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Leaching Characteristics of Metals and Polycyclic Aromatic Hydrocarbons (PAHs) from Asphalt Paving Materials

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Abstract

Asphalt pavement, a major type of road surface, may contain hazardous elements depending on its specific composition. A growing concern has developed regarding the potential leaching of these hazardous constituents from asphalt pavements, particularly when incorporating waste materials and additives. This study investigates the presence of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in leachates from six commonly employed asphalt paving materials. A comprehensive laboratory leaching experiment was conducted on three key sample scales: asphalt binder, asphalt mortar, and asphalt mixture. The impact of the leachates was assessed by the heavy metal pollution index and the toxic equivalency factor based on the benzo[a]pyrene equivalent concentration. The results reveal that leaching tests at the binder

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and mortar scales provided fundamental insights into leaching characteristics within a relatively short timeframe, while the mixture-scale test was more capable of representing pollutant leaching in near-true scenarios. In addition, the results indicate potential adverse health implications associated with the incorporation of hazardous waste, such as bottom ash, into asphalt pavement. These findings hold significant implications for promoting environmentally responsible practices of asphalt pavement.

Keywords: Asphalt pavement; Waste recycling; Metal leachability; PAHs; Health impacts

1. Introduction

Asphalt mixture has been used in roadway construction for centuries. It comprises approximately 95% mineral aggregate, typically gravel, sand, and various recycled materials. The remaining 5% is the binder, termed asphalt cement, asphalt binder, or bitumen, consisting of the refined product of crude oil with optional modifiers [1, 2]. The highway network has rapidly expanded in recent decades due to the increased demand for transport services, especially in developing countries. More than 10,000 km of highways were constructed annually in China from 2016 to 2020, with 94% surfaced with asphalt concrete [3]. In the next 30 years, more than 25 million kilometers of new roadways are expected to be paved globally [4]. The rapid growth of roadway construction continues to bring environmental concerns that attract increasing global attention. The transport system consumes 20% of global energy resources and produces 25% of global greenhouse gas emissions [5]. Moreover, the release of organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) was reported during the high-temperature asphalt pavement construction [6]. Aggregate and asphalt binder may also contain trace metals and metalloids (e.g., Cr, Ni, Cd, and Pb), depending on the sources of the mineral aggregate and crude oil [7, 8]. In addition, a variety of chemical additives have been employed to prepare modified asphalt with the aim of enhancing engineering performance and durability [9, 10]. However, these additives may involve components that pose potential contamination risks. Moreover, there is a growing interest in the construction of sustainable pavements by incorporating recycled waste materials [11, 12], a practice that may introduce external pollutants. The leaching of these pollutants from asphalt pavement into the water environment is a complex process, usually involving a combination of both organic and inorganic substances in the resulting solution.

In recent times, there has been a growing concern regarding the potential leaching of pollutants from asphalt pavement into adjacent environments, including soils, surface and subsurface water bodies. This concern is particularly relevant when waste materials are incorporated into the production of asphalt pavement [13, 14]. Previous research has reported elevated concentrations of pollutants, such as heavy metals and polycyclic aromatic hydrocarbons (PAHs), in the leachate from waste-modified asphalt mixture [15, 16]. These modified asphalt mixtures incorporates asphalt rubber, steel slag, reclaimed asphalt pavement, and bottom ash or fly ash as aggregates [17-19]. Heavy metals could bioaccumulate in organisms and cause physiological issues [20, 21]. Exposure to toxic heavy metals may damage cells, impacting organelles and neurotransmitters, potentially leading to neurotoxicity and cancer [22, 23]. Similarly, exposure to PAHs can result in ecotoxic effects including mutagenicity and carcinogenicity [24, 25]. PAHs could bioaccumulate in adipose tissues, potentially inducing tumor development in various organs [26, 27]. Additionally, PAHs can impact reproductive health, contributing to embryotoxicity and reproductive system anomalies [28, 29]. However, most of these studies primarily involved simple metal leaching tests aimed at assessing the feasibility of integrating such waste materials into asphalt pavement, with a predominant focus on the engineering performance of the resulting asphalt mixtures. Notably, the results of these prior studies are challenging to compare due to variations in sample preparation protocols and test conditions. Consequently, limited research has systematically evaluated the leaching of pollutants from asphalt paving materials under uniform controlled conditions.

To fill this research gap, this study aims to investigate the leaching behavior of pollutants, including heavy metals and PAHs, from six commonly used asphalt paving materials. This investigation is conducted through a comprehensive multi-scale leaching test, encompassing the following scales: the binder scale (involving asphalt binder films), mortar scale (involving loose asphalt mortar), and mixture scale (involving compacted cylindrical asphalt specimens). Concentrations of heavy metals are quantified using inductively coupled plasma-atomic emission spectrometry (ICP-AES), while PAH concentrations are measured using gas chromatography-mass spectrometry (GC-MS). The assessment of heavy metal pollution in the leachates of asphalt pavement is based on the heavy metal pollution index (HPI). Meanwhile, the harmful effects associated with PAHs in the leachates are characterized using the toxic equivalency factor based on the benzo[a]pyrene equivalent concentration (BaP_{eq}-TEF). Furthermore, the impact of solution acidity on the leaching behavior of asphalt pavement was studied by introducing artificial acid rain as the extraction solution in the leaching test. Additionally, the influence of the oxidative aging of bitumen on the leaching properties of asphalt pavement was characterized by utilizing both short-term and long-term aged asphalt samples [30, 31].

2. Experimental Methods

2.1. Raw materials

Six distinct asphalt paving materials, including conventional hot mix asphalt mixture (CA), styrene-butadiene-styrene polymer modified asphalt mixture (SA), crumb rubber modified asphalt mixture (AR), warm mix asphalt mixture incorporating a chemical additive (WC), asphalt mixture prepared with reclaimed asphalt pavement (RA), and asphalt mixture prepared with municipal solid waste incineration bottom ash (BA), were prepared in this study. These asphalt mixtures were selected because they represent various asphalt pavement types widely utilized in practical field applications. Furthermore, it was anticipated that these mixtures would exhibit distinct leaching behaviors, given their composition of diverse materials or additives sourced from different origins. For a comprehensive understanding of the characteristics of these six asphalt paving materials, detailed descriptions are provided in **Table 1**. CA, the conventional asphalt mixture, comprises unmodified asphalt binder and mineral aggregates. SA, on the other hand, is a frequently employed modified asphalt mixture featuring SBS polymer-modified binder to enhance its engineering performance [32, 33]. AR is a green paving material with a longstanding history of usage in road construction. It owes its resistance to cracking and rutting to the incorporation of crumb rubber from end-of-life tires through binder modification [34, 35]. WC represents a low-carbon paving material that utilizes a chemical warm mix additive, permitting a lower construction temperature (typically 20-40°C lower than conventional hot mix asphalt mixture) without compromising mechanical properties [36-38]. RA is a sustainable paving material that incorporates reclaimed asphalt pavement (RAP) to produce new asphalt pavement. In certain areas or states, the utilization of RAP has even become a mandatory practice [39, 40]. Finally, BA serves as a prime example of waste-recycled asphalt pavement, employing municipal solid waste incineration bottom ash (MSWI-BA) as a fine aggregate substitute, thus alleviating the burden of landfill disposal [41, 42].

Table 1 Specifications of the six asphalt paving materials.

Label	Representative	Specification
CA	Conventional hot mix asphalt (HMA) mixture	Unmodified asphalt binder + 100% mineral aggregate
SA	Styrene-butadiene-styrene (SBS) polymer modified asphalt mixture	Asphalt binder modified with 5%# SBS + 100% mineral aggregate
AR	Crumb rubber modified asphalt mixture (asphalt rubber)	Asphalt binder modified with 20%# crumb rubber (d<0.25mm) + 100% mineral aggregate
WC	Warm mix asphalt (WMA) mixture prepared with a chemical additive	Asphalt binder modified with 5%# Evotherm + 100% mineral aggregate
RA	Asphalt mixture with aggregate partially substituted by reclaimed asphalt pavement	Unmodified asphalt binder + 70% mineral aggregate + 30% RAP

BA	Asphalt mixture with aggregate partially substituted by bottom ash	Unmodified asphalt binder + 70% mineral aggregate + 30% BA

[#] Mass percentage by the weight of asphalt binder

In this study, a dense-graded mixture with a nominal maximum aggregate size of 10-14 mm, termed wearing course 10, served as the mix design. This mix design is widely utilized for road surfaces in Hong Kong. The gradation curve for the wearing course 10 mix design is depicted in **Fig. S1** (Supplementary Materials). A neat bitumen with a penetration grade of 60-70 was used in this study. The ratio of binder to sand in asphalt mortar samples was maintained at 19.6%. The asphalt binder content for asphalt mixture samples was maintained at 6.0%. Locally sourced granite rocks were utilized as aggregates. Detailed information regarding the dosages of asphalt modifiers and aggregate substitutes can be found in **Table 1**.

2.2. Sample preparations

Test samples were prepared at binder, mortar, and mixture scales. The asphalt binder sample was prepared by adding 20g of asphalt binder into a rotating borosilicate glass bottle and heated at 150 ºC for 30 minutes, resulting in the formation of thin films with a thickness of approximately 500 μm. The asphalt mortar sample was prepared through the blending of only fine aggregates (d=0.75-2.36mm), mineral filler (d<0.75mm), and asphalt binder at 170°C, ensuring the attainment of a homogeneous mixture. The asphalt mixture sample was prepared using coarse and fine aggregates (d=0.75-14mm), mineral filler (d<0.75mm), and asphalt binder. The mixing and compaction procedures were conducted at 170 ºC and 150 ºC, respectively. A gyratory compactor was employed to compact asphalt mixtures into cylindrical specimens, achieving the targeted air void content of 4 ± 0.5%. The dimensions of the prepared cylindrical specimen were 100 mm (diameter) × 40 mm (height). Modified asphalt binders incorporating specific additives were prepared prior to the mixing phase in the cases of SA, AR, and WC mixtures. The modification procedure involved the blending of these additives with a neat bitumen with a penetration grade of 60-70, using a shear mixer at 180°C for 1 hour. To replicate real-world conditions, both short-term and long-term aging protocols were applied to the asphalt mixtures in the laboratory. These aging procedures were intended to simulate the characteristics of freshly constructed asphalt pavement and the state of asphalt pavement after a service period of 5 to 10 years [30, 31]. In the short-term aging process, a 35g sample of asphalt binder was poured into a glass container, which was then positioned horizontally in a rotating oven. The sample was subjected to a temperature of 163°C and a constant airflow for 85 minutes, with the glass container rotating at 15 r/min. Subsequently, the aged asphalt binder was retrieved from the glass container after the test. For the long-term aging process, a 50g sample of short-term aged asphalt binder was placed on a stainless steel pan and transferred to the pressurized aging vessel. The aging procedure was carried out at 2.1 MPa and 100°C for 20 hours. Asphalt samples were prepared in triplicates for the leaching test and subsequent analysis.

2.3. Leaching tests

The leaching tests encompassed three scales: binder, mortar, and mixture. At the binder scale, 200 ml of extraction solution was introduced into the sample bottle, where a 20 g asphalt binder film had been previously prepared. This solution was gently agitated at 30 rpm for 24 hours at room temperature. In the mortar scale, a similar procedure was followed, with 200 ml of extraction solution added to the sample bottle containing 20 g of loose asphalt mortar. This mix was also agitated at 30 rpm for 24 hours at room temperature. The experimental configurations for both binder and mortar scale tests are depicted in **Fig.1**.

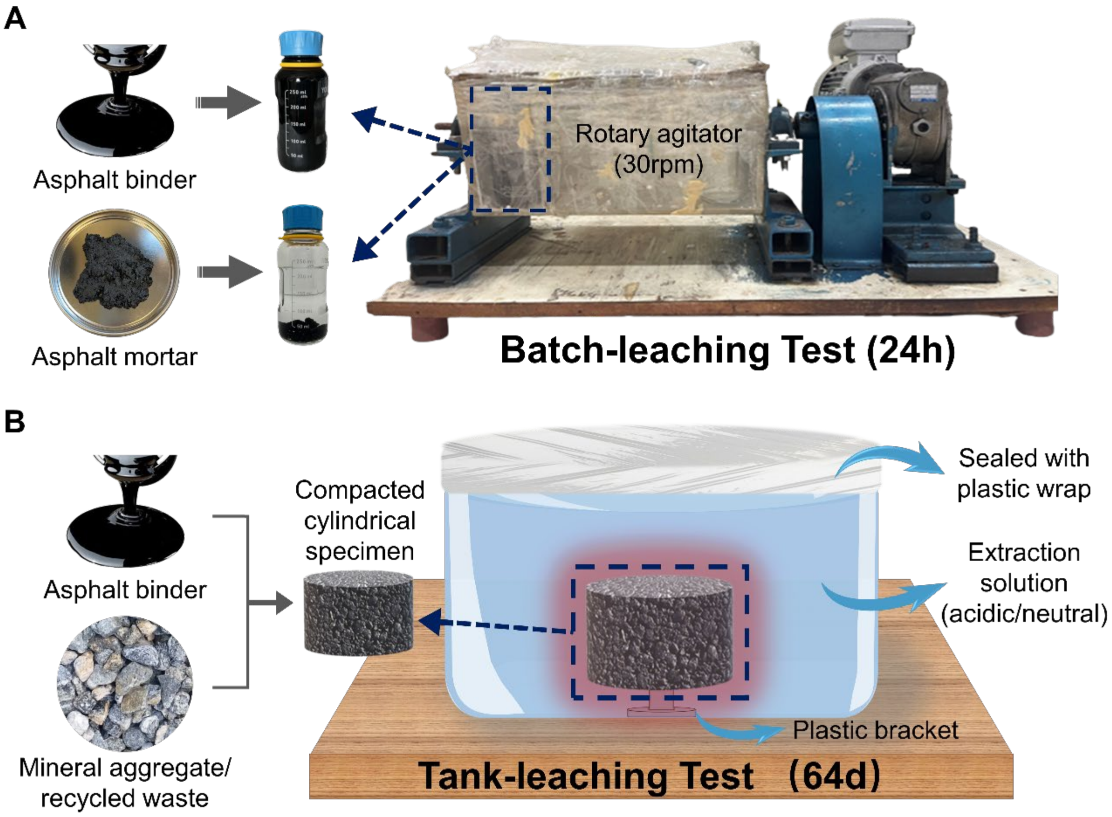

Fig.1. The schematic representation of the experimental setup: a) batch-leaching test and b) tank-leaching test

In the mixture scale, the process was slightly different. Here, a compacted cylindrical asphalt specimen was carefully placed on a plastic bracket within a water tank, ensuring that all surfaces of the specimen were in complete contact with the water. The liquid-to-material mass ratio was maintained at 10:1, consistent with the values employed in the leaching tests for the binder and mortar scales. This leaching test was observed over 64 days at room temperature to enable diffusive leaching to reach an equilibrium state [43]. Two types of extraction solutions, namely neutral and acidic, were utilized to explore the impact of environmental conditions on the leaching of pollutants from asphalt pavement concerning stormwater and runoff acidity. The neutral solution was formulated using deionized (DI) water with a pH range of 6.5-7.0. Conversely, the acidic solution was composed of DI water, sulfuric acid, and nitric acid, both of which are primary constituents of acid rain formed by the presence of sulfur dioxide and nitrogen oxides in the atmosphere. The pH of the acidic solution was maintained at 4.00 ± 0.05 through the use of a 60/40 wt% mixture of sulfuric acid and nitric acid [44]. Upon the completion of the leaching test, the leachates were collected via filtration, employing syringe filters featuring a pore size of 0.45 μm.

2.4. Analytical methods

The concentrations of As, Cd, Cr, Cu, Ni, Pb, Se, and Zn were measured in this study using a Spectro Arcos inductively coupled plasma-atomic emission spectrometry (ICP-AES). Prior to the ICP-AES analysis, a total digestion process was carried out on the collected leachates. The determination of polycyclic aromatic hydrocarbons (PAHs) was accomplished using Agilent gas chromatography-mass spectrometry (GC-MS). To prepare the samples for GC-MS analysis, a three-step liquid-liquid extraction procedure was conducted with dichloromethane (DCM). The ratios of solution to DCM were set at 1:1, 2:1, and 4:1 for the three respective extraction steps. In each extraction process, the leachate and DCM were combined in a borosilicate glass tube and agitated for 90 seconds using a test tube shaker. Subsequently, the tube was sealed and allowed to stand still for 24 hours. The DCM phase was carefully collected, while the water phase was subjected to the subsequent extraction process. The resting times for these processes were 24 hours, 6 hours, and 3 hours, respectively. The DCM phases obtained from the three-step extraction process were dehydrated using anhydrous granulated magnesium sulfate, followed by a condensation process involving a gentle flow of N_2. Lastly, 1 ml of fresh DCM was introduced to the tube and stirred for 120 seconds using a test tube shaker to prepare the final test sample. The GC-MS analysis was immediately conducted upon sample preparation. Further specifics regarding the GC-MS test program can be found in **Table S1**.

3. Results and Discussion

3.1. Leaching of heavy metals

The heavy metal pollution index (HPI) was used in this study to assess the overall water quality concerning heavy metal pollution. The water is considered safe for human health if the HPI value is less than 100 [45]. The HPI was defined by Equation (1).

$$HPI = \sum_{i=1}^{n} \frac{W_i \times Q_i}{W_i} \tag{1}$$

where W_i is the unit weight of each selected parameter as defined in Equation (2), Q_i is the individual quality rating of the ith parameter given by Equation (4), and n is the number of parameters.

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \tag{2}$$

where w_i is the unit weight of the ith parameter, which is inversely proportional to the standard value Si of the corresponding parameter, given by Equation (3).

$$w_i \propto \frac{1}{S_i} = \frac{k}{S_i} = \frac{1}{S_i} \tag{3}$$

where the proportionality factor k equals one for all metals.

$$Q_i = \sum_{i=1}^{n} \frac{|M_i - I_i|}{S_i - I_i} \times 100 \tag{4}$$

where M_i is the measured value of the ith parameter, I_i is the highest desirable value of the ith parameter, and S_i is the standard value of the ith parameter, according to the specifications in the water standard [46].

3.1.1. Asphalt binder scale

Fig. 2 displays the HPI values for the tested asphalt binder samples. It is important to note that four asphalt binder samples were prepared and tested, as both the RA and BA mixtures utilized the same unmodified binder as CA. The HPI values obtained from the leachates of the asphalt binder samples consistently remained below 30, indicating that there were no significant concerns regarding heavy metal pollutants. It was also observed that the AR and WC binders exhibited higher HPI values in the acidic environments compared to neutral environments, suggesting that they contained heavy metals that are more soluble in acidic solutions. These metals were predominantly introduced through the use of waste crumb rubber and chemical additives.

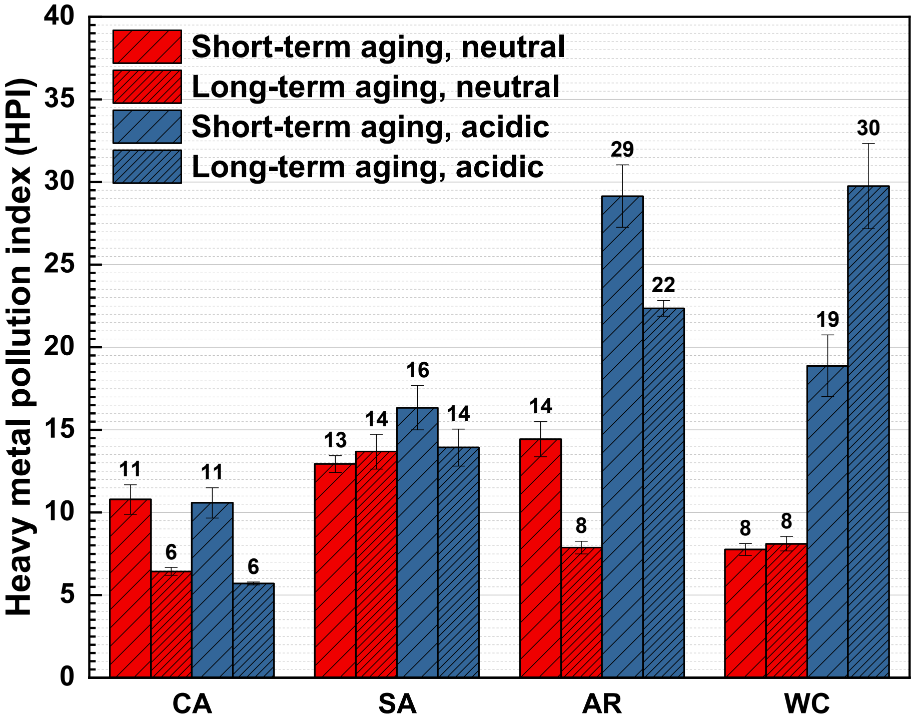

Fig. 2. Leachate HPI values of asphalt binder samples (CA: conventional HMA; SA: SBS-modified asphalt; AR: asphalt rubber; WC: WMA with chemical additive)

Concerning the specific metal content, it is noteworthy that AR and WC binders exhibited notably higher concentrations of Zn in the leachates (**Table S2**). The additional presence of Zn in AR originates from the use of ZnO activator during the rubber vulcanization process. For WC binders, while the ingredients of the commercial chemical additive are confidential, the presence of Zn can likely be attributed to impurities introduced during the manufacturing process. Moreover, AR and WC binders also showed elevated concentrations of heavy metals such as Ni, Pb, and Se in the leachates. At the binder scale, the impact of aging characteristics on the leaching behaviors of asphalt was negligible. No discernible relationship was established between the leachability of metals and the aging characteristics of the samples. In conclusion, the four asphalt binders do not raise significant concerns regarding the leaching of heavy metals. The measured concentrations of heavy metals were consistently well below regulated levels, and the calculated HPI values remained below 30.

3.1.2. Asphalt mortar scale

Fig. 3 depicts the HPI values derived from the leaching tests conducted on six asphalt mortar samples. In the neutral leaching test, CA, SA, AR, WC, and RA exhibited comparable HPI values, with SA recording the lowest values and RA demonstrating the highest HPI values. However, BA displayed considerably higher HPI values than the other mortar samples. This deviation is attributed to the municipal solid waste, which contains substantial amounts of heavy metals like Pb, Zn, Cu, Cr, Mn, and Ni. The combustion process concentrates these metals in the residual bottom ash [47, 48]. SA exhibited lower HPI values than CA, indicating that the modified binder created a solidification effect, preventing the leaching of heavy metals due to enhanced bonding strengths and improved coating performance from the modifier SBS. Conversely, AR and WC showed higher HPI values than CA, suggesting that the incorporation of waste material and chemical additives in the asphalt mixture may lead to increased leaching of heavy metals despite the solidification effect created by binder modifications. RA also displayed higher HPI values than CA, with the released heavy metals stemming from accumulated pollutants in the end-of-life RAP.

In the acidic leaching test, HPI values significantly increased for all asphalt mortar samples due to the greater solubility of metals in acidic solutions. Nevertheless, the overall trends and rankings remained consistent with those observed in the neutral leaching tests. BA exhibited the highest HPI values, surpassing 200 for both short-term and long-term aged samples, signifying the toxicity of BA leachates and their potential harm to human health. The elevated presence of heavy metals within MSWI-BA can be attributed to certain factors. Heavy metals tend to concentrate in residues, particularly within the bottom ash, post-incineration. Studies have shown that over 60% of heavy metals like Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb), and Zinc (Zn) are retained within MSWI-BA after the incineration process [49]. The incorporation of MSWI-BA as a substitute aggregate in asphalt pavement introduces these heavy metals into the mixture. Consequently, during the leaching process, these metals are gradually released from the mixture, resulting in significantly higher HPI values associated with BA samples. CA, SA, AR, WC, and RA generally maintained low HPI values, with AR, WC, and RA releasing slightly more heavy metals than CA and SA due to the presence of pollutants in the waste materials and chemical additives.

At the mortar scale, it appears that most long-term aged samples displayed a slightly increased leachability of heavy metals. Since the batch-leaching test was a dynamic process, the weakened adhesive strength between aged asphalt and aggregate makes the mortar more susceptible to stripping under the influence of water flushing. As the asphalt binder films were stripped away, the solidification effect of bitumen diminished, resulting in the release of more heavy metals from the incorporated waste materials or additives. AR, recognized for its improved aging resistance [50], showed similar HPI values for both short-term and long-term aged samples. However, the influences of aging characteristics on stripping only exist in scenarios involving strong water flush throughout the testing mortar samples, which is unlikely to happen under realistic conditions. Therefore, these findings are not transferable to other asphalt materials under different test conditions.

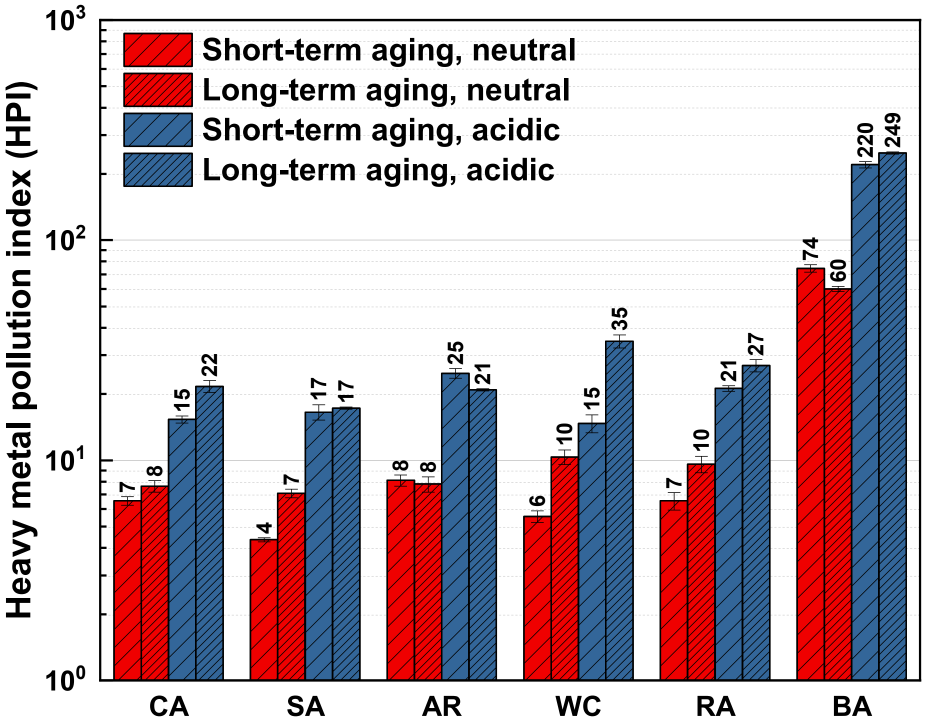

Fig. 3. Leachate HPI values of asphalt mortar samples (CA: conventional HMA; SA: SBS-modified asphalt; AR: asphalt rubber; WC: WMA with chemical additive; RA: 30% RAP-incorporated; BA: 30% bottom ash-incorporated)

In terms of specific metal ions, the concentration of each individual heavy metal in the leachates was generally well below regulatory limits, except for BA. Only trace amounts of Cd, Cu, Pb, Se, and Zn were detected in the leachates of CA, SA, AR, WC, and RA (**Table S3**). However, it is noteworthy that AR exhibited a relatively higher concentration of Zn, primarily originating from residual ZnO present in the crumb rubber. Elevated levels of Cd were found in the leachate of BA, surpassing regulatory limits. Cd is identified as a high-risk metal in bottom ash, with relatively higher leachability under neutral conditions compared to other metals [51]. In the acidic leaching test, a greater amount of heavy metals were present in the leachates, although most remained within permissible limits. AR exhibited slightly higher concentrations of Cr, Cu, Ni, and notably higher concentrations of Zn in the leachates. Findings verified concerns regarding Zn leaching associated with crumb rubber applications, as waste tires typically contain approximately 1–2% Zn by weight [52, 53]. BA displayed significantly higher concentrations of heavy metals, including Cd, Cu, Pb, and Zn, exceeding regulatory thresholds. The increased solubility of contaminants under acidic conditions is responsible for their heightened leachability [54]. Se concentrations in the leachates of CA, SA, AR, WC, and RA were relatively higher compared to other metals. The presence of Se is typically found in minerals and crude oils. Importantly, Se is primarily identified within the bitumen fraction, unlike other potentially toxic trace elements (Ag, As, Be, Cd, Cu, Pb, Sb, Tl, and Zn), which are predominantly associated with the mineral fraction [55]. Therefore, the stronger bondings within the bitumen fraction resulting from asphalt binder modifications in SA and WC may explain their slightly lower Se contents in the leachates, as these strong bondings hinder the diffusion and dissolution of Se from the inner to the outer areas of the particle bodies.

The results also imply that the application of waste materials in asphalt mixtures as modifiers may be more environmentally friendly than as aggregate substitutes. Crumb rubber served as an asphalt modifier in AR, where it was encapsulated by the asphalt binder after modifications. Additionally, the content of crumb rubber used as a modifier was lower. Consequently, AR exhibited acceptable Zn contents in the leachate, even though the added crumb rubber contained substantial amounts of Zn.

3.1.3. Asphalt mixture scale

Fig. 4 presents the HPI values derived from the leaching test results for the six asphalt mixture samples. No discernible trend in the influence of different aging characteristics on the leaching behaviors of asphalt paving materials can be revealed from the test results. Notably, the extended-duration leaching tests conducted on asphalt mixtures yielded higher HPI values compared to the short-batch leaching tests on asphalt mortar samples. This observation suggests that the accelerated batch leaching test might underestimate the total amount of heavy metals that could potentially leach from asphalt pavement in practical applications. However, the ranking of HPI values among the different asphalt paving materials remained consistent with the results from the mortar-scale leaching tests. Specifically, CA exhibited the lowest HPI values among the six materials, while SA and RA had higher yet still acceptable HPI values. Conversely, AR and WC displayed HPI values at harmful levels in the leachate when an acidic extraction solution was used. Furthermore, BA exhibited exceptionally high HPI values in the leachates from both neutral and acidic leaching tests. The concentrations of nearly all heavy metals exceeded regulatory limits in the leachate of BA under acidic conditions (**Table S4**). This result underscores the potential environmental issues associated with using hazardous waste materials like MSWI-BA in asphalt pavement without proper treatment. Additionally, the use of waste crumb rubber and chemical additives in asphalt binder modification amplified the leaching risk of heavy metals. Particular attention is warranted when considering the application of AR and Evotherm-modified warm mix in regions susceptible to acid rain.

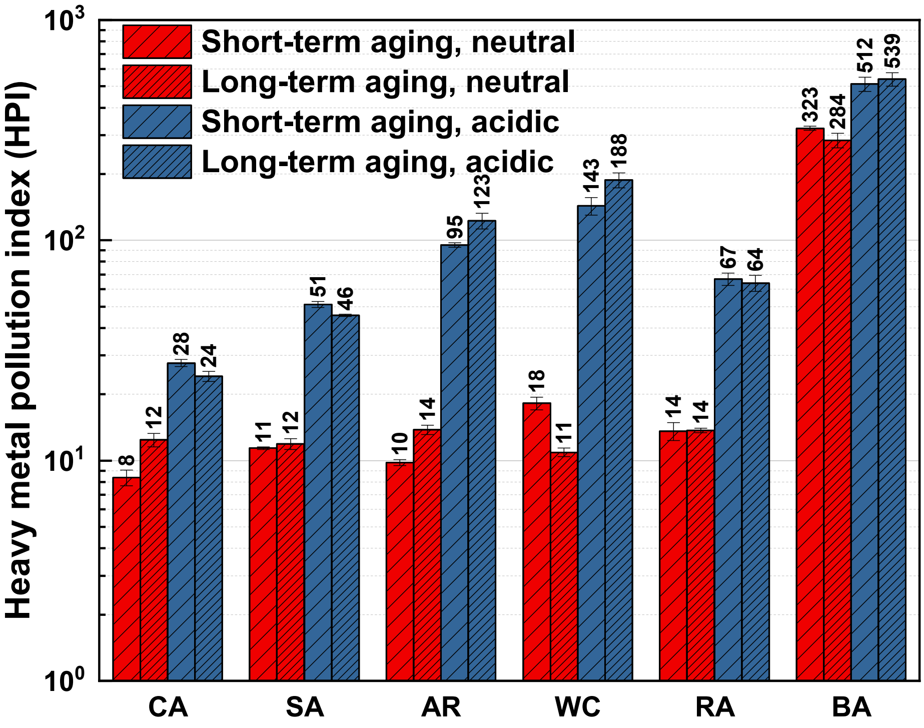

Fig. 4. Leachate HPI values of asphalt mixture samples (CA: conventional HMA; SA: SBS-modified asphalt; AR: asphalt rubber; WC: WMA with chemical additive; RA: 30% RAP-incorporated; BA: 30% bottom ash-incorporated)

3.2. Leaching of PAHs

The concentrations of 16 US EPA priority pollutant PAHs were measured in this study, including acenaphthene (Ace), acenaphthylene (Acy), anthracene (Ant), fluoranthene (Flt), fluorene (Flu), naphthalene (Nap), phenanthrene (Phe), pyrene (Pyr), benz[a]anthracene (BaA), benzo[b] fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[ghi]perylene (BghiP), benzo[a]pyrene (Bap), chrysene (Chr), dibenz[a,h]anthracene (Dba), and indeno[1,2,3-

cd]pyrene (Ip). The impact of PAHs on health can be evaluated by the toxic equivalency factor (TEF), based on the BaP equivalent concentration (BaP_{eq}) that assumes that all carcinogenic PAHs are as potent as BaP [56-58]. The leaching of PAHs is considered at little or no risk for harmful health if the obtained BaP_{eq}-TEF values are at low levels (i.e., less than 0.01 μg/L). The BaP_{eq}-TEF values were calculated by Equation (5):

$$\begin{gathered}\left(BaP_{eq} - TEF\right)_{\Sigma PAH} = \\ [Nap] \times 0.001 + [Acy] \times 0.001 + [Ace] \times 0.001 + [Flt] \times 0.001 + \\ [Phe] \times 0.001 + [Ant] \times 0.01 + [Flu] \times 0.001 + [Pyr] \times 0.001 + \\ [BaA] \times 0.1 + [Chr] \times 0.01 + [BbF] \times 0.1 + [BkF] \times 0.1 + \\ [BaP] \times 1 + [Ip] \times 0.1 + [DbA] \times 1 + [BghiP] \times 0.01 \end{gathered} \tag{5}$$

3.2.1. Asphalt binder scale

The BaP_{eq}-TEF values for the four asphalt binders are presented in **Fig. 5**. It was observed that some long-term aged samples displayed lower BaP_{eq}-TEF values compared to their short-term aged counterparts. This could be attributed to the loss of lightweight PAH compounds through evaporation during the high-temperature laboratory aging process. Significant differences were not detected in the BaP_{eq}-TEF results for CA, SA, and AR binders. In contrast, the WC binder exhibited considerably elevated BaP_{eq}-TEF values in comparison to the other three binders, exceeding them by more than one order of magnitude. This suggests that the chemical warm mix additive Evotehrm comprises organic chemicals that may release PAHs during the leaching process. The BaP_{eq}-TEF values obtained for the leachates of binders CA, SA, and AR were all within safe levels (i.e., less than 0.01 μg/L). Conversely, WC binders demonstrated higher risks, which could potentially lead to toxic effects on human health. The influence of extraction solution acidity on the leaching of PAHs was found to be negligible at the binder scale.

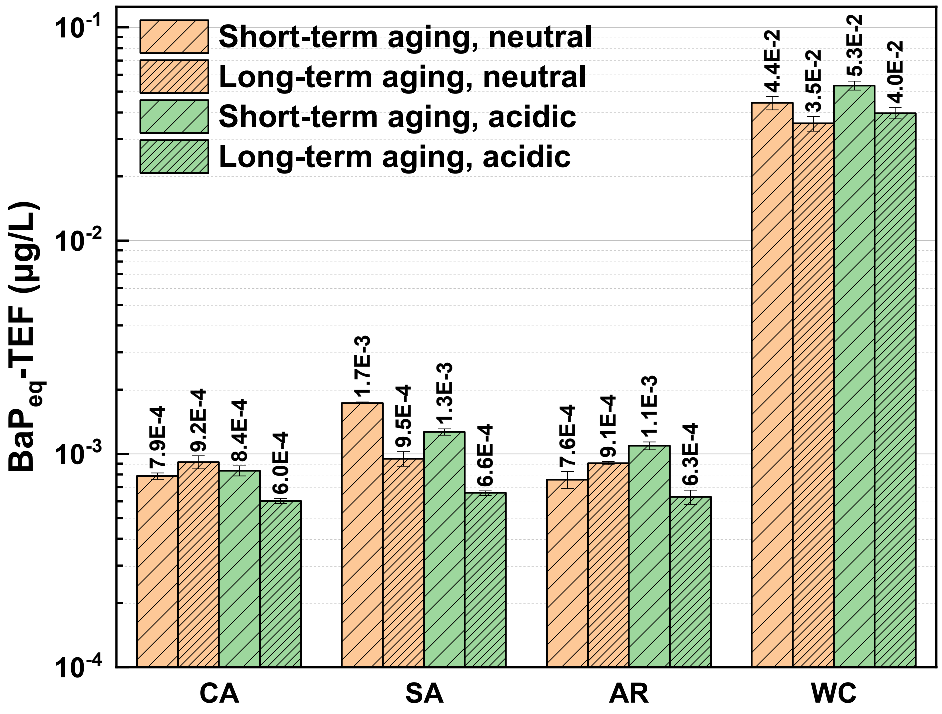

Fig. 5. Leachate BaP$_{eq}$-TEF values of asphalt binder samples (CA: conventional HMA; SA: SBS-modified asphalt; AR: asphalt rubber; WC: WMA with chemical additive)

3.2.2. Asphalt mortar scale

Fig. 6 displays the BaP$_{eq}$-TEF results for the six asphalt mortar samples. WC exhibited the highest BaP$_{eq}$-TEF values, which can be attributed to the inclusion of the chemical additive, aligning with the findings in the binder scale. The leaching of PAHs from WC mortar exhibited a significant reduction compared to WC binder. This discrepancy can be attributed to the composition of mortar samples, which primarily consist of aggregates, with the binder accounting for only 19.6% of the total weight. SA, AR, RA, and BA showed slightly higher BaP$_{eq}$-TEF values than CA, although they generally remained at low levels. Furthermore, the influence of aging on PAH leaching was evident, with long-term aged samples generally exhibiting lower concentrations of PAHs compared to their short-term aged counterparts. At the mortar scale, no discernible relationship could be identified between the BaP$_{eq}$-TEF results and the acidity of the extraction solution.

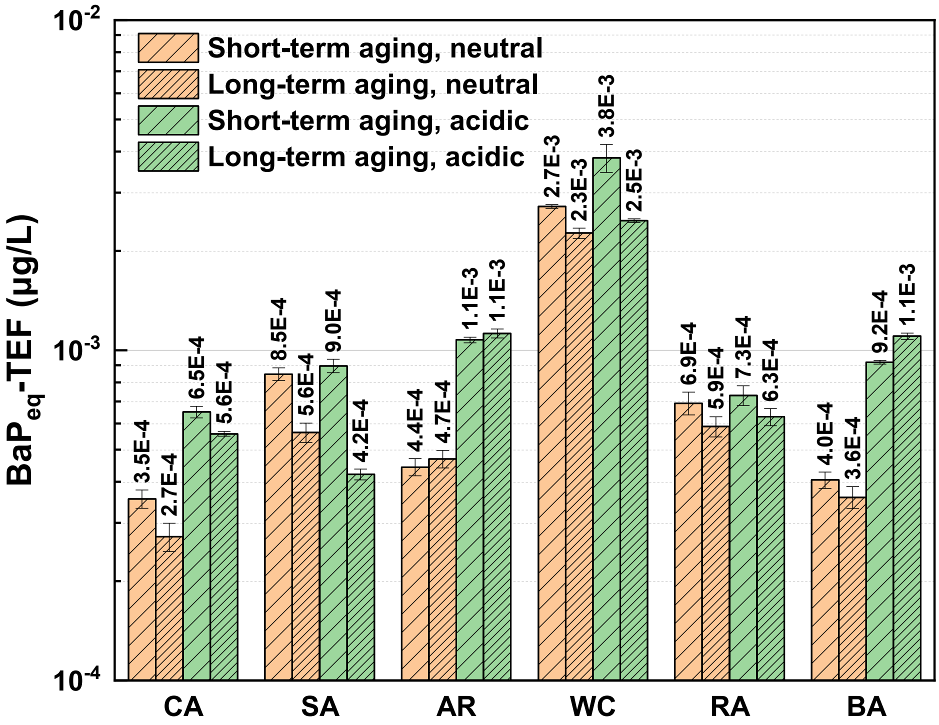

Fig. 6. Leachate BaP$_{eq}$-TEF values of asphalt mortar samples (CA: conventional HMA; SA: SBS-modified asphalt; AR: asphalt rubber; WC: WMA with chemical additive; RA: 30% RAP-incorporated; BA: 30% bottom ash-incorporated)

The comprehensive concentration ranges of PAHs in the leachates from the six asphalt mortar samples are depicted in **Fig. 7**. Among these samples, only eight PAHs were detected at measurable concentrations in CA, SA, AR, RA, and BA leachates, namely Ace, Acy, Ant, Flt, Flu, Nap, Phe, and Pyr. However, the leachates of WC contained two additional PAHs, namely BaA and Chr. It is worth noting that the concentrations of PAHs with lighter molecular weights (such as Nap, Acy, Ace, and Flu) were higher than those with heavier molecular weights (Phe, Ant, Flt, and Pyr). This phenomenon can be attributed to the relatively lower solubility of PAHs in water, where the lighter molecular weight PAHs exhibit greater solubility compared to their counterparts with higher molecular weights. Importantly, the overall concentrations of PAHs in the leachates of all asphalt mortar samples were well below the regulated maximum levels. Furthermore, only PAHs with lighter molecular weights (i.e., containing fewer than five hydrocarbon rings) were present in the leachates, demonstrating minimal toxic effects on human health, as evidenced by BaP_{eq}-TEF values consistently below 0.01 μg/L.

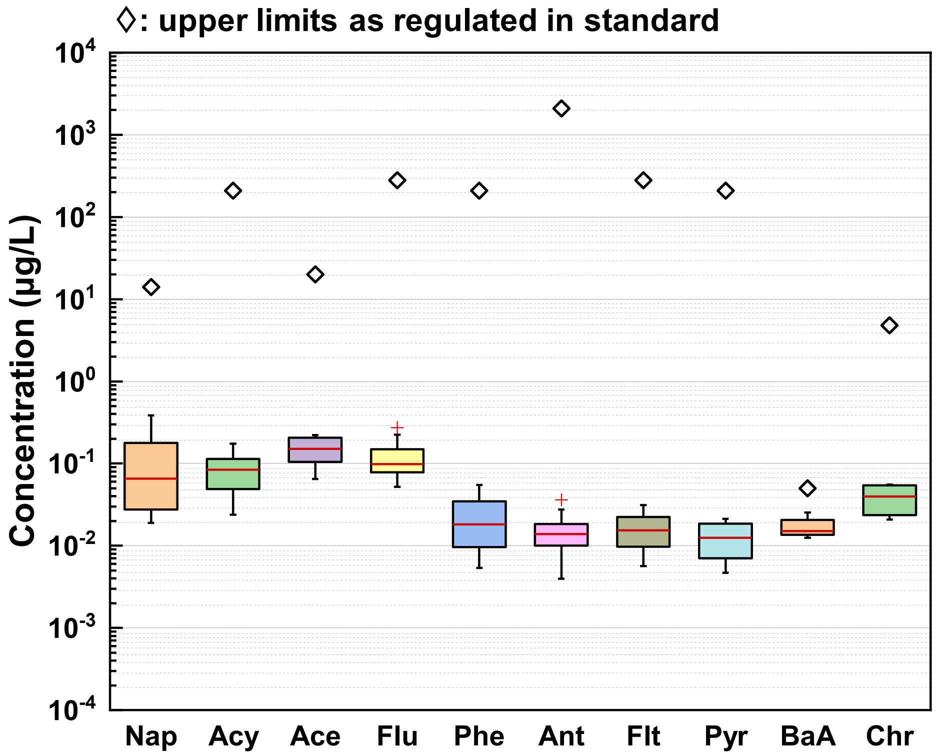

Fig. 7. The concentration range of PAHs in asphalt mortar leachates in comparison to the regulated levels [46].

3.2.3. Asphalt mixture scale

Fig. 8 presents the BaP_{eq}-TEF values of the six asphalt mixture samples. Notably, the BaP_{eq}-TEF values observed in this context exhibited a general decrease when compared to the results obtained in the asphalt mortar scale. One primary factor contributing to this difference is the source of PAH leaching, which was predominantly from the asphalt binder. Consequently, asphalt mortar samples, containing a higher proportion of binder, were expected to release relatively more PAHs than their asphalt mixture counterparts. Another possible reason for this variance could be attributed to differences in their sample preparation processes. In particular, asphalt mortar samples were rapidly dispersed and cooled to room temperature following the mixing process. Conversely, asphalt mixture samples underwent compaction after mixing, and the mixed loose mixtures were maintained at the compaction temperature for a period to ensure effective compaction. Consequently, more lightweight PAHs, which are relatively volatile, may have evaporated during the preparation of compacted asphalt mixture samples, leading to the release of fewer PAHs in the subsequent leaching tests. Importantly, the measured BaP_{eq}-TEF values consistently remained well below 0.01 μg/L. This finding underscores that the leaching of PAHs from compacted asphalt mixtures into the extraction solution occurred at safe levels. In addition, consistent with the test results observed in both the binder and mortar scales, the effects of solution acidity on the leaching of PAHs were insignificant at the mixture scale. This implies that the leaching of PAHs from asphalt pavement is not sensitive to the occurrence of acid rains.

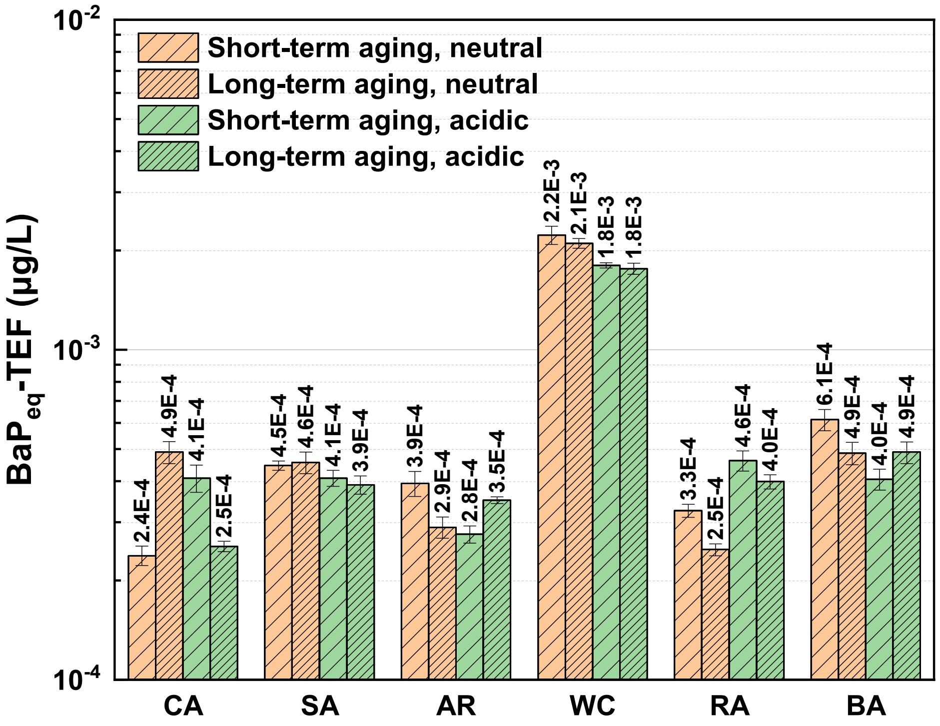

Fig. 8. Leachate BaP_{eq}-TEF values of asphalt mixture samples (CA: conventional HMA; SA: SBS-modified asphalt; AR: asphalt rubber; WC: WMA with chemical additive; RA: 30% RAP-incorporated; BA: 30% bottom ash-incorporated)

Fig. 9 illustrates the comprehensive concentration ranges of PAHs in the leachates of the six asphalt mixture samples. Consistent with the findings in the asphalt mortar scale, the leachates from CA, SA, AR, RA, and BA predominantly contained measurable concentrations of Ace, Acy, Ant, Flt, Flu, Nap, Phe, and Pyr. However, the leachates from WC also featured the presence of BaA and Chr. Notably, there was a noticeable reduction in the concentrations of lightweight PAHs, such as Nap, Acy, Ace, Flu, and Phe, when compared to the asphalt mortar scale. In contrast, the concentrations of heavier molecular weight PAHs, including Ant, Flt, BaA, and Chr, either matched or exceeded the results obtained in the asphalt mortar scale.

These observations confirmed the likelihood of the evaporation of lightweight PAHs during the mixing and compaction processes involved in preparing the asphalt mixture samples. Notably, the measured BaP_{eq}-TEF values for the six asphalt paving materials consistently remained well below 0.01 μg/L, signifying the absence of concerns related to PAH pollution, except for the WC binder, which exhibited elevated BaP_{eq}-TEF values potentially causing toxic effects on human health. Despite the higher content of organic pollutants in WC binder, its application in asphalt pavement significantly reduced the leachability of PAHs, ensuring the safety of WC mortar and mixture without PAH pollution concerns.

The overall results indicate that the leachates of asphalt pavements pose minimal to no risk of harmful health effects, primarily because PAHs are less frequently encountered in water due to their low solubilities when compared to air and soil. However, it is essential to note that while the BaP_{eq}-TEF results demonstrate the minimal health risks associated with human exposure to PAH pollutants from the leachates of asphalt pavements, there are still potential health concerns linked to contact with asphalt fumes. PAHs can be emitted from asphalt mixtures into the air, particularly during the high-temperature construction process of asphalt pavement. A comprehensive investigation of PAHs exposure from contact with asphalt fumes is beyond the scope of this study, and interested readers can refer to previous studies related to PAH emissions in asphalt fumes for further information [59-61].

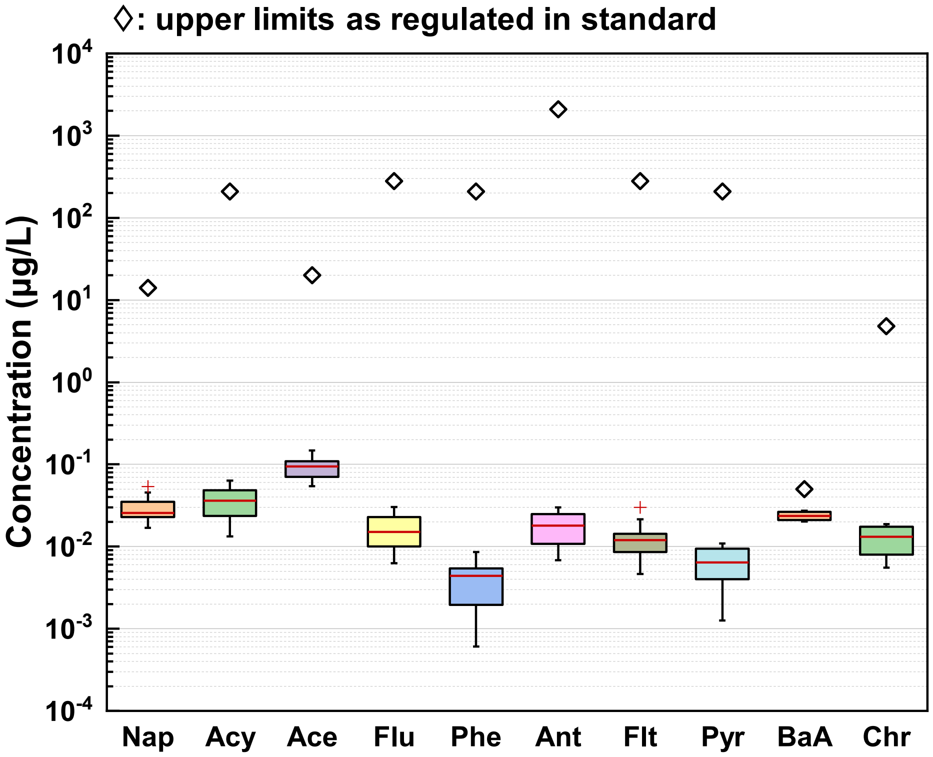

Fig. 9. The concentration range of PAHs in asphalt mixture leachates in comparison to the regulated levels [46].

4. Conclusion

In summary, this study conducted an extensive investigation into the leaching behaviors of six distinct asphalt paving materials, employing samples prepared at three different scales: asphalt binder film, loose asphalt mortar, and compacted asphalt specimens. The study focused on quantifying the levels of heavy metals and PAHs in the leachates of asphalt mixtures and assessing their potential health risks by utilizing HPI and BaP_{eq}-TEF values. The key conclusions drawn from this study are as follows:

- The leaching tests conducted at the asphalt binder and mortar scales offer a rapid assessment of pollutant levels in the leachate. However, these tests might not fully capture the long-term release of heavy metals. As a precautionary measure, especially in areas prone to acid rain events, it is advisable to complement these evaluations with asphalt mixture scale leaching tests when dealing with recycled materials known to contain metal pollutants.

- The leaching of heavy metals from CA, SA, AR, WC, and RA occurred at low levels in neutral environments. However, the elevated metal leaching from AR and WC was observed in acidic environments, the application of AR and WC in regions prone to acid rain events may heighten the leaching risk of heavy metals into the environment.
- BA exhibited significantly increased heavy metal contents in the leachate, with HPI values of BA mixtures reaching around 300 in neutral environments and 500 in acidic environments. This implies that employing hazardous waste materials such as MSWI-BA in asphalt pavement, without appropriate treatment measures, may result in severe heavy metal leaching into the environment, potentially causing adverse effects on human health.
- The overall leaching of PAHs from asphalt pavement was minimal. Most leachates contained only eight lightweight PAHs (i.e., Ace, Acy, Ant, Flt, Flu, Nap, Phe, and Pyr). WC displayed the leaching of two additional PAHs, BaA and Chr, at concentrations well below regulatory limits. The obtained BaP_{eq}-TEF values consistently remained within safe levels (<0.01 μg/L), with no exceedances of individual PAH concentrations compared to the standard.

These findings contribute to an enhanced understanding of the environmental performance of asphalt paving materials, thereby informing more sustainable approaches to the design and maintenance of asphalt pavement. As this study focused on investigating the leaching behaviors of undamaged asphalt pavements. It is recommended to explore the leaching characteristics of deteriorated asphalt pavements affected by issues like cracking, rutting, raveling, and moisture damage in further investigations. In addition, alternative mix design types of asphalt pavement should be studied in the future to further investigate the influences of different mixture compositions. Lastly, field measurements are recommended to explore the influence of environmental conditions on the leaching properties of asphalt pavements in future studies.

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