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Occurrence and risk assessment of PAHs from athletic fields under typical rainfall events

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ABSTRACT

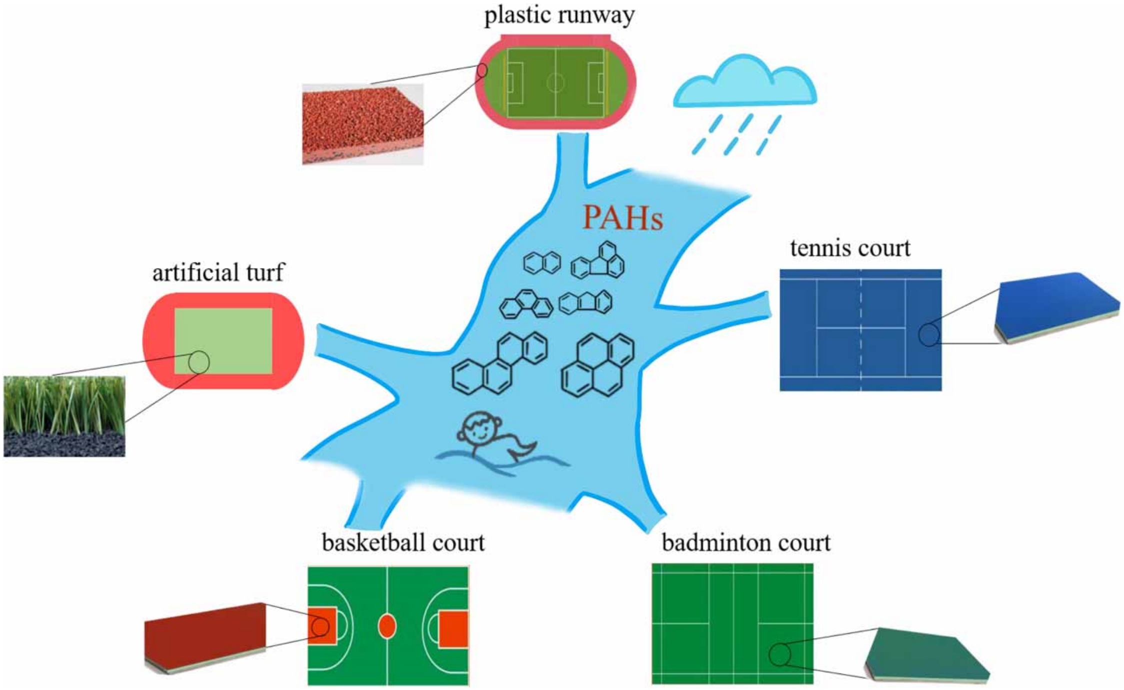
Six polycyclic aromatic hydrocarbons (PAHs) including naphthalene (Nap), fluorene (Flu), phenanthrene (Phe), fluoranthene (Fla), pyrene (Pyr), and chrysene (Chr) were detected in runoff from five athletic fields during three rainfall events. The event mean concentration (EMC) of $\sum_6$PAHs ranged from 3.96 to 23.23 μg/L, which was much higher than the EMC in urban traffic area runoff. Except for Nap, the PAH concentrations followed in the order of artificial turf > badminton court > basketball court > plastic runway > optennis court. The surface characteristics of the athletic fields, such as the composition of materials and roughness, played an essential role in the release of PAHs. $\sum_6$PAHs concentration during the 2nd rainfall event (July 22nd) was the highest among the three rainfall events, indicating that high rainfall intensity facilitated the PAHs release. PAHs during three rainfall events showed little first flush effect except for the artificial turf during the 2nd (22nd July) and 3rd (29th July) rainfall events. The first flush effect could be affected by rainfall characters, PAH properties, and surface characteristics of athletic fields. Ecological risk assessment showed that PAHs in runoff corresponded to moderate-to-high risk, while health risk assessment showed that PAHs could pose a potential carcinogenic danger to human health via dermal contact.

Key words: athletic fields, EMC, PAH, risk assessment, runoff

HIGHLIGHTS

- The event mean concentration of $\sum_6$PAHs in athletic field runoff ranged from 3.96 to 23.23 μg/L.
- 4-ring PAHs were more significant than 2- and 3-ring PAHs.
- High rainfall intensity facilitated the PAHs release.
- The first flush effect was affected by rainfall, PAH properties and athletic field surface characters.
- PAHs in runoff corresponded to moderate-to-high risk but pose a potential carcinogenic danger to human health via dermal contact.

GRAPHICAL ABSTRACT



1. INTRODUCTION

With increasing living standards, people's demand for sports fields is increasing. An artificial athletic field has many advantages over an open grass field. As they do not require a growing season, fertilizers, pesticides, or both, they use less water and require less time, labor, and effort to produce (Claudio 2008). As such, the number of artificial athletic fields is increasing, and their application scope is expanding, from schools and sports fields to parks, communities, and public entertainment venues. More than 13,000 artificial turf courts and 47,000 small-scale courts were used for football training in the EU in 2016, and this number continues to increase (ECHA 2017). The United States has thousands of synthetic turf fields (especially for children and adolescents) that many people frequently use. As an essential part of artificial athletic fields, surface materials are directly in contact with the users. Depending on the sports functions such as running, playing basketball, playing football, etc., surface characteristics such as composed materials and roughness vary from different athletic fields. For example, the surface materials of artificial turf are composed of plastic grass and rubber particles, while the surface materials of badminton courts are mainly composed of rubber. For economic reasons, rubber materials are mainly produced from discarded car tires (Cheng *et al.* 2014). According to the European Chemicals Agency (ECHA), 43% of the waste rubber is used for artificial turf (including fillers), and 45% of the waste rubber is used for sports fields such as track and field fields, tennis courts, and basketball courts. About 21% of the waste tire-derived rubber particles in Europe are used as fillers for artificial turf (Verschoor *et al.* 2021). Because different chemical compounds (benzene, phthalates, alkylphenols, etc.) and additives (activators, plasticizers, vulcanizers, etc.) are employed in the manufacture of tires, it is a sophisticated procedure (Bocca *et al.* 2009). In addition, in the production and laying process, some organic additives such as antioxidants and pigments are also added to the surface materials (Li *et al.* 2010). With the increasing use of sports grounds, the degradation of materials caused by exogenous processes (e.g., rainfall, weathering, and mechanical wear) inevitably leads to the release of chemical substances such as polycyclic aromatic hydrocarbons (PAHs), metals, and volatile organic compounds (VOCs) (Zhang *et al.* 2021). Although several nations and areas have established rules and regulations to limit the use of dangerous chemicals in the rubber for making artificial turf, the rubber itself may still include a number of dangerous elements (Canepari *et al.* 2018; Gomes *et al.* 2021), which could potentially leach out of the materials during use, pollute the environment, and endanger human health.

Environmental contaminants known as PAHs are pervasive, bioaccumulative, and hazardous. Early in the 1980s, the United States Environmental Protection Agency (U.S. EPA) identified 16 PAHs as priority pollutants that the International Agency for

Research on Cancer (IARC) had also identified as potential human carcinogens. Outdoor conditions such as oxidants, sunlight, high temperatures, and rain can weaken the mechanical resistance of the surface materials of sporting grounds (Wachtendorf *et al.* 2017). Consequently, toxic substances such as PAHs are likely released from athletic field materials into air and runoff, which impose potential health risks via inhalation or dermal absorption, in addition to ecological risks by ending up in sewage waters, groundwater, and natural surface waters (Krüger *et al.* 2013). Celeiro *et al.* (2018) found 14 kinds of PAHs in the air above artificial turf. In addition, eight PAHs including naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, and chrysene were detected in the runoff samples, with a total concentration of 0.68–1.55 μg/L. The partial distribution of PAHs in the air and runoff was then demonstrated. Schneider *et al.* detected high concentrations of heavy metals, PAHs, and VOCs in rubber crumbs, including aluminum (5,383 mg/kg), cobalt (168 mg/kg), benzothiazole (48 mg/kg), 2-(2-hydroxyphenyl) benzothiazole, and 4-tert-octylphenol (14 mg/kg) (Schneider *et al.* 2020). Kalbe *et al.* (2013) used particles grained from artificial turf surface materials to study the leaching behavior of PAHs in a column experiment. They found that the artificially aged turf materials could release PAHs and the leaching concentration increased over aging time.

Numerous safety evaluations have found no danger of chemical exposure from recycled rubber used in artificial fields. However, it may still cause a series of health concerns. For example, some toxic compounds (specify these compounds here) were frequently detected in human urine after playing over the athletic fields (van Rooij & Jongeneelen 2009). As a result, there are growing concerns about the safe use of artificial fields, particularly those using surface materials made of recycled rubbers. Unfortunately, previous studies on the health risks of recycled rubber's health risks have some limitations, including small sample numbers and little analysis of pertinent exposure routes and situations (Peterson *et al.* 2018). In addition, to our best knowledge, previous studies mainly focused on investigating pollutants from specific fields such as artificial turf. Different athletic fields may result in various pollutant distribution partners due to the varying materials composition, surface structure, catchment area, rainfall characteristics, etc. However, the occurrence of PAHs in different types of athletic fields remains understudied. Especially, the risk assessment of PAHs released from athletic fields other than artificial turf remains inadequate.

In our previous study, we investigated heavy metal pollution in the runoff from artificial athletic fields and found that the health and environmental risks could not be neglected (Zhang *et al.* 2021). To further assess the risks of pollutants in stormwater runoff from artificial athletic fields, this study aimed to investigate the occurrence and health risks of PAHs in runoff (under three typical rainfall events) from various types of athletic fields, including artificial turf, badminton, basketball, plastic runway, and tennis court (Zhang *et al.* 2021). The specific objectives were (i) to distinguish the distribution of PAHs in runoff from various kinds of artificial sports fields; (ii) to study the effect of rainfall characteristics on the distribution and first flush behavior of PAHs in runoff from different types of athletic fields, and (iii) to assess the ecological and health risk of PAHs in runoff from various athletic fields.

2. MATERIALS AND METHODS

2.1. Sampling sites

Five commonly used athletic fields with different functions and underlying surfaces, namely artificial turf, badminton court, basketball court, plastic runway, and tennis court at a university campus in Daxing District, Beijing, China, were selected as the sampling sites. The main characters of the five athletic fields were summarized in Table S2. The sampling points were located at the drain outlet of each athletic field. Sampling was conducted during three specific rainfall events in the summer of 2019 (5th, 22nd, and 29th July), and 20 samples in total were collected. The drought period before the three rainfall events was 40, 4, and 7 days, respectively, according to the data from the Daxing District Meteorological Bureau (Beijing, China). The rainfall duration was 90, 60, and 90 min, and the total rainfall was 8.2, 9.6, and 8.0 mm, respectively (Zhang *et al.* 2021). Sampling was conducted at different time intervals during a particular rainfall event at the selected sampling points of the athletic fields (Figure 1). When runoff was generated, the first runoff sample was collected (defined as time 0 min). The runoff was then measured every 30 min until the rain ceased. Each group of samples was collected in duplicate (300 mL per sample) and stored in brown glass sampling bottles without leaving headspace. Natural rain samples (rainfall without touching the ground surfaces) were also collected as the control for each rainfall event. Samples were then stored in a fridge at 4 °C for further analysis.

2.2. Laboratory analysis

The liquid–liquid extraction method was used to extract PAHs from the runoff samples (Kruger *et al.* 2011). Before the extraction, 200 mL of the sample was filtered through 0.45 μm glass fiber filters (GF/F, Whatman, pre-combusted at 450 °C for 4 h) and added with 5 ng of 2-fluorobiphenyl and 4–4′-terphenyl-d_{14} (o2si, USA). Then, 15 mL of dichloromethane (CNW,

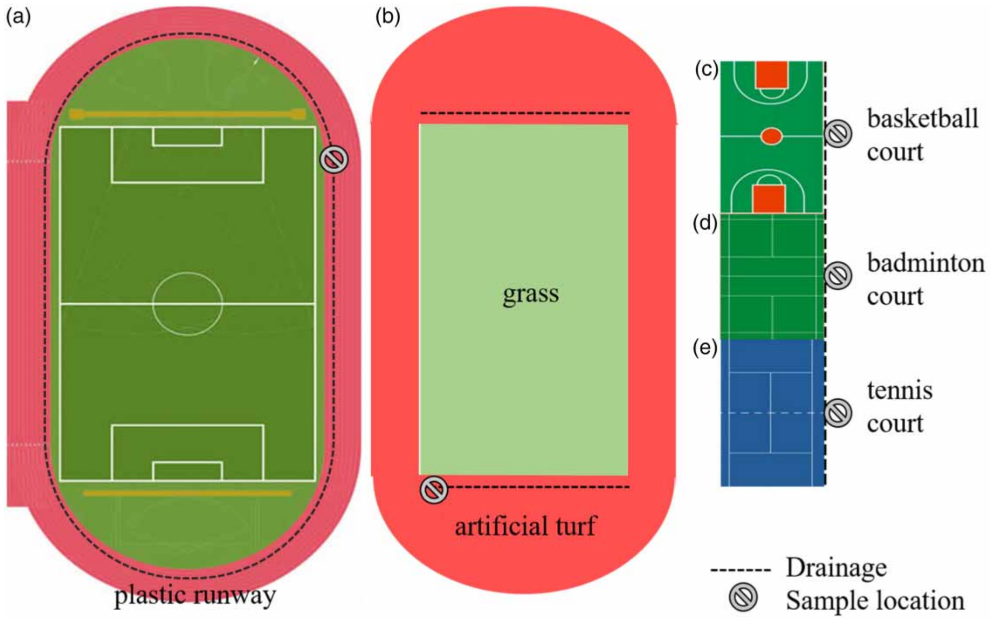


Figure 1 | Sampling sites of five athletic fields located at a university campus in Daxing District, Beijing, China.

Germany) was combined with each sample in a separating funnel. The organic phase was separated 15 min later after moderate shaking. The extraction was repeated once with 15 mL fresh dichloromethane. The organic phases were combined into a single mixture, dried with anhydrous sodium sulfate, and then concentrated with a nitrogen blower until almost dry. The concentration was transferred to a C18 cartridge for solid-phase extraction (SPE) (CNW LC-C18 SPE). Each C18 cartridge was prepared with 5 mL of dichloromethane and 5 mL of n-hexane (CNW, Germany) before sample loading and was then dried in a vacuum. The analytes on the cartridge were eluted three times with 5 mL of n-hexane. The extract was then evaporated to almost dryness with a moderate nitrogen flow, and it was then reconstituted with n-hexane to a final volume of 1 mL. Sixteen priority PAHs' mixed standards were bought from o2si, USA. After that, a gas chromatograph–mass (GC–Mass) spectrometer (Agilent 7890B-5977C) was used to quantify the PAHs in the extracts.

The calibration curves were established with six data points (0.05, 0.1, 0.3, 0.5, 1.0, and 5.0 g/mL) that were used to create the calibration curves. For GC separation, a DB-5 ms silica-fused capillary column was used. The temperature of the GC oven was initially set at 40 °C for 2 min, raised to 300 °C at a rate of 10 °C/min, and then kept at 300 °C for 10 min. The recovery of the standards at each calibration point was monitored and served as quality control. In the dichloromethane:N-hexane solvent (1:3, v/v), the recovery was achieved from standards of known concentrations with acceptable linearity ($r^2 = 20.997$). The mean recovery percentages ranged from 95.2 to 99.5%. The relative standard deviation (i.e., coefficient of variation) varied from 0.2 to 4.5%. Recovery rates between 50 and 120% and a coefficient of variation value under 20% are considered to be within acceptable limits (Yuan *et al.* 2019). Thus, the quality assurance in this study was adequately confirmed. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated based on 3 and 10 times the standard deviations. The LOD values ranged from 0.001 to 0.020 μg/L, while the LOQ values ranged from 0.002 to 0.091 μg/L. Statistical analysis was conducted with SPSS and Origin 2018. The analytical parameters for each PAH are shown in Table S1.

2.3. Calculation of event mean concentration

The event mean concentration (EMC) is an essential indicator for evaluating the degree of pollution of surface runoff, which is calculated as per Equation (1) (Brezonik & Stadelmann 2002):

$$\mathrm{EMC} = \frac{M}{V} = \frac{\int_0^t C_t Q_t d_t}{\int_0^t Q_t d_t} \tag{1}$$

where M is the total amount of pollutants (mg), V is the total volume of runoff (m^3), C_t is the mass concentration of contaminants at time t (μg/L), and Q_t is the runoff at time t (m^3/s).

2.4. Identification of first flush events

The first flush effect was analyzed with M–V curves constructed from the dimensionless cumulative pollution load M (t) and the dimensionless cumulative runoff V (t), which are determined according to Equations (2) and (3), respectively (Li *et al.* 2007):

$$M(t) = \sum_{i=1}^{n} C_i Q_i \Delta t_i / M \tag{2}$$

$$V(t) = \sum_{i=1}^{n} Q_i \Delta t_i / V \tag{3}$$

where Q_i and C_i are the respective flow rate and concentration at a time; t_i corresponds to the ith measurement of an event having n the number of measurements. M and V are the total pollutant load and the total runoff volume discharged, respectively.

2.5. Ecological and health risk assessments

The toxic equivalent quotient (TEQ) of PAHs about benzopyrene (BaP) was utilized to evaluate the ecological risk. This approach is frequently used to assess the environmental risk of PAHs in sediments and aquatic habitats (Tsai *et al.* 2009), as shown in Equation (4):

$$\text{TEQ}_{\text{CARC}} = \Sigma C_i \times \text{TEF}_i \tag{4}$$

where C_i is the concentration of PAHs i in the runoff sample (μg/L) and TEF_i is the toxic equivalency factor of PAHs i relative to BaP.

The lowest risk concentration of BaP was converted to a TEQ of 0.0005 μg/L (TEQ_{QV}). The ecological risk level was calculated by $\text{TEQ}_{\text{CARC}}/\text{TEQ}_{\text{QV}}$, which was divided into four grades: no risk (<0.1), low risk (0.1–1), low-to-moderate risk (1–10), moderate-to-high risk (10–100) and high risk (≥100) (Ravindra & Mor 2019).

Health risk assessment was evaluated by a lifetime carcinogenic risk (ILCR) model proposed by the U.S. EPA to assess the potential carcinogenic risk of PAHs to humans through skin contact (Zhang *et al.* 2015). ILCRs formula is shown in Equation (5):

$$\text{ILCRs}_{\text{Dermal}} = \frac{\text{CS} \times \left(\text{CSF}_{\text{Dermal}} \times \sqrt[3]{\frac{\text{BW}}{70}}\right) \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times 10^6} \tag{5}$$

where CS is the sum of *BaP* equivalent concentrations; $\text{CSF}_{\text{Dermal}}$ is the carcinogenic slope factor (1/(mg/kg/day)); BW is the average body weight (kg); SA is the surface area of the skin that contacts the water (L/day); AF is a skin adherence factor; ABS is the dermal absorption factor; EF is the exposure frequency (days/year); ED is the exposure duration (year); and AT is the average life span (days).

3. RESULT AND DISCUSSION

3.1. Distribution of PAHs in different athletic field runoffs

Compared with the average concentration, the EMC also considers the impact of runoff flow on the concentrations of pollutants. Therefore, the EMC is a crucial event-specific parameter representing the actual time variations in concentrations (Perera *et al.* 2021). The EMC of PAHs in runoff from each athletic field is presented in Table 1. A total of 6 out of the 16 EPA PAHs were detected in all the samples, namely naphthalene (Nap), fluorene (Flu), phenanthrene (Phe), fluoranthene (Fla), pyrene (Pyr), and chrysene (Chr). This indicates that PAHs were ubiquitous in athletic field runoffs. The sources of PAHs in the runoff could be mainly from the surface materials of athletic fields. The EMC of $\sum_6$PAHs in the five athletic

Table 1 | EMC of PAHs in different athletic field runoffs (μg/L)

PAHs	Artificial turf	Badminton court	Basketball court	Plastic runway	Tennis court
Nap	0.24	0.18	0.16	0.22	0.22
Flu	0.28	0.05	0.05	0.04	0.03
Phe	1.31	0.54	0.63	0.18	0.11
Fla	1.32	0.88	0.67	0.23	0.09
Pyr	0.94	0.29	0.21	0.14	0.09
Chr	2.14	0.75	0.46	0.25	0.03
$\sum_6$PAHs	23.23	22.51	14.11	8.42	3.96

fields ranged from 3.96 to 23.23 μg/L, which was several times higher than the EMC (a few micrograms) of runoff in urban traffic areas (Zheng *et al.* 2014).

In addition, the surface of the athletic field is often made from rubber polymer, reinforcing elements (such as carbon black), aromatic extender oils, antioxidants, pigments, etc. (Perkins *et al.* 2019). Ethylene propylene diene monomer (EPDM) is frequently used as rubber fillers in sporting grounds. In use, PAHs may be released during the pyrolysis of the surface materials. PAHs are semi-volatile and highly hydrophobic. Thus, there are more PAHs distributed in the gas phase than in the water phase. The thermal stability of the athletic field surface material is much weaker than the road surface. Especially in summer, high temperatures will accelerate the release of organic compounds from the surface material (Jim 2017). Besides, the athletic field could undergo UV, ozone, and mechanical force during use. These processes can accelerate the cracking and peeling of the polymer matrix, so the internal additives and other pollutants containing PAHs could be released (Wachtendorf *et al.* 2017). Celeiro *et al.* (2018) have demonstrated that watering the surfaces of athletic fields contributed to the PAHs leaching from the rubber material.

Except for Nap, the concentrations of five PAHs, including Flu, Phe, Fla, Pyr, and Chr, in the athletic field runoff followed in the order of artificial turf > badminton court > basketball court > plastic runway > tennis court. To promote the reuse of waste resources, most of the rubber used in surface materials of athletic fields is recycled tires. Magnusson & Mácsik (2017) show that recycled tires are more susceptible to cracking than new tires. PAHs are one of the byproducts of tire cracking (Quek & Balasubramanian 2012). Thus, PAHs are inevitably released from the surface with rubber, causing a higher amount detected in the runoff from the artificial turf and badminton court. In addition, the smaller the size of the filling particle, the easier it releases contaminants (Menichini *et al.* 2011; Kim *et al.* 2012). In the artificial turf, the surface is composed of small rubber particles, while the badminton court is composed of compacted, smooth surfaces. Thus, the release of PAHs from the artificial turf was higher than that from the badminton court. The PAHs concentration in the plastic runway and tennis court was lower than that in other fields. The reason might be due to the lower release from surface materials. Unlike rubber as the main composition in artificial turf, the surface materials of the plastic runway and tennis court mainly comprised EPDM and siloxane-modified polyurethanes. Even though EPDM and siloxane-modified polyurethanes could release PAHs during pyrolysis, their release could be much less than from rubber. Therefore, the concentration of PAHs in the plastic runway runoff was lower. The PAHs concentration in the tennis court was the lowest, which might be due to its compact surface. Unlike other fields, the surface of the tennis court is smoother, where PAHs might not be released from that compact surface as quick as from the rough surface of the other fields.

The PAHs distribution in the athletic fields is compared with reported data in the literature. Celeiro *et al.* (2021) analyzed PAH concentrations in the runoff from eight football fields. They found that the average concentrations of Flu, Chr, Fla, and Nap were 0.03, 0.04, 0.07, and 0.04 μg/L, respectively, which were much lower than the concentrations (specify the values here) detected in this study. For Pyr, the concentration detected in the present study was 0.09–0.94 μg/L, which was similar to the concentrations (0.05 –0.9 μg/L) detected in eight football fields by Celeiro *et al.* (2021). The comparison shows that the distribution of PAH in athletic fields is highly dependent on athletic fields' locations, types, and sampling points.

3.2. Profiles of PAHs composition

The total PAHs concentration in most of the runoff was lower than 7.0 μg/L. From the distribution ratio perspective, the samples' distribution was mainly concentrated in two regions (marked in red, Figure 2). The first region was located in the

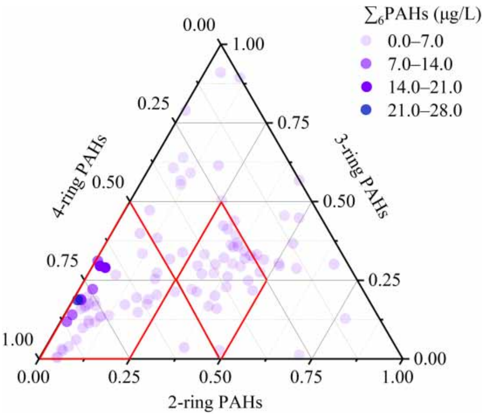


Figure 2 | Triangular diagram of percentage concentration for the six PAHs in the five athletic field runoffs on a university campus. Please refer to the online version of this paper to see this figure in colour: https://dx.doi.org/10.2166/wst.2023.092.

middle of the triangular diagram, where the proportions of 2-, 3-, and 4-ring PAHs were the same, accounting for 25–50% of the total PAHs. The second region was located on the left bottom of the triangular diagram, where 4-ring PAHs accounted for a large proportion, more than 50% of the total PAHs. Samples with concentrations higher than 7.0 μg/L all appeared in this area.

2-ring PAHs have poor stability in an aqueous solution (Zhang *et al.* 2019). Therefore, the proportion of 2-ring PAHs in the runoff was relatively low. The relatively high distribution of 3- to 4-ring PAHs in all the samples could be originated from rubber polymer, aromatic extender oil, antioxidants, processing aids, plasticizers, etc., from the surface materials of the athletic fields (Lopes *et al.* 2000). The previous analysis showed that the samples with higher total concentrations were located in the artificial turf area, and the proportion of 4-ring PAHs was more significant. Celeiro *et al.* (2021) detected seven kinds of PAHs leaching from the material of artificial turf, and the total concentration was 6.0–54.0 μg/g and the largest portion was Pyr (4-ring PAHs), which reached a concentration of 30.0 μg/g. The dominance of 4-ring PAHs in athletic runoff in this study is consistent with the previous survey.

3.3. Temporal variation of PAHs concentration under different rainfall events

Under various types of rainfall events, the temporal change of $\sum_6$PAHs concentration displayed diverse patterns (Figure 3). Generally, the $\sum_6$PAHs concentration under the 2nd rainfall event (July 22nd) was the highest (i.e., 0.30–24.23 μg/L), followed by the 3rd and then 1st rainfall events. The average rainfall of the three events was observed in the order of the 2nd (9.6 mm) $>$ 1st (8.2 mm) $>$ 3rd (8.0 mm), and the duration of the rainfalls followed in the order of 1st (90 min) $\approx$ 3rd (90 min) $>$ 2nd (60 min). Due to the vigorous rainfall intensity of the 2nd rainfall, the erosion effect on surface materials was more prominent. The stronger the scouring impact, the more the pollutants were released. Besides, the high amount of $\sum_6$PAHs during the 2nd rainfall might also be due to the higher temperature on July 22nd than a few days before and after. From Table 2, the ambient temperature of the 2nd rainfall was the highest (35 °C) compared with the 1st and 3rd rainfall (30 and 29 °C, respectively). High temperatures could facilitate the release of pollutants especially for VOCs from the ground surface. Therefore, high PAHs concentrations were detected, especially during the 2nd rainfall.

There was no clear rule between rainfall duration and PAHs concentration under a particular rainfall event, except for the 2nd rainfall event. During the 2nd rainfall event, except for the tennis court, the PAHs concentration increased first and then decreased over time in the early stages of the rainfall (0–30 min). This suggests that scouring had a more significant effect on the PAHs in runoff in the early rainfall stage. At this time, the primary source of PAHs may be the release of surface particulate matter. During the later period of rainfall, the concentration of pollutants increased again. The concentration was positively related to the rainfall intensity during the 2nd rainfall event. This suggests that surface materials released PAHs into runoff environments (Wachtendorf *et al.* 2017). However, during the 1st and 3rd rainfall events, the PAHs concentration seemed random during the sampling process for the five types of athletic fields. Generally, except for the tennis court, the concentration of PAHs from all the athletic fields under the 2nd rainfall event was the highest. It seems that rainfall duration only exerted a significant influence on high concentrations but not on low concentrations.

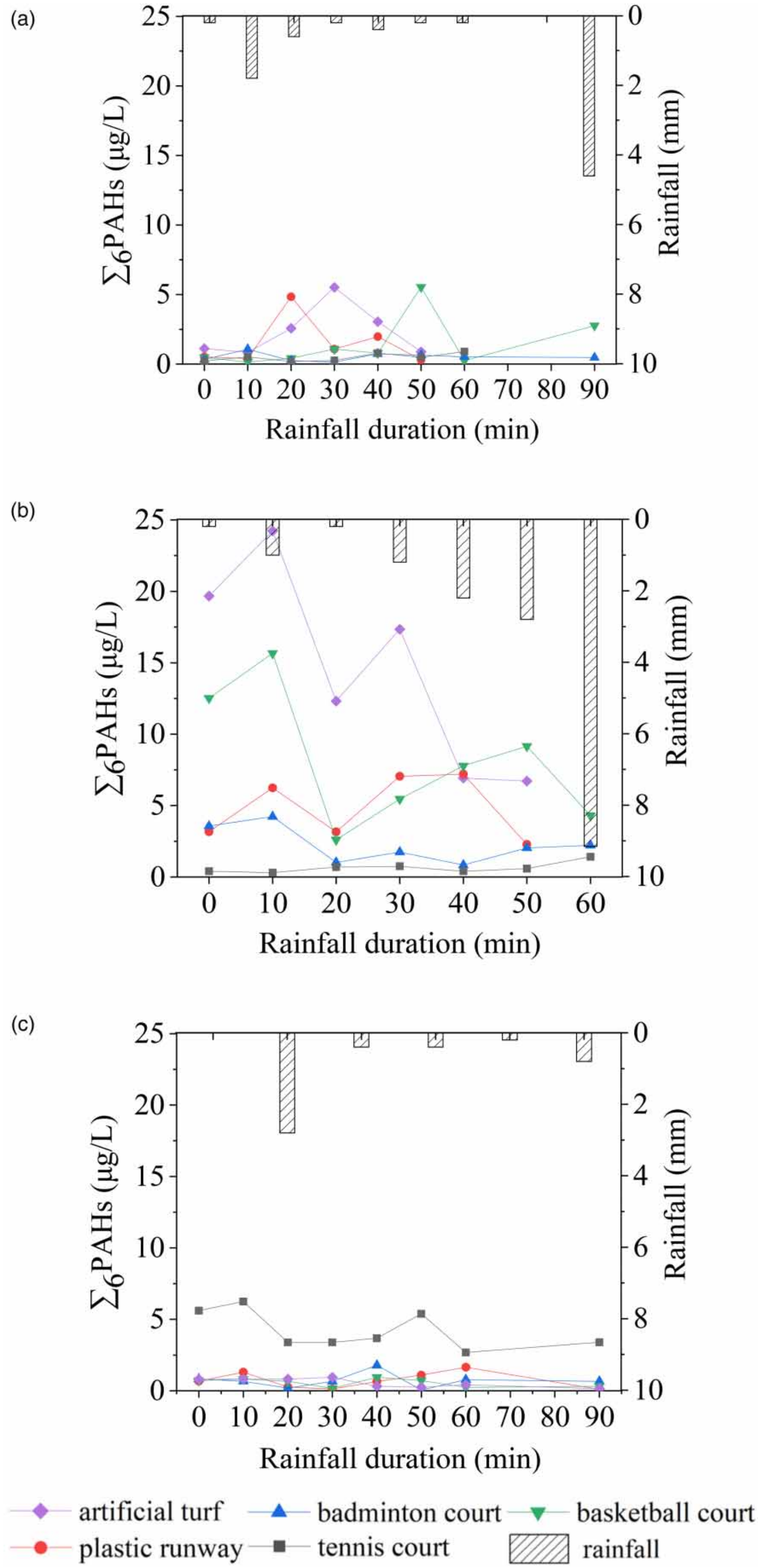


Figure 3 | Concentrations of PAHs under different rainfall events in five athletic fields: (a) 1st rainfall event (July 5th, 2019), (b) 2nd rainfall event (July 22nd, 2019), and (c) 3rd rainfall event (July 29th, 2019).

3.4. First flush effect analysis

The existence of the first flush effect can be identified in the *M*–*V* curves if there are points above the 45°line, i.e., the rate of pollutant load is higher than that of stormwater runoff (Li *et al.* 2007). Generally, PAHs under the three rainfall events showed little first flush effect (data now shown), except for the artificial turf under the 2nd and 3rd rainfall events (Figure 4). Specifically, a strong first flush effect of three PAHs including Phe, Fla, and Pyr and four PAHs including Nap, Phe, Fla, and Pyr was observed in the artificial turf runoff in the 2nd and 3rd rainfall events, respectively (Figure 4). The concentrations of Flu and Chr in the runoff of some fields were too low to perform the first flush effect analysis. The first flush effect could be affected by multi-factors, including rainfall characters, PAHs properties, and the surface characteristics of athletic fields. During the 2nd rainfall event, the PAHs concentration in all the fields' runoff was much larger than that during the 1st and 3rd rainfall events. Li *et al.* (2007) showed that the first flush effect was weak if a vigorous rainfall intensity appeared later during a rainfall event. Besides the rainfall characteristics, the field materials' roughness and the degree of imperviousness may also have an impact on the first flush effect. Most PAHs in the runoff show little first flush effect. In the second rainfall event, the concentration of PAHs increased first and then decreased with time, which was more obvious in the areas of artificial turf, badminton court, basketball court, and plastic runway. At this time, the main source of PAHs may be the precipitation of pollutants in the surface material. However, conventional pollutants such as heavy metals usually show a significant initial washing effect, which may be caused by the difference in the adsorption of pollutants by surface materials. Gomes *et al.*'s study of rubber fillings from six countries (the United States, the Netherlands, Norway, Portugal, Spain, and Italy) showed that the potential of rubber fillings to release pollutants depends on the type of rubber, while the release of zinc (n.d. – $14{,}150 \pm 1{,}344$ mg/kg) is much higher than that of pyrene (n.d. – 4.31 ± 3.95 mg/kg) (Gomes *et al.* 2021). Lee *et al.* (2002) concluded that when the fraction of impervious was large, the initial flush happened forcefully. The impervious area (catchment area) of the five athletic fields decreased in the order of artificial turf (17.3 m^2) > plastic runway (16.1 m^2) > basketball court (2.9 m^2) > tennis court (1.82 m^2) > badminton court (1.45 m^2) (Table 1). Therefore, the first flush effect of PAHs was only observed in the artificial turf runoff, which passed the highest impervious area.

3.5. Ecological and health risk assessments

The TEQ_{CARC} values of PAHs in the five athletic field runoffs ranged from 0.0008 to 0.0255, with an average value of 0.0091 μg/L. The ecological risk level calculated by TEQ_{CARC}/TEQ_{QV} at the different athletic fields was followed in the order of artificial turf > badminton court > plastic runway > basketball court > tennis court (Figure 5). According to the risk classification, the ecological risk level of PAHs in the artificial turf, badminton court, and plastic runway corresponded to moderate-to-high risk. In contrast, the ecological risk level in the basketball court and the tennis court corresponded to low-to-moderate risk. The environmental risk level of the artificial turf runoff was significantly higher than the levels of other athletic fields, which might be due to the highest concentration of Chr.

The ILCRs were calculated to estimate the potential human health risks caused by PAHs exposures through dermal contact. The ILCRs calculated for each sampling sites are presented in Figure 6. According to the U.S. EPA, a cancer risk index between 10^{-6} and 10^{-4} indicates a potential health risk, and a risk index higher than 10^{-4} indicates a high risk (Chen & Liao 2006).

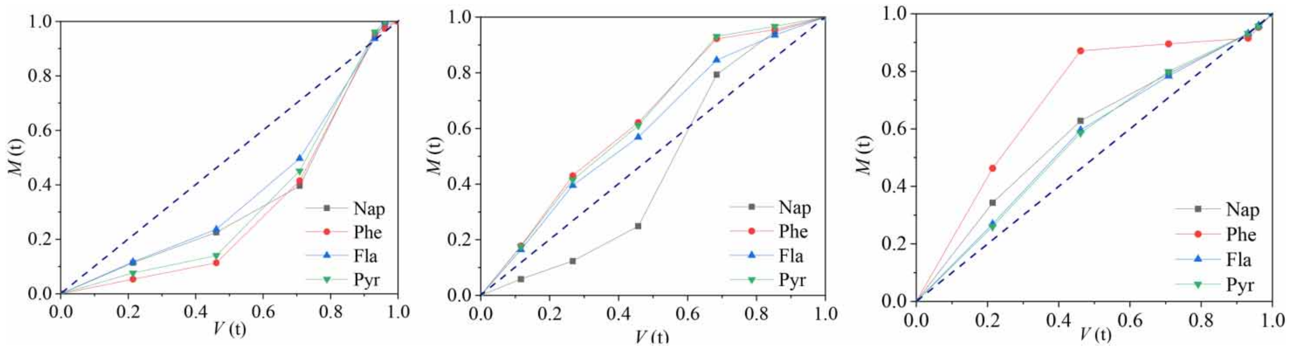


Figure 4 | Normalized cumulative curves for Nap, Phe, Fla, and Pyr in artificial turf runoff: (a) 1st rainfall event (July 5th, 2019), (b) 2nd rainfall event (July 22nd, 2019), and (c) 3rd rainfall event (July 29th, 2019).

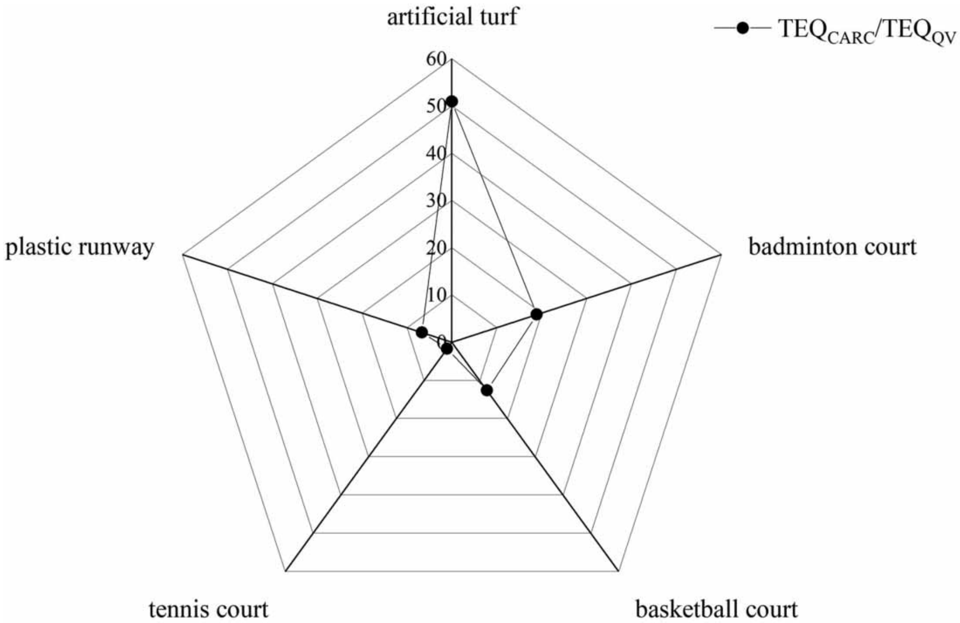


Figure 5 | TEQ_{CARC}/TEQ_{QV} values of PAHs in five athletic field runoffs.

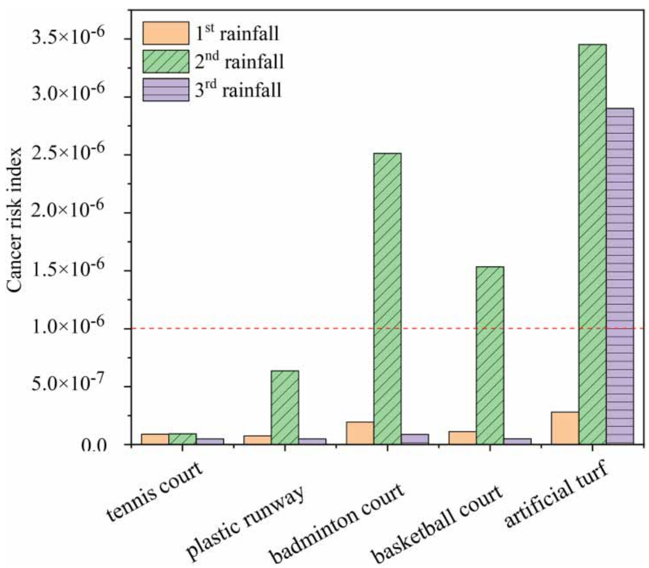


Figure 6 | Health risk of PAHs in five athletic field runoffs.

The carcinogenic risk indexes of runoff from the five athletic fields are presented in Figure 6. Among them, the cancer indexes of the badminton and basketball court runoff during the 2nd rainfall event and the indexes of the artificial turf runoff under the 2nd and 3rd rainfall events were higher than 1.0×10^{-6}. This indicates that the artificial turf, badminton, and basketball court runoff could pose a health concern to the users. The EMC of the PAHs in those fields was also the highest (Section 3.1), suggesting a positive relationship between health risk and the concentration of PAHs. Therefore, the use of recycled materials in badminton courts, basketball courts, and artificial turf should be strictly controlled to reduce the potential human health risk. The carcinogenic risk was not found under the remaining rainfall events. Nonetheless, the migration of PAHs into the surrounding environment via runoff and their cumulative effect may have a significant impact on the surrounding environment.

4. CONCLUSIONS

This study investigated and compared the distribution and risks of PAHs in runoff from five representative athletic fields (artificial turf, badminton court, basketball court, plastic runway, and tennis court) under three typical rainfall events. Six out of 16 PAHs in the U.S. EPA's priority pollutant list were detected in all the samples, namely Nap, Flu, Phe, Fla, Pyr, and Chr. The sources of PAHs in the runoff could be mainly from the surface materials of athletic fields. The EMC of Σ_6PAHs in the five athletic fields ranged from 3.96 to 23.23 μg/L, which was dozens of times higher than the EMC of runoff in urban traffic areas. These results indicate that PAH pollution was ubiquitous in the athletic field runoffs. Four-ring PAHs (Pyr and Chr, $>$30%) were more significant than 2-ring and 3-ring PAHs. Except for Nap, the PAHs concentrations followed in the order of artificial turf $>$ badminton court $>$ basketball court $>$ plastic runway $>$ tennis court. The surface character of the athletic fields, such as the composition of materials and roughness, played a crucial role in the release of PAHs. Besides, strong rainfall intensities facilitated the release of PAHs, and the first flush effect was weak if a vigorous rainfall intensity appeared later during a rainfall event. Ecological risk assessment showed that PAHs from the artificial turf, badminton court, and plastic runway runoff corresponded to moderate-to-high risk. Health risk assessment showed that PAHs from the artificial turf, badminton court, and basketball court runoff could pose a potential carcinogenic risk to humans via dermal contact. Therefore, using recycled materials to construct badminton courts, basketball courts, and artificial turf should be adequately controlled to reduce potential hazards to human health.

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AUTHOR'S CONTRIBUTIONS

X.Z. performed the design of experiment, conducted date analysis and funding acquisition, wrote the original draft, reviewed and edited the article. Y.G. and Y.W. performed sampling, sample analysis, and data analysis, wrote the original draft, reviewed and edited the article. J.L. reviewed and edited the article. Y.J. did sampling. Y.T. performed graphical abstract. Z.Z. reviewed the article. C.T. and Y.W. investigated sample analysis. H.L. conducted funding acquisition. Y.H. conceptualized and revised the article.

All authors contributed to the preparation of the manuscript.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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