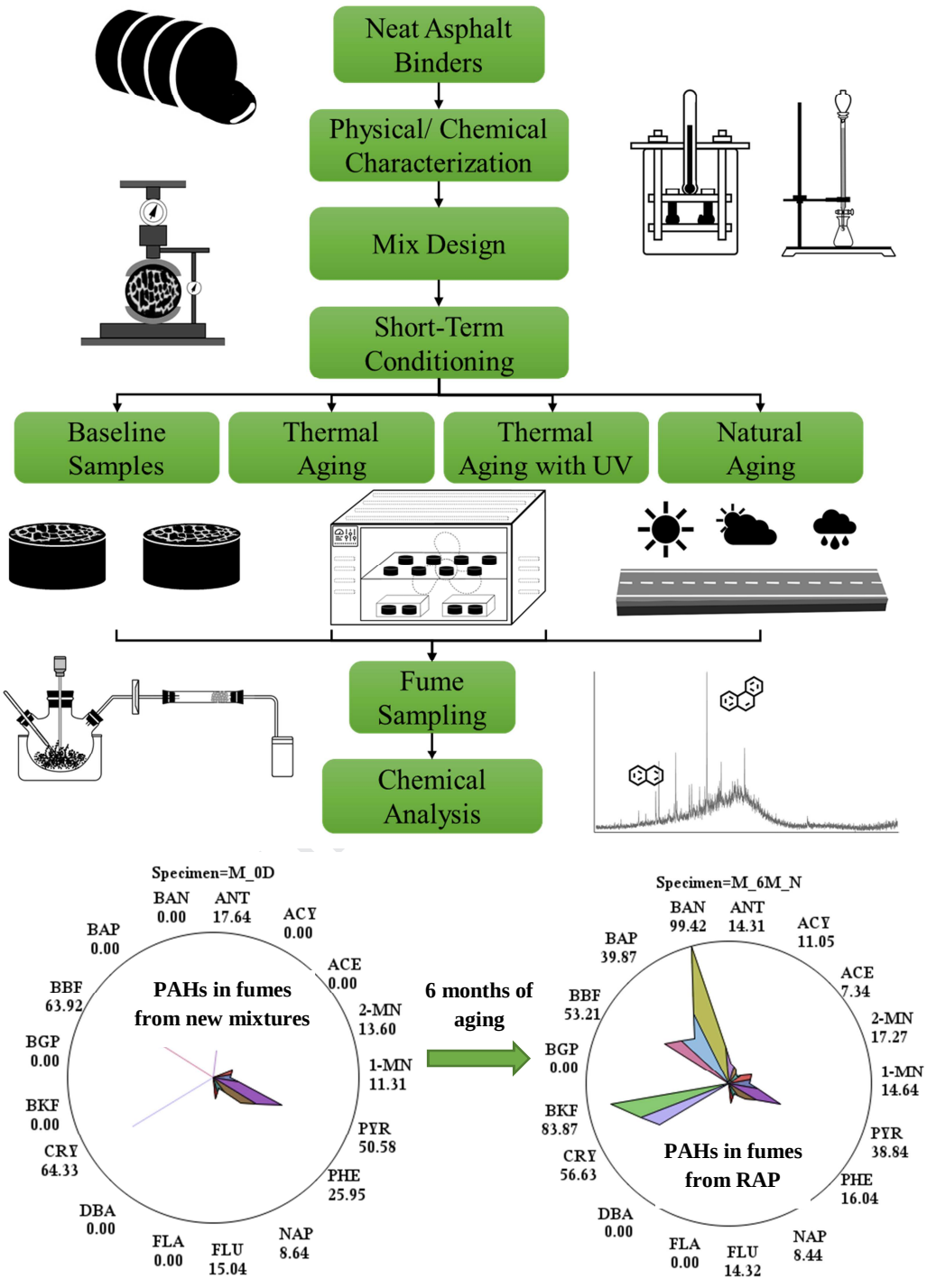
Shicong Mo: performing the experiments, writing the initial draft. Yuhong Wang: formulation of research goals and aims, design of methodology, data analysis. Feng Xiong: Supervision. Chunjin Ai: Development of test method, validation of experimental results. Dawei Wang: Acquisition of financial support. Giin Yu Amy TAN: provision of assistance on experiments and analysis software.

Graphical Abstract



Changes of asphalt fumes in hot-mix asphalt pavement recycling

Shicong Mo[1]; Yuhong Wang[2*]; Feng Xiong[3]; Chunjin Ai[4], Dawei Wang[5], Giin Yu Amy TAN[6]

Abstract: Hot-mix asphalt pavement recycling is widely practiced for its economic and environmental benefits. Existing studies are mainly focused on the engineering properties of reclaimed asphalt pavement (RAP) materials, without considering their impacts on the generated asphalt fumes—a widely recognized environmental hazard. The effects of using RAP on asphalt fumes are systematically studied in this research. Asphalt binders from different sources were used to create RAP materials in three aging conditions. Asphalt fumes were generated and collected from non-aged asphalt materials as well as RAP materials, followed by gravimetric and chemical analysis of the collected asphalt fumes. RAP materials were found to generate greater amount of particulates in asphalt fumes as compared with non-aged ones. RAP materials are also associated with increase in the types and concentrations of polycyclic aromatic hydrocarbons (PAHs) in asphalt fumes, especially those PAHs with more than three aromatic rings. PAHs increase in asphalt fumes is particularly noticeable for RAP created in the natural aging condition. It is reasonable to conclude that asphalt fumes generated from RAP become more hazardous, hence deserving more attention from researchers and practitioners. The mechanisms of the increase in PAHs are discussed, in addition to field exposure studies and mitigation measures.

Keywords: asphalt fumes, reclaimed asphalt pavements, polycyclic aromatic hydrocarbons, oxidation, health

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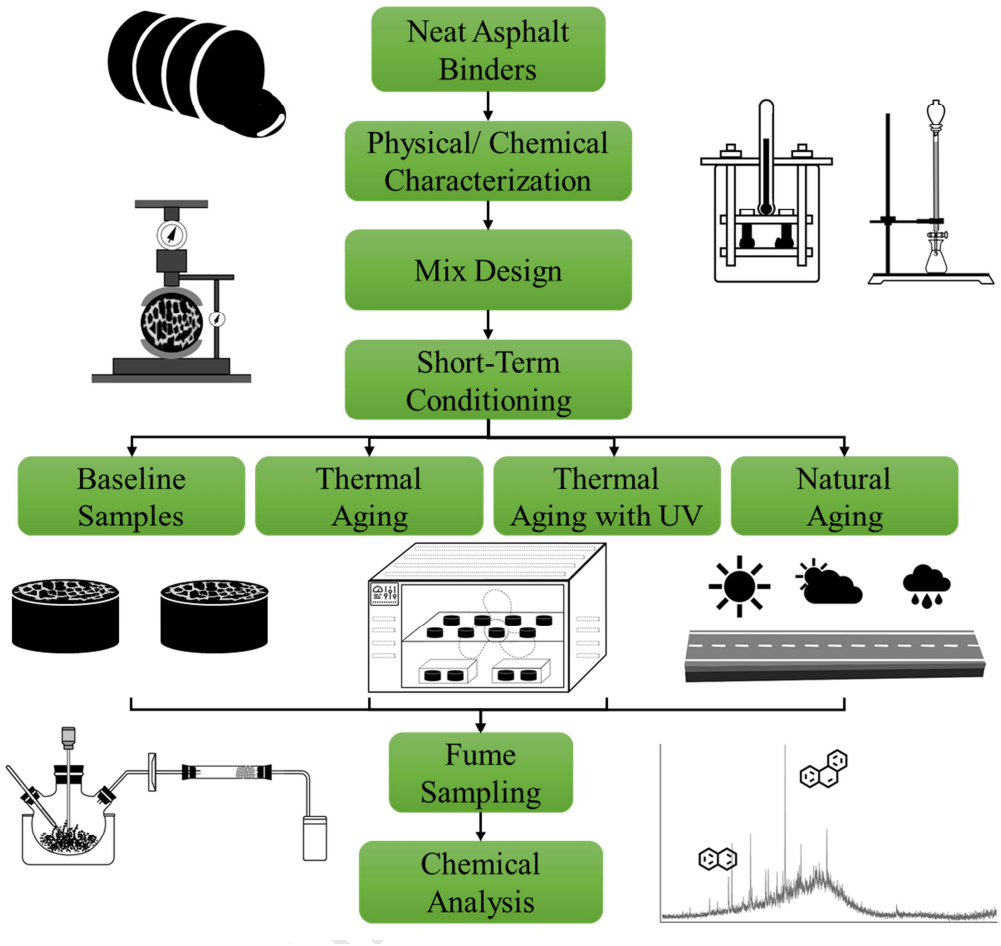
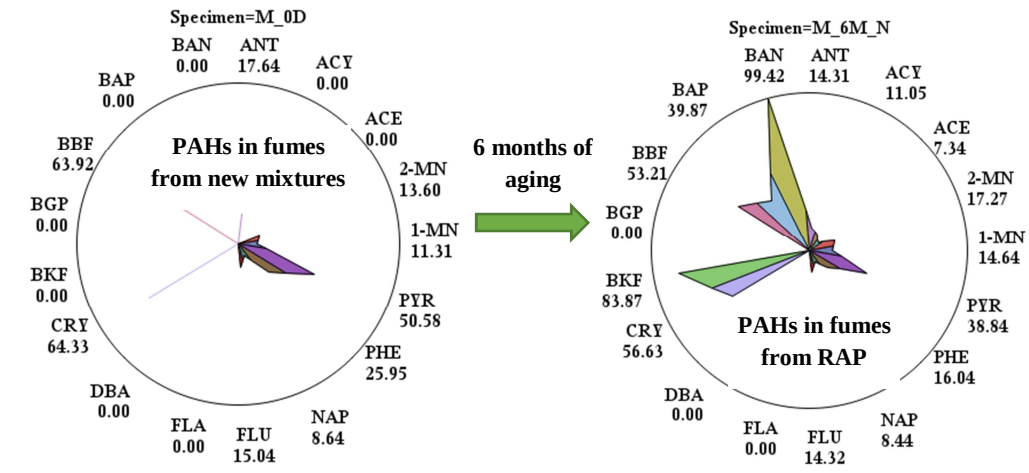
Graphical Abstract





Abbreviations

Analytes in the standard PAHs mixture

Analyte	Abbr.	MM (g/mol)	Analyte	Abbr.	MM (g/mol)
Naphthalene	NAP	128.17	Pyrene	PYR	202.26
2-Methylnaphthalene	2-MN	142.20	Benzo(a)anthracene	BAN	228.29
1-Methylnaphthalene	1-MN	142.20	Chrysene	CRY	228.29
Acenaphthylene	ACY	152.20	Benzo(b)fluoranthene	BBF	252.32
Acenaphthene	ACE	154.21	Benzo(k)fluoranthene	BKF	252.32
Fluorene	FLU	166.22	Benzo(a)pyrene	BAP	252.32
Phenanthrene	PHE	178.23	Indeno(1,2,3-cd)pyrene	IND	276.34
Anthracene	ANT	178.23	Dibenzo(a,h)anthracene	DBA	278.35
Fluoranthene	FLA	202.26	Benzo(g,h,i)perylene	BGP	276.34

*Abbr.: Abbreviation; MM: Molecular Mass

1 Introduction

The majority of paved roads around the world are surfaced with hot-mix asphalt (HMA) pavements (Mallick et al., 2017), which are also widely used for the construction of airport runways, parking lots, and other facilities. It is estimated that about 1.6 trillion metric tons of asphalt mixtures are produced annually for the construction, rehabilitation, and maintenance of the paved civil infrastructures (NAPA and EAPA, 2011). The life expectancies of HMA pavements range from a few years to several decades. At the end of their service lives, HMA pavements need to be demolished, creating a large amount of wastes. In the United States alone, for instance, about 100 million tons of asphalt pavements are milled off annually in road resurfacing and widening (MAPA, 2019). The demolished pavements, however, still contain valuable aggregate and asphalt binder. If unattended, they form a significant source of inert solid wastes. Therefore, asphalt pavement recycling has become a common practice for cost saving and environmental conservation (Alam et al., 2010; Wang, 2016).

Different technologies are available for asphalt pavement recycling. A simple approach is to use reclaimed asphalt pavement (RAP) materials as a granular road base. A more value-added approach is to mix RAP with virgin materials in a HMA plant to produce new mixtures. The typical amount of RAP added to the new mixtures ranges from less than 10% to 30% (Williams et al., 2018). The extreme scenario is 100% hot in-place recycling (Lo Presti et al., 2016; Zaumanis et al., 2014). Existing literature on HMA containing RAP is mainly focused on their engineering properties.

There have been persistent concerns over health risks associated with HMA construction. HMA pavement needs to be placed and compacted at high temperatures ranging from 135 °C for conventional HMA to 260 °C for special ones (Read and

Whiteoak, 2006). At high temperatures, enormous volatile organic compounds (VOCs) and aerosols are emitted, collectively known as asphalt fumes. The hazardous nature of asphalt fumes is widely recognized (Chong et al., 2018; Mickelsen et al., 2006; NIOSH, 2000). Although the use of RAP promotes sustainable development by reducing waste, saving unrenewable materials, and cutting down carbon footprint, it aggravates concerns on workers' health. RAP-containing HMA mixtures typically need to be heated to even higher temperatures to compensate for the fluidity loss of asphalt binder due to aging. The amount of generated asphalt fumes is found to be closely related to HMA temperature (D'Angelo et al., 2008; Mo et al., 2019). In a field study, McClean et al. (2004) found that HMA mixtures with high RAP content are associated with a five-time increase in inhalation polycyclic aromatic compounds (PAC) exposures as compared with mixtures with low RAP content. Moreover, aging causes chemical changes in asphalt binders. How such changes affect the quantity and hazardous potential of asphalt fumes remains unknown. Health is an important component in the social dimension of sustainable development; therefore, it is necessary to investigate how the extensive use of RAP affects asphalt fumes that will be breathed by workers.

This study aims to examine possible changes in asphalt fumes generated from RAP. The study arises from concerns expressed by road construction workers and managers, who feel that asphalt fumes generated from HMA mixtures with high RAP content are more obnoxious (Li, 2017). The study is focused on possible changes in those 16 Environmental Protection Agency (EPA) priority polycyclic aromatic hydrocarbons (PAHs) and 2 other PAHs in asphalt fumes generated from RAP, as compared with those generated from virgin asphalt mixtures (EPA, 2014). A rigorous experimental

procedure was designed and followed to assist the investigation, which is summarized below:

(1) Asphalt binders from different manufacturers around the world were used for experiments. The chemical compositions of asphalt binders, which vary greatly with their origins, affect the chemical compositions of generated asphalt fumes (Mo et al., 2019). This study is interested in understanding if asphalt binders of different origins show similar trends in producing asphalt fumes before and after aging.

(2) A standard HMA mixture was designed and prepared, and subsequently treated in different aging conditions to create RAP. The longest treatment is 184 days of aging in a field pavement exposed in natural conditions. The uniform mixture design and systematic aging treatments make the prepared RAP materials and generated asphalt fumes more comparable.

(3) A new set of equipment was built to generate and collect asphalt fumes.

(4) Asphalt fumes collected from the aged samples were analyzed and compared for gravimetrical and chemical differences.

The HMA paving industry employs a large number of workers. In the U. S. alone, there were about 300,000 paving workers (NIOSH, 2000). Understanding the working environment of the workers and making it less hazardous are very important. With the increasing use of RAP, it becomes necessary to evaluate its effects on generated asphalt fumes. This study reveals how PAHs in asphalt fumes change as fresh HMA materials turn into RAP. The results can be combined with future field sampling efforts to help the industry understand the risk of using RAP and take measures to control such risks.

2 Methodology

2.1 Experimental procedures

The experimental procedure is shown in Fig. 1. Four neat (not modified by any modifiers) asphalt binders were collected, and their physical and chemical properties were characterized. A standard HMA mix design was used to produce uniform HMA mixtures. After being mixed and short-term aged, the loose mixtures were compacted by using a Marshall compaction machine. The entire process is to simulate the actual process of HMA mixture production, transportation, placement and compaction in construction. Parts of the compacted specimens serve as baseline materials for generating asphalt fumes, and the rest were subjected to three aging treatments: (1) 30 days of aging at 60°C and in a dark environment, (2) 30 days of aging at 60°C and under ultraviolet (UV) light, and (3) 184 days of aging in a field pavement. The purpose of using different methods to create RAP is to investigate how different aging conditions affect the chemical compositions of asphalt fumes generated from RAP. After the aging treatments, the samples were broken loose and placed in a specially developed apparatus to generate asphalt fumes in a uniform condition. The collected fumes were subsequently analyzed gravimetrically and chemically

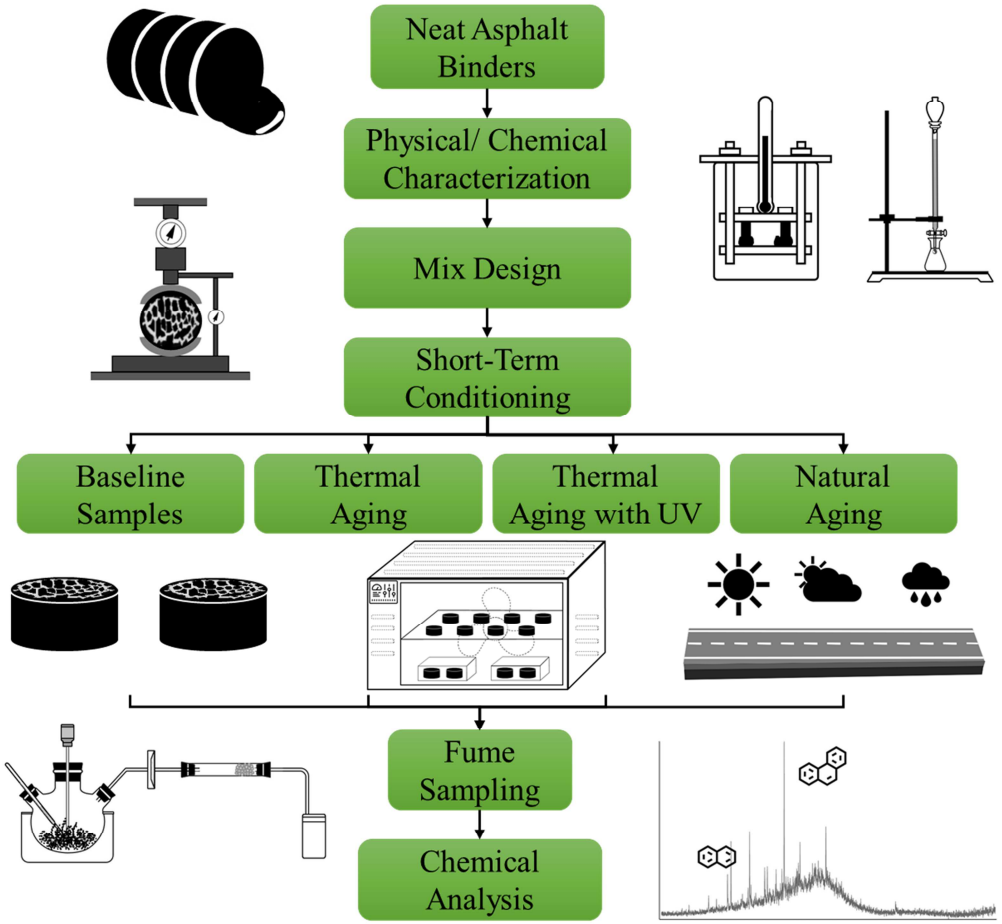


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Fig. 1 Diagram of the experimental procedure

2.2 Materials

2.2.1 Asphalt binders

Four neat asphalt binders were obtained from different suppliers: Shell Pen 60/70 (designated as S60/70) is commonly used in some Southeast Asian countries and regions, Nynas Pen 70/100 (N70/100) is commonly used in Europe, Sinopec JL70 (JL70) and Sinopec MM70 (MM70) are commonly used in mainland China. The typical engineering properties of those asphalt binders are shown in Table 1, including: penetration, softening point, and viscosity. The properties suggest that S60/70 is the softest among all the asphalt binders at the usage temperature, while MM70 is the hardest. At 135 °C, however, N70/100 has the lowest viscosity. The asphalt binders apparently vary in consistency at a same temperature as well as in consistency sensitivity to temperature.

Table 1 Physicochemical characterization of the selected asphalt binders

Physicochemical characterization		Unit	Shell Pen 60/70 (S60/70)	Nynas Pen 70/100 (N70/100)	Sinopec MM70 (MM70)	Sinopec JL70 (JL70)
Engineering	Penetration (25 °C)	0.1mm	68.0	64.0	56.6	63.2
	Softening Point, R&B	°C	46.2	47.0	50.3	48.9
	Viscosity (135 °C)	Pa.sec	0.413	0.410	0.519	0.570
Corbett Fraction	Saturates	wt%	12.58%	20.04%	17.96%	14.84%
	NA	wt%	43.51%	39.29%	41.73%	46.42%
	PA	wt%	20.10%	14.43%	15.79%	16.22%
	Asphaltenes	wt%	23.81%	26.24%	24.52%	22.52%

Asphalt contains numerous types of organic molecules that vary with crude oil source, manufacturing process, and aging states. Hence, no attempt has been made to separate

and identify the individual asphalt molecules (Petersen, 2009). Instead, asphalt is usually separated into some general fractions in chemical analysis. A commonly used fraction scheme is Corbett fraction (ASTM, 2018; Thenoux et al., 1988), by which asphalt is divided into four fractions in accordance with the rising polarity of the molecules, including: saturates, naphthene aromatics (NA), polar aromatics (PA), and asphaltenes. Saturates and NA are the fluid phase, while asphaltenes are colloidal particles peptized by PA. The Corbett fractions of the four asphalt binders are also shown in Table 1. The results suggest that S60/70 has the highest aromatic fractions (NA+PA), while N70/100 has the lowest ones. Conversely, N70/100 has the highest asphaltene and saturate contents.

2.2.2 Asphalt mixtures

To facilitate the comparison of asphalt fumes generated from different materials, only one type of aggregate was used to create HMA mixtures, and a standard mix design was followed. The chosen mix design is a commonly used surface mixture for highways. The gradation of the mix design is shown in Table 2. The asphalt binder content is 6%, determined through the Marshall mixture design method.

Table 2 Aggregate gradation

B.S. Sieve (mm)	14	10	5	2.36	1.18	0.6	0.3	0.15	0.075	<0.075
% Passing	100	96	74	53	38	26	17	11	6.5	6.5

The HMA mixtures were produced at a temperature of 155 °C. The loose mixtures were subsequently conditioned at 135 °C in an oven for 4 hours to simulate the short-term aging of HMA mixtures during production, transportation, and placement. After conditioning, the Marshall apparatus was used to create compacted HMA mixtures.

192 The freshly produced Marshall samples were cooled for 24 hours. The baseline
193 samples were placed in a freezer to prevent further aging. The rest were subjected to
194 three types of aging treatments, as introduced below.

195 *2.3 Aging Treatments*

196 RAP is the result of asphalt mixture aging in the field. The predominant aging
197 mechanism in field pavements is asphalt oxidation (Lau et al., 1992; Petersen, 1986;
198 Wang et al., 2014; Zou et al., 2013). As introduced previously, three aging treatments
199 with different durations were applied to the Marshall samples.

200 The schematic diagram of a chamber specifically designed and built for this study is
201 shown in Fig. 2. The chamber consists of an upper and a lower compartment
202 separated by a rack and a layer of aluminum foil. UVA lamps were used to generate
203 UVA radiation in the upper compartment. UVA accounts for about 94% of terrestrial
204 UV radiation from sunlight (Diffey, 2002). The wavelength of the radiation light is
205 365 nm and the exposure intensity is approximately 7,500 μWcm^{-2}. The lower
206 compartment was used to simulate aging in a dark environment. In addition to
207 protection by the foil reflector, shield boxes were used to further protect the samples
208 from UV radiation. The aging temperature was set to be 60 °C, which is a commonly
209 seen temperature of asphalt pavement surfaces in summer months.

210

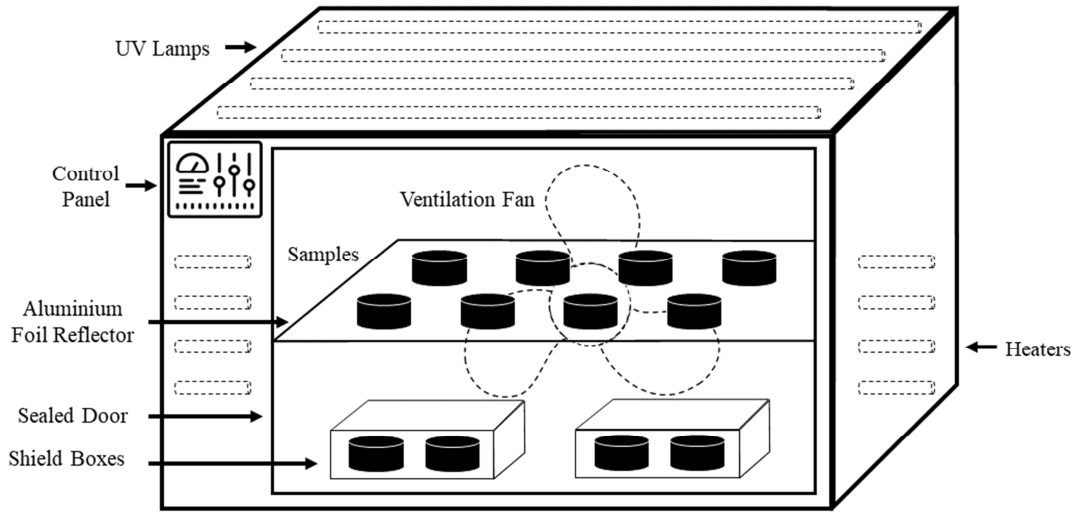


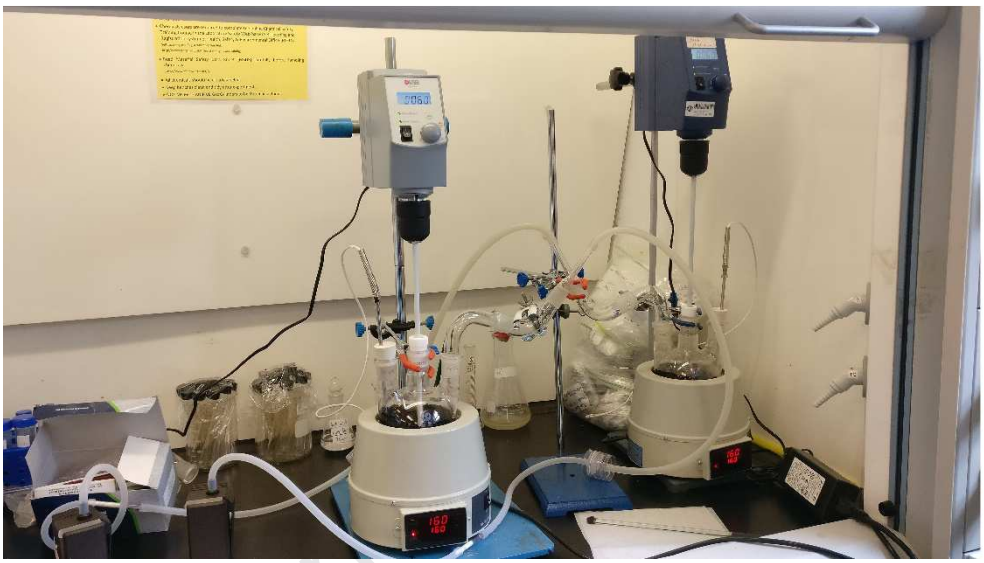
Fig. 2 Schematic diagram of the photo- and thermal-oxidation chamber

Natural aging treatment was conducted on an unused road pavement in Hong Kong. Holes slightly larger than the Marshall samples were drilled into the existing pavements. The Marshall samples were then inserted into the drilled holes. The gap between the Marshall samples and the existing pavements was filled with sand. Due to the limited supply of asphalt binders, only three types of asphalt binders were used to create samples for natural aging, including S60/70, MM70 and JL70. Natural aging was conducted from March 29 to September 28 in 2018. According to weather data from the Hong Kong Observatory, air temperature ranged from 12.1 °C to 36.4 °C during the aging treatment period, with 126 out of 184 days having the maximum air temperature above 30 °C. The pavement surface temperature is usually much higher than the air temperature. The total rainfall in the region was 1883.9 mm during the observation period.

2.4 Fume generation and collection

A fume generator was used for generating asphalt fumes from asphalt mixtures and collecting the fumes for further analysis (see Fig. 3). It contains two major components: (1) a mixing and fume generation system that controls the mixture

230 temperature and agitates the mixtures to simulate the action of augers in an asphalt
231 paver in field construction, and (2) an asphalt fume collection system similar to the
232 setup used for collecting air-borne samples for the analysis of PAHs in accordance
233 with NIOSH 5515 (NIOSH, 1998b). More detailed descriptions on the fume generator
234 are provided by Mo et al. (2019).
235



236
237 **Fig. 3** Photo of the asphalt fume generator and collector
238

239 The compacted asphalt mixtures were first broken loose. They were then placed in the
240 asphalt fume generator, where the mixtures were reheated to 160 °C and mixed with a
241 propeller at 50-60 rpm. The fume generation and collection process lasts for 4.5 hours.
242 The sampling condition remains consistent for all the samples.

243 *2.5 Fume analysis*

244 2.5.1 Reagents and instruments for fume analysis

245 A certified standard solution of the 18 PAHs Mix (CRM 47543, TraceCERT®, lot no.
246 XA26145V) was purchased from Supelco (Sigma-Aldrich, Bellefonte, U.S.).
247 Acetonitrile, solvent for asphalt fume extraction, is HPLC grade supplied by Duksan
248 Pure Chemicals (Ansan, South Korea). Disposable syringes (3 ml, NORM-JECT®,

Henke Sass Wolf GMBH, Tuttlingen, Germany), PTFE syringe filters (0.45μm, hydrophobic, Membrane Solutions, Dallas, U.S.), and glass pasteur pipettes (Brand GMBH, Wertheim/Main, Germany) were supplied by the Oriental Chemicals & Lab. Supplies Ltd (Hong Kong, China).

The ultra-microbalance is Sartorius MC5 (sensitivity 0.001 mg, Sartorius GMBH, Gottingen, Germany). The ultrasonic bath is KQ-50D (Kunshan Ultrasonic Instruments Co., Kunshan, China). The GC-MS is Agilent 7890B Gas Chromatography with 5977B Single Quadruple Mass Spectrometer (Agilent Technologies, Palo Alto, U.S.).

2.5.2 Analysis procedures

The gravimetric analysis of total particulates (TP) in asphalt fumes was performed by dividing the mass of TP deposited on the filter membranes with the volume of fume-containing air, measured by the air pump in the fume collection system. An environmental chamber was used for conditioning the filter membranes before and after sampling (at ambient temperature of 25 ± 0.5 °C and relative humidity of 40 ± 1%) for 24 h. The mass of TP was obtained by measuring the mass increase of filter membranes.

The process of extracting organic soluble matters and the operation of GC/MS are described in Mo et al. (2019). The confirmation of PAH compounds was based on the comparision of retention time between the GC-chromatography of the sample and that of the standard PAH reference. For a positive confirmation, the retention time of a particular PAH analyte in the sample has to be within ± 0.1 min of the target analyte in the standard mixture (Shang et al., 2014).

The standard PAH solution was diluted by $10^{\wedge 2}$, $10^{\wedge 2.5}$, $10^{\wedge 3}$, $10^{\wedge 3.5}$, $10^{\wedge 4}$, and $10^{\wedge 4.5}$ times in acetonitrile and analyzed by using GC/MS. The peak values of each PAH

compound in the chromatograms of the diluted solutions were used to produce calibration curves, as shown in Table 3. The curves were used for quantitatively analysis of PAHs, and duplicate specimens were tested.

277 **Table 3** Calibration curves for the PAH compounds

Compounds	Retention time (min)	Calibration curve*	R^2	Detection limit (ug/mL)	Limit of quantification (ug/mL)
NAP	14.583	$y = 4{,}347.464x^{1.474}$	0.994	0.061	0.194
2-MN	17.701	$y = 2{,}239.999x^{1.454}$	0.996	0.060	0.191
1-MN	18.120	$y = 2{,}811.727x^{1.531}$	0.996	0.063	0.199
ACY	21.736	$y = 2{,}181.865x^{1.345}$	0.995	0.066	0.208
ACE	22.566	$y = 3{,}133.622x^{1.491}$	0.995	0.063	0.199
FLU	25.004	$y = 1{,}643.036x^{1.523}$	0.996	0.063	0.199
PHE	29.426	$y = 3{,}138.131x^{1.485}$	0.996	0.063	0.199
ANT	29.667	$y = 2{,}168.803x^{1.337}$	0.995	0.064	0.201
FLA	34.973	$y = 1719.701x^{1.409}$	0.995	0.063	0.198
PYR	35.972	$y = 2{,}322.573x^{1.459}$	0.994	0.066	0.209
BAN	41.653	$y = 737.761x^{1.405}$	0.998	0.198	1.598
CRY	41.812	$y = 2{,}314.158x^{1.309}$	0.995	0.064	0.201
BBF	46.336	$y = 786.087x^{1.367}$	0.997	0.196	1.615
BKF	46.428	$y = 1{,}015.932x^{1.331}$	0.998	0.201	1.575
BAP	47.602	$y = 899.188x^{1.207}$	0.998	0.187	1.694
IND	51.664	$y = 801.715x^{1.048}$	0.998	0.198	1.598
DBA	51.830	$y = 737.355x^{1.081}$	0.996	0.203	1.558
BGP	52.510	$y = 1{,}243.051x^{1.096}$	0.995	0.200	1.581

278 * x = concentration of analyte compound (ug/mL); y = peak height of analyte compound.

3 Results

3.1 Total particulates

Fig. 4 shows the concentrations of TP in asphalt fumes generated from the asphalt mixtures at 160 °C. Evidently, TP concentration varies with the source of asphalt binder: The concentration of TP generated from S60/70, MM70 and JL70 ranges from 19.970 mg/m^3 to 74.876 mg/m^3, while that generated from N70/100 ranges from 152.130 mg/m^3 to 160.392 mg/m^3. It also appears that aging increases the TP concentration. Aging by a combination of thermal and UV treatments seemingly resulted in the highest TP concentration increase as compared with the baseline, while aging in the natural condition resulted in the lowest TP concentration increase.

In spite of the small sample size, paired t-tests reject the null hypothesis (at the significance level of 0.05) that the TP concentrations of asphalt fumes generated from the non-aged asphalt mixtures are equal to (1) those from thermal-aged mixtures and (2) those from thermal- and UV-aged mixtures. The difference between the non-aged and natural-aged asphalt mixtures is not statistically significant, due to the even smaller sample size. Aging apparently plays an important role in the TP concentration of asphalt fumes. It is noted that natural aging treatment in this study only lasted for 6 months. On actual roads, pavements may be aged from 10 to 50 years before recycling and hence are more severely aged.

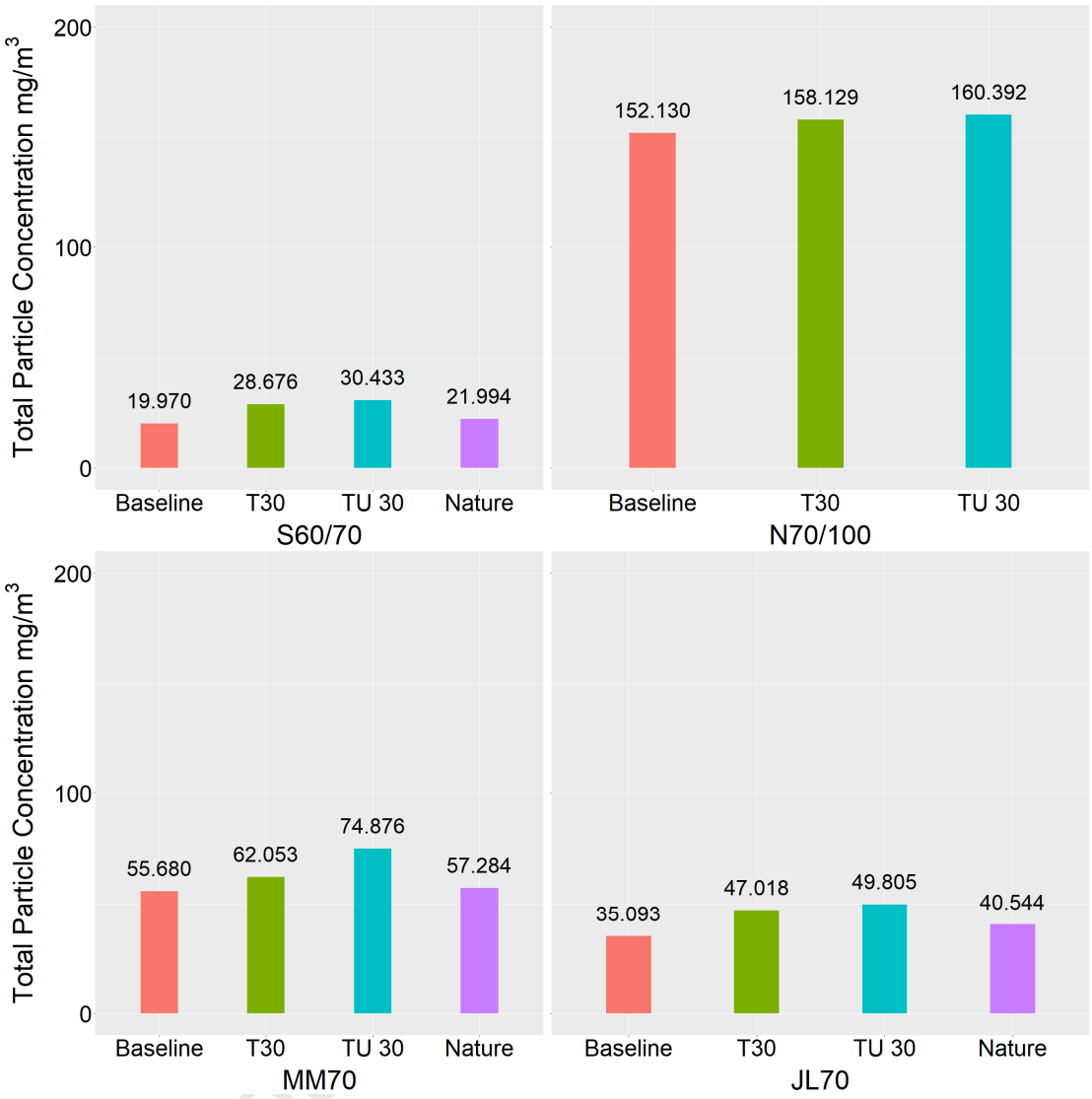


Fig. 4 TP concentrations of asphalt fumes (mg/m^3)

3.2 Identification of the PAH compounds

The GC chromatograms of one set of asphalt fume samples (S60/70) are shown in Fig. 5 for illustration purpose. As mentioned previously, a positive confirmation is made if the retention time of the suspected PAH compound is within ± 0.1 min of the retention time of the corresponding PAH compound in the reference chromatogram (Shang et al., 2014). According to this criterion, PAHs are identified (see Table 4 to Table 7) and summarized in Table 8. Several observations can be made from the results:

(1) Seven types of PAHs are found to be present in all the fume samples generated from mixtures made with different types of asphalt binders and of different aging states, including: NAP, 2-MN, 1-MN, PHE, ANT, PYR, and CRY.

(2) The types of detectable PAHs in asphalt fumes vary with the types of asphalt binders. For non-aged asphalt mixtures, N70/100 generates the largest number of identifiable PAHs as compared with others.

(3) Aging creates more identifiable PAH compounds. In general, asphalt mixtures subjected to natural aging generate the largest number of identifiable PAHs, followed by asphalt mixtures subjected to a combination of thermal and UV aging.

(4) Certain PAHs such as ACE, FLA, and BKF are only detected in aged asphalt mixtures. One notable PAH is BAP, which is a toxic compound classified as Group I *"carcinogenic to humans"* (IARC, 2018). While BAP can be found in asphalt fumes generated from all the asphalt mixtures made from N70/100, it can only be found in asphalt fumes generated from aged mixtures for asphalt binder S60/70, MM70, and JL70.

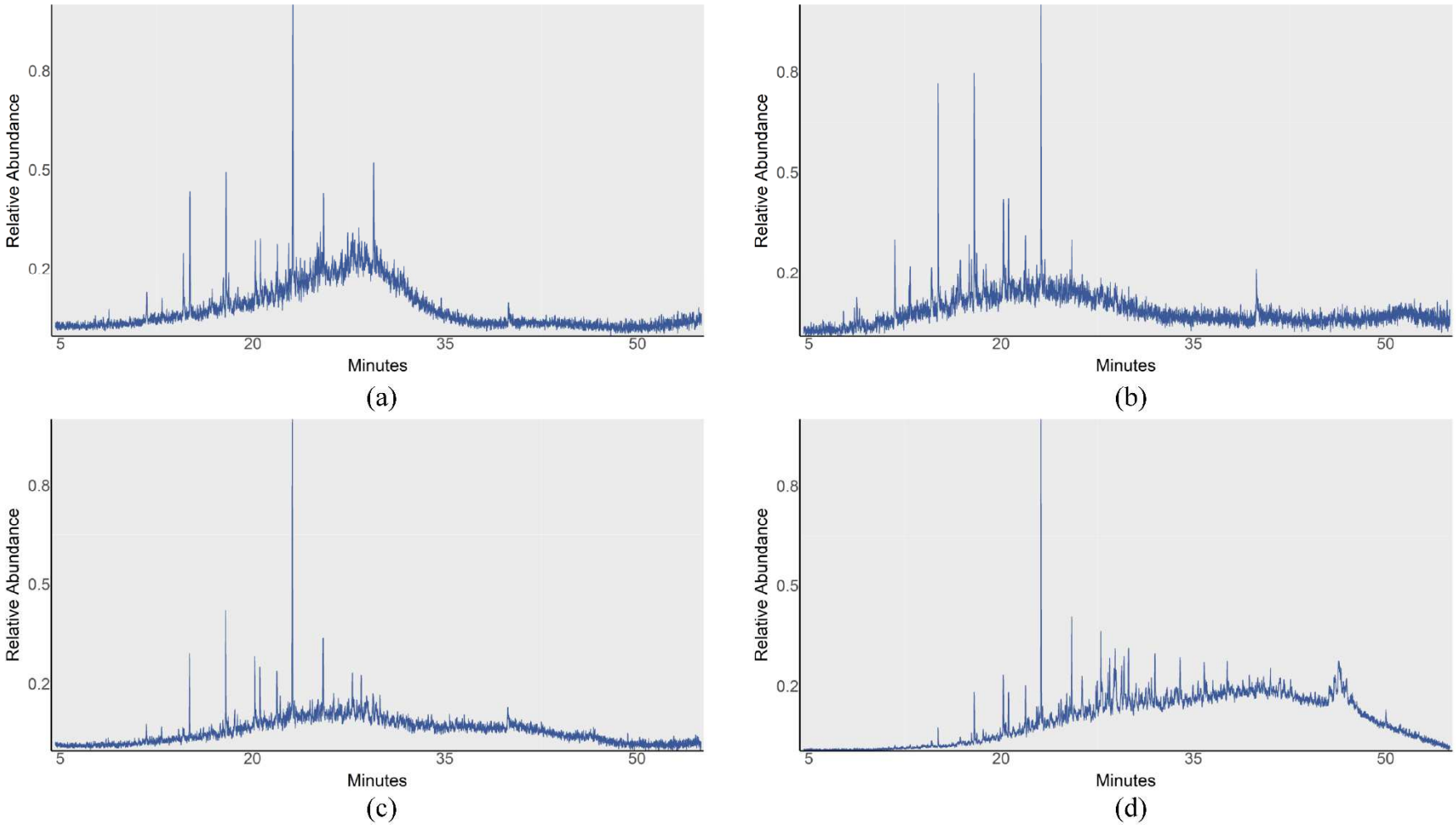


Fig. 5 The GC-chromatography of organic compounds in asphalt fumes generated from S60/70 asphalt mixture: (a) baseline, (b) 30 days of thermal aging, (c) 30 days of thermal and UV aging, and (d) 6 months of natural aging.

327 **Table 4** Retention time and deviation range of the PAHs for S60/70 Unit: minute

	RT	0 day		30 of days thermal oxidation		30 days of thermal with UV		6 months natural aging	
		RT	DTR	RT	DTR	RT	DTR	RT	DTR
NAP	14.583	14.570	-0.013	14.565	-0.018	14.565	-0.018	14.570	-0.013
2-MN	17.701	17.694	-0.007	17.688	-0.013	17.694	-0.007	17.683	-0.018
1-MN	18.120	18.114	-0.006	18.104	-0.016	18.109	-0.011	18.109	-0.011
ACY	21.736	--	--	21.839	0.103	21.741	0.005	21.824	0.088
ACE	22.566	--	--	--	--	22.561	-0.005	22.654	0.088
FLU	25.004	24.994	-0.010	25.025	0.021	24.979	-0.025	24.984	-0.020
PHE	29.426	29.420	-0.006	29.436	0.010	29.404	-0.022	29.404	-0.022
ANT	29.667	29.664	-0.003	29.653	-0.014	29.653	-0.014	29.659	-0.008
PYR	35.972	35.952	-0.020	35.947	-0.025	35.958	-0.014	35.947	-0.025
BAN	41.653	--	--	--	--	--	--	41.655	0.002
CRY	41.812	41.769	-0.043	41.759	-0.053	41.800	-0.012	41.748	-0.064
BBF	46.336	--	--	46.325	-0.011	46.330	-0.006	46.345	0.009
BAP	47.602	--	--	--	--	47.658	0.056	47.601	-0.001

328 * RT, retention time;

329 ** DTR, deviation in analyte retention time between the fume sample and the standard PAHs mixture

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331 **Table 5** Retention time and deviation range of the PAHs for JL70 Unit: minute

	RT	0 day		30 of days thermal oxidation		30 days of thermal with UV		6 months natural aging	
		RT	DTR	RT	DTR	RT	DTR	RT	DTR
NAP	14.583	14.570	-0.013	14.575	-0.008	14.575	-0.008	14.570	-0.013
2-MN	17.701	17.709	0.008	17.694	-0.007	17.688	-0.013	17.683	-0.018
1-MN	18.120	18.129	0.009	18.119	-0.001	18.119	-0.001	18.103	-0.017
ACY	21.736	21.730	-0.006	21.730	-0.006	21.673	-0.063	21.761	0.025
FLU	25.004	--	--	--	--	24.984	-0.020	24.989	-0.015
PHE	29.426	29.420	-0.006	29.441	0.015	29.415	-0.011	29.410	-0.016
ANT	29.667	29.674	0.007	29.679	0.012	29.653	-0.014	29.659	-0.008
PYR	35.972	35.953	-0.019	35.952	-0.020	35.953	-0.019	35.963	-0.009
BAN	41.653	--	--	41.650	-0.003	41.639	-0.014	41.665	0.012
CRY	41.812	41.759	-0.053	41.743	-0.069	41.759	-0.053	41.790	-0.022
BBF	46.336	--	--	46.366	0.030	46.345	0.009	46.345	0.009
BAP	47.602	--	--	47.622	0.020	47.606	0.004	47.616	0.014

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335 **Table 6** Retention time and deviation range of the PAHs for MM70 Unit: minute

	RT	0 day		30 of days thermal oxidation		30 days of thermal with UV		6 months natural aging	
		RT	DTR	RT	DTR	RT	DTR	RT	DTR
NAP	14.583	14.580	-0.003	14.581	-0.002	14.586	0.003	14.575	-0.008
2-MN	17.701	17.688	-0.013	17.699	-0.002	17.694	-0.007	17.694	-0.007
1-MN	18.120	18.119	-0.001	18.114	-0.006	18.124	0.004	18.104	-0.016
ACY	21.736	--	--	21.824	0.088	21.699	-0.037	21.684	-0.052
ACE	22.566	--	--	--	--	22.587	0.021	22.493	-0.073
FLU	25.004	24.989	-0.015	24.984	-0.020	24.994	-0.010	24.984	-0.020
PHE	29.426	29.420	-0.006	29.425	-0.001	29.420	-0.006	29.415	-0.011
ANT	29.667	29.653	-0.014	29.674	0.007	29.664	-0.003	29.653	-0.014
PYR	35.972	35.963	-0.009	35.952	-0.020	35.953	-0.019	35.947	-0.025
BAN	41.653	--	--	41.665	0.012	41.639	-0.014	41.670	0.017
CRY	41.812	41.764	-0.048	41.758	-0.054	41.753	-0.059	41.769	-0.043
BBF	46.336	46.356	0.020	46.345	0.009	46.366	0.030	46.371	0.035
BKF	46.428	--	--	--	--	--	--	46.475	0.047
BAP	47.602	--	--	47.559	-0.043	47.591	-0.011	47.663	0.061

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338 **Table 7** Retention time and deviation range of the PAHs for N70/100 Unit: minute

	RT	0 day		30 of days thermal oxidation		30 days of thermal with UV	
		RT	DTR	RT	DTR	RT	DTR
NAP	14.583	14.575	-0.008	14.586	0.003	14.570	-0.013
2-MN	17.701	17.683	-0.018	17.694	-0.007	17.694	-0.007
1-MN	18.120	18.114	-0.006	18.114	-0.006	18.098	-0.022
ACY	21.736	--	--	21.694	-0.042	21.808	0.072
ACE	22.566	--	--	22.566	0.000	22.566	0.000
FLU	25.004	--	--	25.01	0.006	24.911	-0.093
PHE	29.426	29.415	-0.011	29.446	0.020	29.404	-0.022
ANT	29.667	29.664	-0.003	29.679	0.012	29.659	-0.008
FLA	34.973	--	--	34.961	-0.012	34.951	-0.022
PYR	35.972	35.953	-0.019	35.952	-0.020	35.953	-0.019
BAN	41.653	41.644	-0.009	41.644	-0.009	41.644	-0.009
CRY	41.812	41.753	-0.059	41.758	-0.054	41.743	-0.069
BBF	46.336	46.335	-0.001	46.345	0.009	46.335	-0.001
BKF	46.428	--	--	46.454	0.026	46.491	0.063
BAP	47.602	47.611	0.009	47.606	0.004	47.606	0.004

DBA	51.830	51.830	0.000	51.845	0.015	51.887	0.057
BGP	52.510	52.525	0.015	52.525	0.015	52.502	0.010

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352 **Table 8** The detected PAHs in the samples

Compounds	S60/70				N70/100			MM70				JL70			
	Baseline	T30	TU30	Nature	Baseline	T30	TU30	Baseline	T30	TU30	Nature	Baseline	T30	TU30	Nature
NAP	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
2-MN	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
1-MN	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
ACY		✓	✓	✓		✓	✓		✓	✓	✓	✓	✓	✓	✓
ACE			✓	✓		✓	✓			✓	✓				
FLU	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓			✓	✓
PHE	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
ANT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
FLA						✓	✓								
PYR	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
BAN				✓	✓	✓	✓		✓	✓	✓		✓	✓	✓
CRY	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
BBF		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
BKF						✓	✓				✓				
BAP			✓	✓	✓	✓	✓		✓	✓	✓		✓	✓	✓
DBA					✓	✓	✓								
BGP					✓	✓	✓								
Total	8	10	12	13	12	17	17	9	12	13	14	9	11	12	12

353 *T30: 30 days of thermal oxidative aging; TU 30: 30 days of thermal oxidative with UV radiative aging; Nature: 6 months natural aging

354 *3.3 Quantitative analysis of PAHs in collected asphalt fumes*

355 3.3.1 PAH concentrations

356 Fig. 6 shows the total concentrations of all the detected PAHs in the collected asphalt
357 fumes. It is obvious that the concentrations of PAHs are affected by asphalt type.
358 PAH concentrations in fume samples from N70/100 asphalt mixtures are much higher.
359 Aging also apparently increases the total concentrations of those detected PAHs
360 except for 30-day thermal aging of binder N70/100. Paired t-tests do not yield
361 statistically significant difference (at the 0.05 significance level) due to small sample
362 size and large variation.

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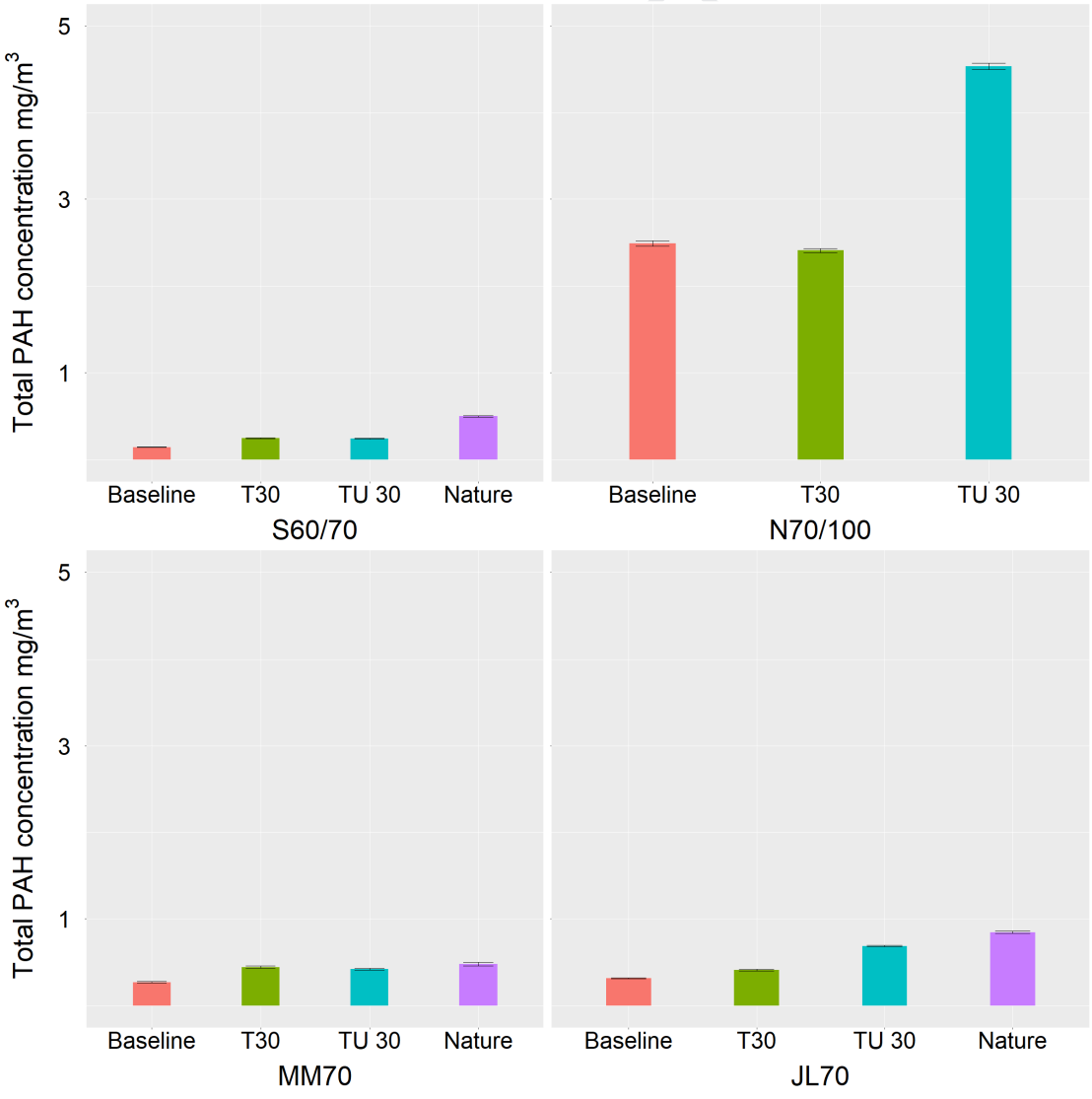

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Fig. 6 Total identifiable PAH concentrations in asphalt fumes (mg/m^3) (n=3)

Ratios between the total amount of detected PAHs and the total particulates (TP) are shown in Fig. 7. Note that the ratios do not represent the concentrations of PAHs in TP, because part of the PAHs are also from the vapor phase collected by the sorption tube (SKC, 226-30-04). In addition, not all the PAHs in the TP are detected and counted. Nevertheless, the ratios provide a general indication of the PAHs in asphalt fumes. As shown in Fig 4, the ratios between the detected PAHs and TP ranges from 0.48% to 2.83%. The ratios also vary with asphalt type, with MM70 being the lowest while N70/100 being the highest. Aging generally drives up the ratios, except for 30 days of thermal aging of asphalt N70/100 and JL70. The most noticeable changes of the ratios occur on natural aging.

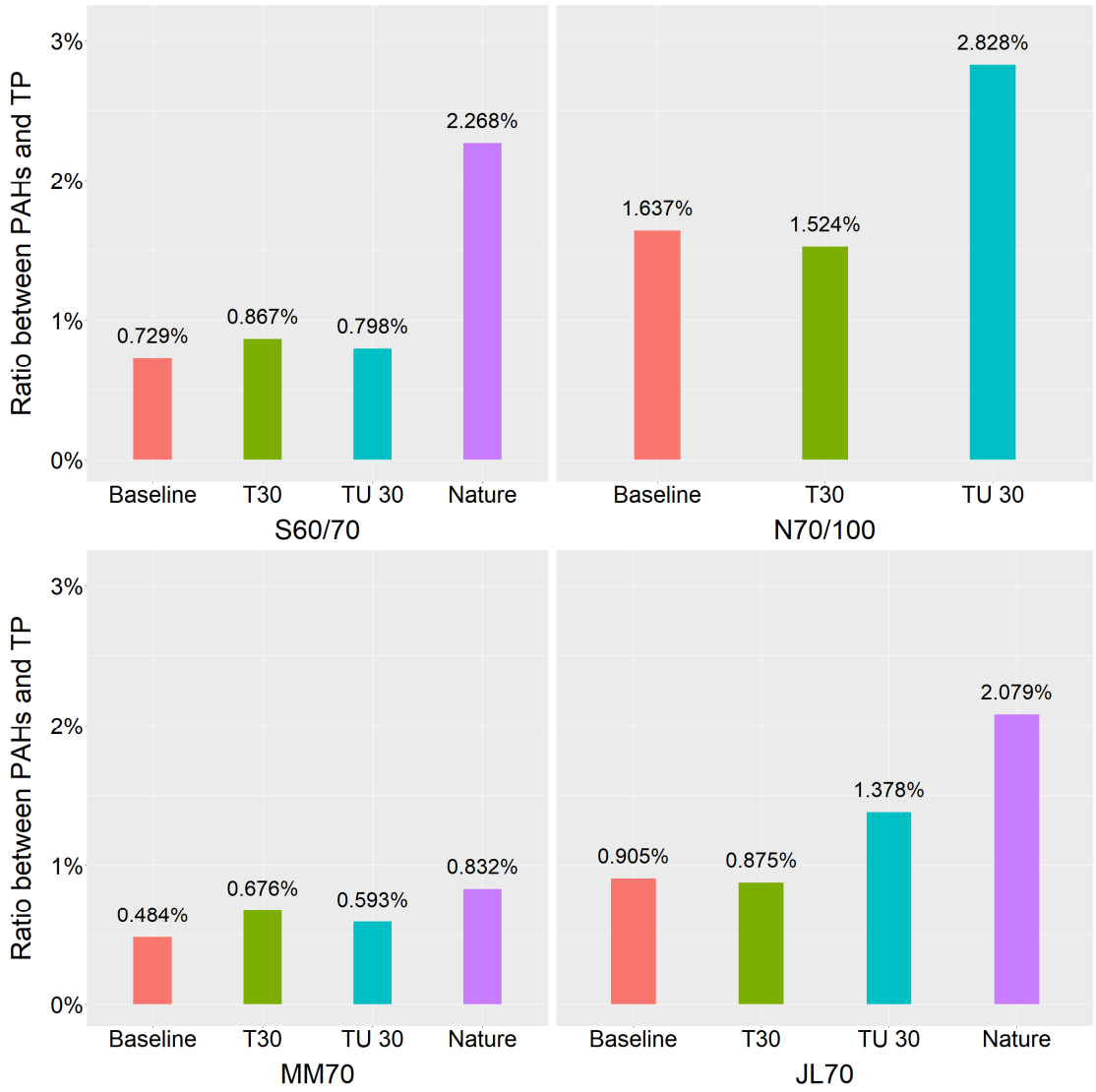


Fig. 7 The ratios between the total amount of detected PAHs and the total particulates

The detected PAHs are further divided into two groups based on the number of rings they contain. It is anticipated that groups with less than or equal to three rings (less rings) are dominant in the vapor phase while those with more rings are dominant in TP (Hanedar et al., 2014; Krugly et al., 2014; Masiol et al., 2012). The amounts of the PAHs in the two groups are presented in Fig. 8. It appears that those PAHs with less rings vary little with asphalt type and aging states, as compared with those with more rings.

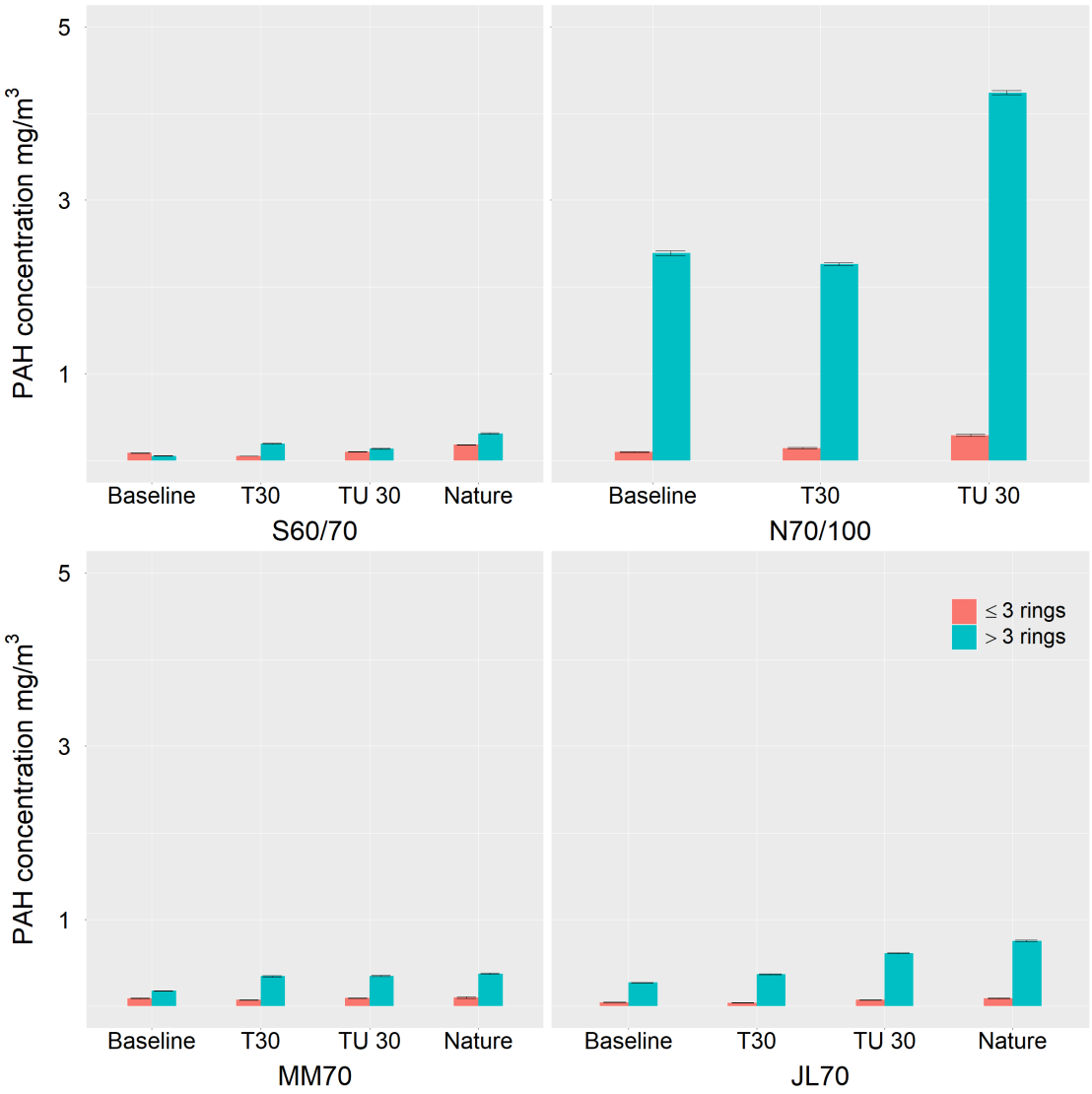


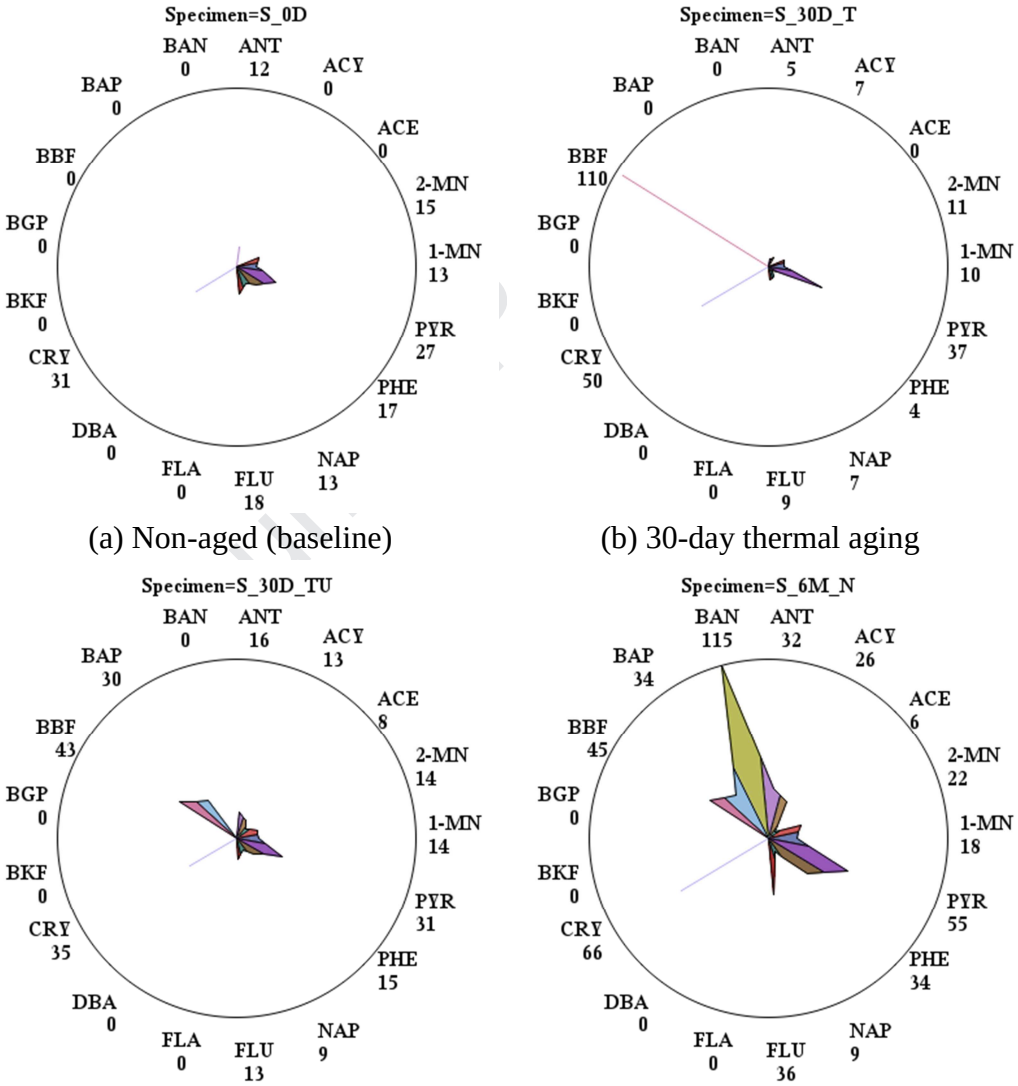
Fig. 8 Total identifiable PAH concentrations separated by number of aromatic rings (n=3)

3.3.2 Concentrations of individual PAH compounds

The concentrations of individual PAH compounds in asphalt fumes (in ug/m^3 of air sample) are presented as star plots in Fig. 9-12. The plots not only indicate the changes of each PAH compound in the asphalt fume samples, but also vividly display an overall profiles of the PAHs in each sample. For asphalt fumes from a same type of asphalt binder, the areas of the polygons in the plots also indicate the amount of the PAHs. However, the areas in the plots from different types of asphalt binders are not

comparable because the scales are different. It is evident from the plots that aging generally leads to an increase in PAH concentrations in asphalt fumes for all the asphalt types.

For asphalt S60/70, 30 days of thermal aging leads to a significant increase in BBF and 30 days of thermal and UV aging leads to a significant increase in BBF and BAP. A noticeable difference related to 6 months of natural aging is the relatively large amount of BAN generated.

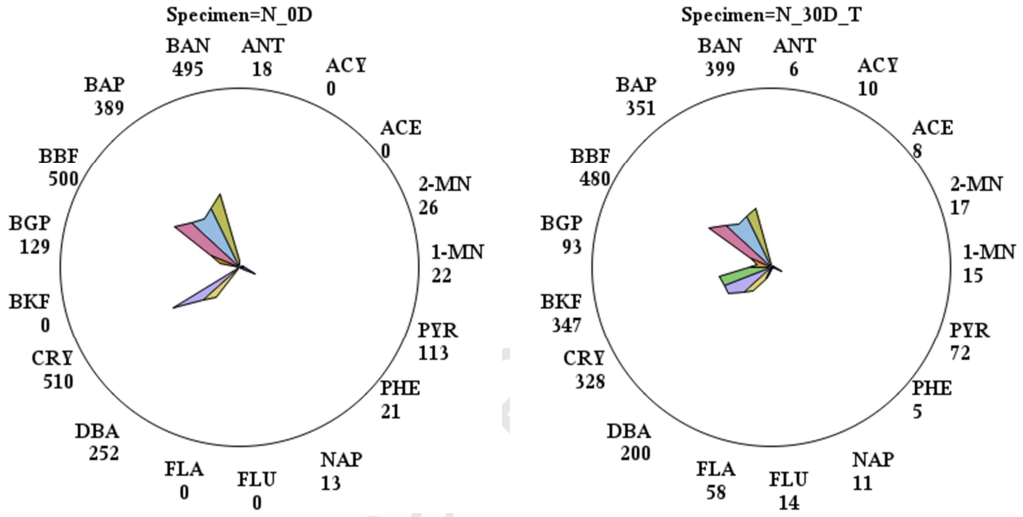


(a) Non-aged (baseline) (b) 30-day thermal aging

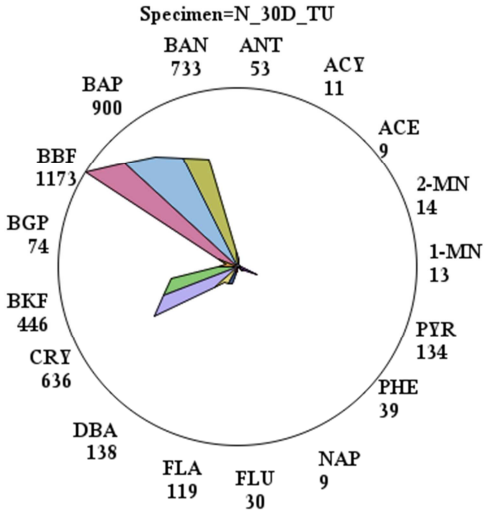
(c) 30-day thermal and UV aging (d) 6-month natural aging

Fig. 9. The concentrations of PAHs in asphalt fumes generated by mixtures made of asphalt S60/70 (ug/ m^3)

For asphalt N70/100, asphalt fumes from non-aged asphalt mixtures already contain a wide variety of PAHs. Therefore, 30 days of thermal aging does not greatly alter the composition of the PAHs, except for the added BKF. A combination of thermal and UV aging for 30 days, however, leads to a significant increase in BBF, BAP, and BAN.



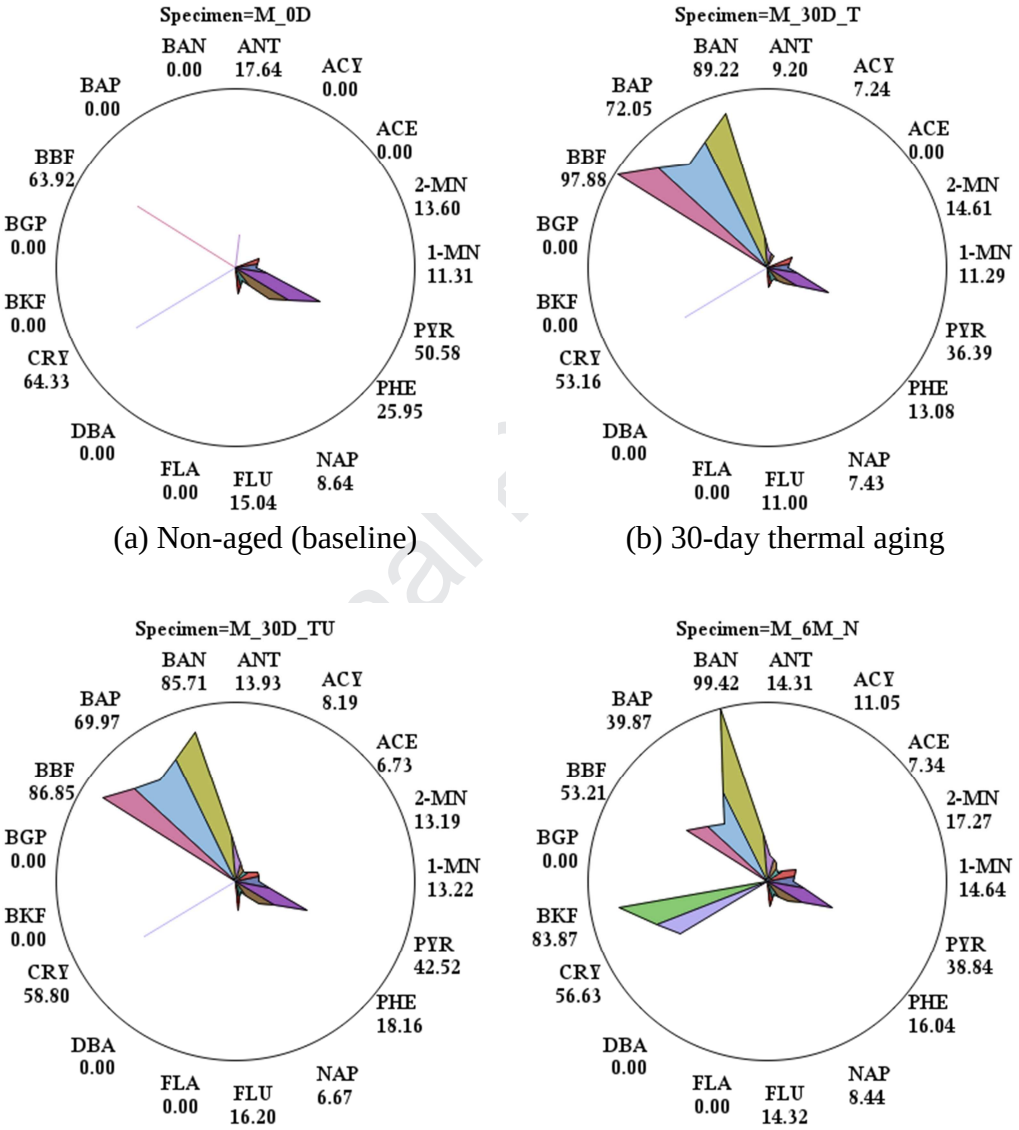
(a) Non-aged (baseline) (b) 30-day thermal aging



(c) 30-day thermal and UV aging

Fig. 10. The concentrations of PAHs in asphalt fumes generated by mixtures made of asphalt N70/100 (ug/ m^3)

For asphalt MM70, 30 days of thermal aging adds BAP and BAN to the detectable list of PAHs. The effect of combined thermal and UV aging appears to be similar to that of thermal aging. Natural aging by 6 months, however, creates an apparently different profiles of PAHs. In particular, BKF is detected and BAN becomes proportionally more than BBF and BAP.

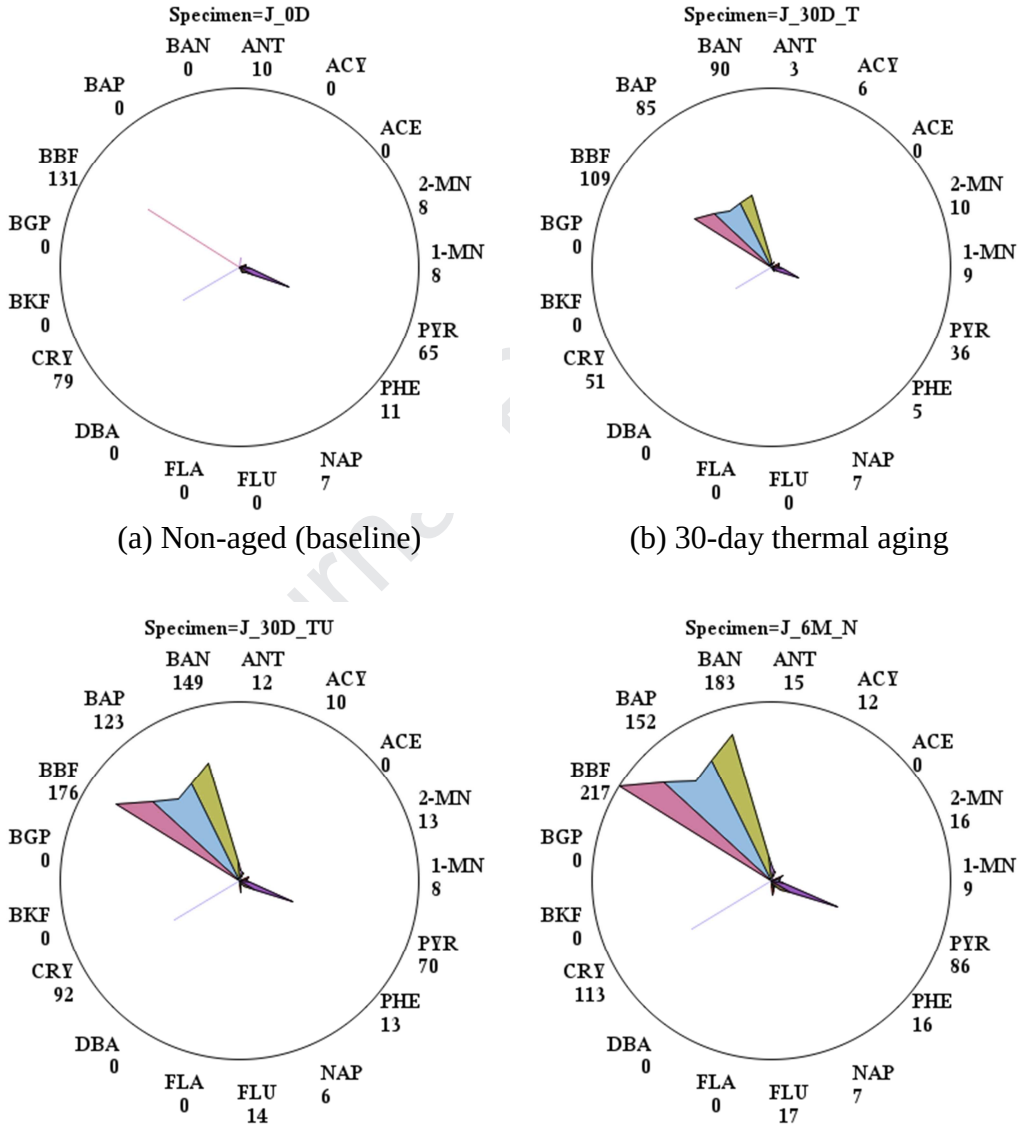


(a) Non-aged (baseline) (b) 30-day thermal aging

(c) 30-day thermal and UV aging (d) 6-month natural aging

Fig. 11 The concentrations of PAHs in asphalt fumes generated by mixtures made of asphalt binder MM70 (ug/ m^3)

For asphalt JL70, 30 days of thermal aging also adds BAP and BAN to the detectable list of PAHs. Judged from the shape of the star plots, the profiles of the PAHs associated with the three aging treatments are similar. However, natural aging creates the highest amount of BBF, BAP, and BAN, followed by the combination of thermal and UV aging.



(a) Non-aged (baseline) (b) 30-day thermal aging

(c) 30-day thermal and UV aging (d) 6-month natural aging

Fig. 12 The concentrations of PAHs in asphalt fumes generated by mixtures made of asphalt binder JL70 (ug/ m^3)

In summary, aging of asphalt mixtures affects the compositions of PAHs in asphalt fumes. The responses of those PAHs to aging, however, are different. Some PAHs of small-to-medium molecular mass such as NAP, 1-MN, PYR already exist in asphalt fumes generated from non-aged asphalt mixtures. Aging does not necessarily increase the amount of such PAHs. However, some PAHs of medium-to-heavy molecular mass such as BKF, BBF, BAP, and BAN typically exhibit a significant increase after aging. In particular, BKF is below the detection limit in all those asphalt fumes generated from non-aged asphalt mixtures, but it emerges in asphalt fumes from N70/100 asphalt after both aging treatments and in asphalt fumes from MM70 asphalt after natural aging. BBF, BAP, and BAN either rises from undetectable amounts or increase significantly after aging treatments. In general, PAHs of medium-to-heavy molecular mass become proportionally more after aging treatments. In view of the increased amount and types of PAHs in asphalt fumes generated from RAP, especially the obvious increase of PAHs of medium-to-heavy molecular mass, it is reasonable to conclude that the asphalt fumes from RAP are more hazardous.

4 Discussion

4.1 Mechanisms of Asphalt Fume Changes Caused by Asphalt Binder Aging

The findings above indicate that asphalt aging can change the quantity and composition of fumes generated in hot asphalt mixtures. We conducted a literature review to understand the possible mechanisms of such changes. To our best knowledge, studies on relationships between asphalt aging and asphalt fumes are non-existent. One study by Petersen et al. (1998), however, discusses the mechanisms of oxidative aging on the chemical property changes of asphalt binders. Petersen divides the oxidative aging of asphalt binders into two stages: a spurt reaction stage during

which oxidation occurs very rapidly and a slow reaction stage that follows the first one. The major chemical reactions during the spurt stage were illustrated by Petersen using dihydroanthracene as a model molecule. One of the end products of the reactions is anthracene. The mechanisms of oxygen reacting with hydroaromatics in asphalt are also discused by other researchers (Mill, 1996).

The aging mechanisms proposed by Petersen suggest that PAHs can be generated in asphalt binders through the oxidative reactions of hydroaromatics. According to Fig. 6 to Fig. 12, a commonly detected PAH after ashphalt aging is benz(a)anthracene (BAN). We use Fig. 13 to illustrate the reactions that generate BAN from 3,4-dihydrobenz(a)anthracene, based on the mechanism proposed by Petersen. The PAHs generated in asphalt binder during the aging process are likely emitted in asphalt fumes at high temperatures.

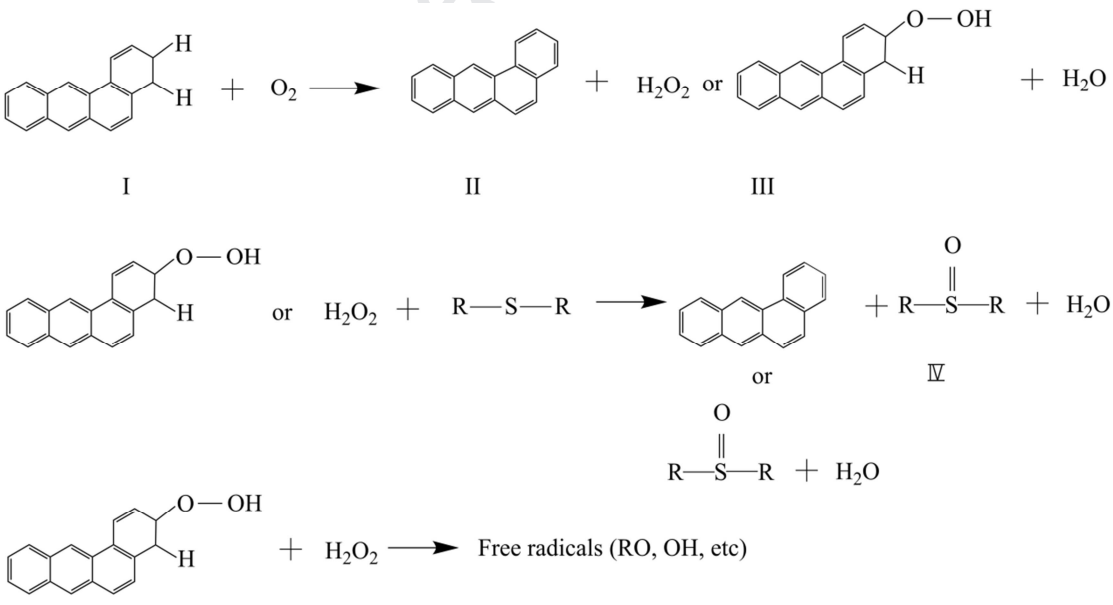


Fig. 13 Oxidation that leads to the generation of PAHs in asphalt binder, illustrated for 3,4-Dihydrobenz(a)anthracene (adapted from Petersen et al. (1998))

In addition to oxidation, other possible mechanisms may cause the chemical changes of asphalt binders in the field. For instance, biodegradation of petroleum products including asphalt have been extensively and continuously studied (Kim and Crowley, 2007). However, the relationship between biodegradation and PAHs in asphalt binder during the field aging process remains to be studied.

4.2 Field Measurements and Implications on Exposure Limits

This study is focused on laboratory assessment of asphalt fumes generated by HMA mixtures before and after aging. Because the point of interest is the effect of asphalt binder aging in RAP on generated asphalt fumes, mixture samples were prepared and tested at controlled conditions. The results shown above indicate that asphalt binder aging affects the amount and compositions of asphalt fumes.

Actual exposures and hazards received by paving workers, however, need to be evaluated through field studies. A through discussion on the current field sampling methods and exposure limits is made by (Chong et al., 2018). Currently, the Occupational Safety and Health Administration (OSHA) does not specify an exposure limit for asphalt fumes, but provides an exposure limit to PAHs in asphalt fumes (0.2 mg/m^3) (ATSDR, 1995). In addition, there is a Permissible Exposure Limit (PEL) of 5 mg/m^3 (8-hr time weighted averages, or TWA) for "respirable" particulates by OSHA (1989). NIOSH's recommended exposure limit to asphalt fumes is 5 mg/m^3 determined during any 15-min period (NIOSH, 1998a).

In practices, asphalt fume exposures are seldom tested. Even less tested are the chemical compositions of asphalt fumes, due to the complicated sampling and testing procedure. It is evident from this study that RAP is associated with increases in not only PAH concentrations, but also the more hazardous PAH species. Therefore, the

exposure limit by OSHA and NIOSH may be revisited for RAP-containing HMA mixtures.

4.3 Methods for Improvements

The increased health risks of using RAP calls for effective mitigation methods, which may be approached from three aspects: use of personal protection equipment (PPE) by workers, modification of construction equipment, and use of alternative materials.

Commonly used PPE for air-borne particles is respirators. There are three types of filters on respirators: N-series, R-series, and P-series (NIOSH, 1995). N-series is not resistant to oil and hence is not suitable. The other two types have the ability to remove at least 95% of particles when oil aerosols are present. Tests from Janssen and Bidwell (2006) indicate that these two types of respirators provide acceptable filtration of exhaust in workplaces. Respirators, however, are generally not used by paving workers likely due to several reasons. Firstly, the working environment for paving is hot and laborious, and wearing respirators making workers feel more uncomfortable. Secondly, the R-series and P-series filters, costing at least 3 U. S. dollars (USD) per one 8-hr working shift, are more expensive than the commonly used N-series ones. Thirdly, there exists ignorance of the health risks by jobsite workers and managers. However, if the workers and managers are informed of the concentrations, compositions, and hazards of asphalt fumes generated from RAP, their attitude toward using respirators may change.

In a paving crew, the persons who are subject to the highest asphalt fume exposures are paver operator and screedman. Several equipment manufacturers supply pavers with fume extraction systems, such as Volvo's extractor for bituminous fumes and the FXS® fume extraction from Roadtec. The price for a paver is about 400,000 USD (ESCNJ, 2018). As compared with traditional pavers, the cost of adding the fume

548 extraction system is about 10,000-20,000 USD. Existing study suggests that exposure
549 to asphalt fumes is significantly lowered after using the fume extraction systems
550 (Mickelsen et al., 2006).

551 Another approach is to modify the paving materials. One possible way is to add
552 chemicals that suppress asphalt fumes, but the effectiveness such chemicals has not
553 been well documented. Another way is to reduce HMA paving temperature by using
554 warm-mix technology. Warm-mix technology is mainly used to reduce energy use
555 and facilitate pavement constructability, but reduction in asphalt mixture temperature
556 can significantly reduce the amount of asphalt fumes (Mo et al., 2019). Both water-
557 based method and chemical additives can be used to produce warm mix asphalt
558 (EAPA, 2014). The former needs to make investment on equipment in a mixture plant
559 ($100,000-$120,000 USD) (Middleton and Forfylow, 2009), while the latter requests
560 the purchase of warm-mix additives. For instance, the use of Sasobit® (an organic wax)
561 causes a $1.30-$3.00 increase in mixture cost per ton while the use of Evotherm® (an
562 emulsion) causes a $3.5-$4.00 increase in mixture cost per ton (Kristjansdottr et al.,
563 2007).

564 In summary, increased health risk by asphalt fumes generated from RAP may be
565 controlled at the different stages of mixture production and construction. In mixture
566 production, warm mix technology can be used to reduce mixture temperature. In
567 construction, fume extraction systems installed on pavers can be used to reduce fume
568 exposures. As a last line of defense, R- or P-series respirators can be used to filter out
569 the particulate phase of asphalt fumes. The wide adoption of these controlled
570 measures is subject to further field exposure studies and risk analysis.

571

5 Summary and Conclusion

Asphalt pavement recycling is widely practiced for its economic and environmental benefits. The oxidative aging or biodegradation of asphalt binders induces chemical changes in binders (Daniel et al., 2005; Kim and Crowley, 2007; Petersen, 1998). Therefore, in working with RAP, it is important to understand whether the chemical changes in asphalt binders translate into the chemical changes in fumes, and how such possible changes affect the hazard potentials of asphalt fumes. In this study, three methods were used to age asphalt mixtures to create RAP. Asphalt fumes were generated and collected from the created RAP as well as from non-aged asphalt mixtures in uniform conditions. The collected asphalt fume samples were analyzed gravimetrically and chemically, with emphasis on PAHs.

The following conclusions are drawn from the study:

1) RAP mixtures are associated with greater amount of total particulates in asphalt fumes, as compared with non-aged asphalt mixtures of the same materials.
2) In general, RAP mixtures are associated with increases in the types and concentrations of PAHs in asphalt fumes, especially those PAHs with more than three aromatic rings.
3) Increases in PAHs in asphalt fumes are particularly noticeable for RAP created in natural aging conditions.
4) Overall, asphalt fumes from RAP become more hazardous as compared with fresh asphalt mixtures using virgin materials.

Currently, the hazardous potentials of asphalt fumes are typically evaluated without differentiating material characteristics. This study suggests that asphalt fumes from

RAP warrant more attentions, perhaps worth being evaluated separately. There are several limitations of this study:

1) Asphalt binders in RAP from the field are typically more severely aged than the ones used in this study.
2) RAP-containing asphalt mixtures may be paved at temperatures different than that used in this study.
3) RAP mixtures are commonly blended with fresh asphalt mixtures.

These limitations, however, do not preclude the concerns on asphalt fumes generated from RAP. Detailed field studies may be conducted in the future to evaluate asphalt fumes generated from RAP or RAP-containing asphalt mixtures.

Acknowledgements

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- Particulate concentration in asphalt fumes is increased in aged asphalt mixtures.
- Total PAHs in asphalt fumes from aged asphalt mixtures are increased.
- PAHs in asphalt fumes from aged mixtures contain more aromatic rings.
- Asphalt fumes in hot-mix asphalt pavement recycling are likely more hazardous.

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: