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Profiling and assessing soil-air exchange of polycyclic aromatic hydrocarbons (PAHs) in playground dust and soil using ex situ equilibrium passive sampling

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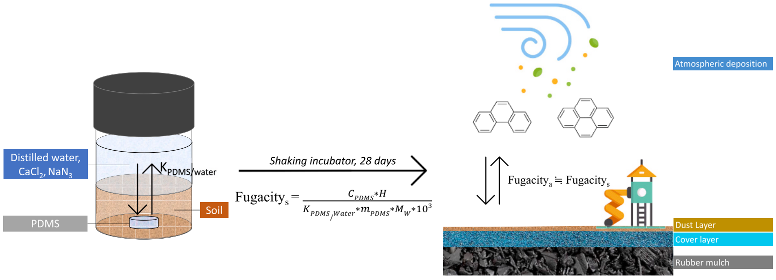
HIGHLIGHTS

- Total concentration of Σ16 PAH in dust was approximately 5 times higher than soil.
- Bioavailable fraction of PAHs was evaluated using passive samplers.
- Fugacity analysis indicated that PAHs in dust/soil are mainly from atmospheric deposition.
- Source apportionment suggests the main source of PAHs from petrogenic combustion.
- PAHs in dust/soil showed weak correlations with TOC.

GRAPHICAL ABSTRACT



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ABSTRACT

Cancer risk can be associated with exposure to polycyclic aromatic hydrocarbons (PAHs) in playground dust and soil. This study investigated the profiles and sources of PAHs from poured rubber-surfaced playground dust and uncovered playground surface soil, by applying an *ex-situ* equilibrium passive sampling technique. Surface dust and soil samples were collected from 15 different playgrounds in Seoul, Republic of Korea. The total 16 EPA PAHs concentrations in surface dust and soil varied from 198 to 919 μg kg^{-1} dw and 68–169 μg kg^{-1} dw, respectively. 4- to 6-ring PAHs were dominant, accounting for approximately 53.8%–94.5% of the total PAHs in surface dust and soil. The diagnostic ratios and principal component analysis suggested that a mixed coal combustion and vehicular emission was likely the main source of PAHs in the surface dust and soil. The higher total organic carbon content can explain the higher PAH accumulation and lower fugacities of PAHs. The fugacity comparison of phenanthrene and pyrene in dust, soil, air, and playground surface material indicated that atmospheric deposition is the main source of PAHs in the dust and soil on rubber-surfaced and uncovered surfaced playgrounds. This study contributes to the understanding of PAHs sources in dust and soil samples in children's playground and helps policymaker determine the right contamination sources for risk management.

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1. Introduction

Polycyclic aromatic hydrocarbon (PAH) pollution, alongside increasing industrialization, has caused serious concern. PAHs are an important group of organic pollutants released into the environment, primarily through incomplete combustion of fossil fuels and biomass (Yu et al., 2019). Children spend more time outdoors, coming in close contact with dust and soil, and may face increased PAH exposure as compared to adults. Numerous studies have focused on the PAH concentrations in surface dust and soil in roadsides, busy streets, and industrial areas, to study the risks of PAHs on the environment and human health (Liu et al., 2019; Marquez-Bravo et al., 2016; Tarafdar and Sinha, 2018; Yadav et al., 2018; Zhang et al., 2016).

Outdoor playground surfaces can be made of natural soil or poured rubber installation, which largely consists of crumb rubber (cushion layer), covered by materials (wear layer) such as ethylene propylene diene monomer (EPDM), styrene-butadiene (SBR), or thermoplastic vulcanizate (TPV) granules. It has been reported that rubber tire materials contain aromatic extender oil and have a PAH content of 300–700 mg kg^{-1} (Aatmeeyata and Sharma, 2010). Previous studies of PAH concentrations in natural soil playgrounds in Bratislava, Slovakia (Hiller et al., 2015) and Gwangju, Republic of Korea (Islam et al., 2018) indicated mean childhood cancer risks of 1.09×10^{-7} and 3.6×10^{-7}, respectively. Contrastingly, Tarafdar et al. (2019) reported that the cancer risk was marginally higher than the standards set by US Environmental Protection Agency ((EPA 1990)) in the dust from poured rubber-surfaced playgrounds in Seoul, Republic of Korea. PAHs concentrations were four to five times higher in dust from the covered playground than in the natural soil playground (Tarafdar et al., 2019). Bioavailability of the higher concentration of PAHs in dust in covered playgrounds is uncertain as the natural soil playgrounds. Higher total PAH concentration in dust can be attributed to PAH migration from the rubber mulch of the poured rubber surface. Therefore, investigating the sources of PAHs in dust and soil particles from playground surfaces and rubber mulch is necessary to further understand the risk associated with PAH uptake and formulate appropriate management strategies.

Soil-air exchange is a key diffusive process governing the fate of hydrophobic organic pollutants, including PAHs (Cousins et al., 1999). Atmospheric deposition is a significant source of PAHs in surface dust and soil (Murakami et al., 2005; Suman et al., 2016; Wild and Jones, 1995). Semi-volatile PAHs may re-volatilize from surface dust and soil and re-enter the atmosphere. To evaluate the risk associated with environmental contamination and human exposure, it is important to understand the soil-air exchange of PAHs. Existing soil-air partitioning methods involve grab sampling (Bidleman and Leone, 2004; Wang et al., 2014). This approach may be inefficient in defining the soil exchange layer, and the compound levels extracted with organic solvents may surpass the levels freely exchanged with air (Wang et al., 2015).

In situ passive sampling is a low cost, efficient, and convenient method (Zhang et al., 2011) as compared to grab sampling, because it can be used to calculate freely dissolved or gas-phase concentrations of semi-volatile compounds in water and air (Donald et al., 2018). Several studies have measured fugacity gradients at the soil-air interface using polyurethane foam passive samplers (Wang et al., 2017; Zhang et al., 2011). Alternatively, soil-air partitioning could be conducted in a laboratory, using the soil-air fugacity based on the freely dissolved concentrations, C_{free}, by mixing soil with passive samplers in batch systems under no-depletion conditions (Arp et al., 2014; Enell et al., 2016; Hawthorne et al., 2011). Upon all phases (water, soil/sediment, colloids, and polymer coating of a passive sampler) achieving equilibrium, C_{free} is calculated using the target chemical concentration in the passive sampler and predetermined equilibrium polymer−water partition constants. This approach is useful for evaluating the bioavailable fraction and fugacity of PAHs in dust, soil, and rubber samples.

The main objectives of this study were to investigate the total concentration, spatial distribution pattern, and emission sources and to determine the soil-air exchanges of the 16 PAHs in surface dust and soil from 15 children's playgrounds. This study will be useful in characterizing playground dust and soil and understanding the risks of rubber surfaces to support decision making in selecting suitable surface materials for children's playgrounds.

2. Material and methods

2.1. Chemicals and materials

A standard mixture containing 16 EPA PAHs (product code: 36,979) and an internal standard mixture (product code: CRM46955) containing acenaphthene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, naphthalene-d_8, perylene-d_{12}, and phenanthrene-$d_{10,}$ were purchased from Supelco (Bellefonte, PA, USA). The abbreviations of the 16 PAHs used in this study are presented in Table S1, Supplementary Material. Dichloromethane (DCM) and *n*-hexane were obtained from Daejung Chemicals (Siheung, Republic of Korea), and water was obtained from Honeywell Burdick & Jackson (Charlotte, North Carolina, USA). All organic solvents and water used were of HPLC-grade. Sodium sulfate, calcium chloride, and sodium azide were purchased from Sigma-Aldrich (St. Louis, MO, USA). Silica gel (0.04–0.063 mm) was obtained from Merck KGaA (Darmstadt, Germany). Recycled rubber mulch (model number: RM16ET) was purchased from IMC Outdoor Living (St. Louis, MO, USA).

2.2. Samples and TOC measurement

Surface dust and soil samples were collected from 15 different children parks in Seoul, from November 2019 to February 2020 (Figure S1, Supplementary Material). The samples were collected according to the guidelines of the Environmental Hazards Assessment Program of the California Environmental Protection Agency (Sava, 1994). Approximately, 50 g of dust particles on 50–100 m^2 of poured rubber playground surfaces was collected using brushes and dustpans. Because particles on covered playgrounds rarely contained soil grain, we defined those as dust particles. Surface soil samples at a depth of approximately 2 cm were collected from the four uncovered playgrounds, using a stainless-steel shovel. Eight sub-samples per site were collected, pooled, and mixed thoroughly to provide a representative sample for each site. All samples were stored in 250 mL amber vials with a Teflon-lined cap for laboratory transportation. After the samples were air-dried at room temperature for 48 h, gravel and plant residues were manually removed from the samples. All samples were gently crushed, homogenized, sieved through a 2 mm sieve, and stored at 4 °C until analysis.

The moisture content and total organic matter (TOM) of 2 g of dust and soil were measured. Dust and soil moisture content was determined by drying the samples at 105 °C for 16 h. These samples were placed in an electric furnace (Model: SJ-DF5, Sejong Scientific Co., Bucheon, Republic of Korea) for TOM determination by measuring their loss upon ignition at 550 °C for 6 h. Total organic carbon (TOC) content was then estimated by multiplying 0.58 with TOM content (Nelson and Sommers, 1983).

2.3. Soxhlet extraction and cleanup

The 5 g dust or soil sample was spiked with 50 μL (20 μg mL^{-1}) of the internal standard mixture and air-dried for 24 h. The samples were mixed with 5 g of anhydrous sodium sulfate and placed in a glass extraction thimble. Sodium sulfate was dehydrated for 6 h at 600 °C in a muffle furnace, prior to the experiment. The samples were then Soxhlet extracted with 150 mL of DCM for 24 h. The extracts were concentrated to 3–5 mL using a rotary vacuum evaporator (N-1200A, Shanghai Eyela Co., Ltd., Shanghai, China). The aliquot was then filtered through a column packed with 2 g and 0.5 g of dehydrated silica gel and anhydrous sodium sulfate, respectively. The column was preconditioned with 10 mL of DCM and *n*-hexane. The PAH fraction was eluted with 20 mL of

DCM and then concentrated to 3–5 mL using a rotary vacuum evaporator. The concentrates were dissipated to 1 mL under a gentle stream of nitrogen gas. The samples were then preserved at 4 °C, prior to gas chromatography-mass spectrometry (GC-MS) analysis.

2.4. *Fugacity determination using passive sampling*

Medical-grade polydimethylsiloxane (PDMS) sheets with a thickness of 125 μm (Specialty Silicone Products, Inc., Ballston Spa, NY, USA) were cut into 6 cm diameter disks and washed with acetone: *n*-hexane (1:1, v/v), followed by methanol. A 5 g homogenized soil sample, a PDMS disk, and 20 mL aqueous solution containing 0.001 M $CaCl_2$ and 0.015 M NaN_3, were placed in a 20 mL glass vial with a Teflon-lined cap. There was only a 0.5 mL headspace in a vial. The vials were then placed in a shaking incubator at 25 °C and 150 rpm in the dark. Equilibrium was achieved after 28 days (Arp et al., 2014; Enell et al., 2016), and the PDMS disks were removed with a tweezer, rinsed with ultrapure water, and wiped dry with a tissue. They were then placed in a clean 5 mL vial, with 2 mL of DCM and 50 μL of the internal PAH solution. The vials were placed in a shaking incubator for 48 h at 150 rpm. After shaking, the solution was concentrated to 100 μL under a gentle nitrogen stream, transferred to a 200 μL GC vial, and immediately analyzed using GC-MS. PAH depletion by the polymer was negligible, accounting for less than 5% of the total amount. This prevents an artefactual reduction of freely dissolved concentrations, C_{free} (μg L^{-1}). At equilibrium, C_{free} was calculated from PAH concentrations in PDMS, C_{PDMS} (μg kg^{-1}), using the obtained PDMS-water partition constants in the literature, $K_{PDMS/W}$ (L_{free} $kg^{-1}{}_{PDMS}$) (Table S2, Supplementary Material) for 16 PAHs (Kwon et al., 2007).

Fugacity is a measure of the tendency of a chemical to escape from its medium (Mackay, 1979). In this study, the PAH concentrations in the dust, soil and aqueous phases were at equilibrium. Therefore, the fugacity of PAHs in dust and soil (f_S, Pa) was equal to that in aqueous phase, which is given by

$$f_W = \left(C_{free} \times H\right) / \left(M_W \times 10^3\right) \tag{1}$$

where, M_W is the PAH molecular weight (g mol^{-1}), and H is Henry's law constant (Pa m^3 mol^{-1}) (Table S2).

PAHs fugacity in air (f_G, Pa) is given by:

$$f_G = 10^{-9} C_G RT / M_W \tag{2}$$

where, R is the universal gas constant (8.314 Pa m^3 K^{-1} mol^{-1}), T is the temperature (K), and C_G is the gas phase concentration (ng m^{-3}).

2.5. *GC-MS analysis*

PAHs were separated on an Agilent DB-5MS column (30 m × 0.25 m × 0.25 μm film thickness) using an Agilent 7890A gas chromatograph, coupled with an Agilent 5975C mass detector. The temperature program of the GC oven was as follows: (1) 40 °C for 1 min, (2) 120 °C (ramp: 25 °C min^{-1}), (3) 160 °C (ramp: 10 °C min^{-1}), (4) 230 °C (ramp: 5 °C min^{-1}), 285 °C (ramp: 1.5 °C min^{-1}), and (5) 300 °C (ramp: 5 °C min^{-1}), held for 3 min. The inlet and detector temperatures were 250 and 280 °C, respectively. Two microliters of sample were injected using an Agilent 7683B series injector autosampler in splitless mode, and helium was used as the carrier gas (1 mL min^{-1}). The analyte identification was confirmed using the peak retention times in GC-MS and qualifier ions (Table S1). The most abundant ions were quantified.

2.6. *Principal component analysis (PCA)*

PCA, the multivariate analytical tool, was used to reduce a set of original variables (measured PAHs content in the dust and soil samples) and to extract a small number of latent factors (principal components, PCs) for analyzing relationships among the observed variables. Data submitted for the analysis were arranged in a matrix, with each column corresponding to one PAH component and each row representing a playground location (i.e., number of playgrounds). PCA was used to evaluate data matrices, allowing the summarized data to be further analyzed and plotted. According to Kaiser's rule, the number of factors extracted from the variables was determined by a scree test. Only factors with eigenvalues greater than one were retained based on this criterion. PCA was performed using GraphPad Prism 9.2.0 for Windows (GraphPad Software, San Diego, CA, USA).

2.7. *Quality control*

A laboratory blank was included for every 15 samples in the analytical procedure. None of the analytical blanks had detectable contamination of the monitored PAHs; thus, all data were reported without recovery corrections. According to the International Conference on Harmonization (ICH) guidelines (Harron, 2013), the detection limit (DL) and the quantitation limit (QL) can be expressed as DL = 3.3 σ/S and QL = 10 σ/S, respectively, where σ is the standard deviation of the response and S is the slope of the calibration curve. The slope S was estimated from the calibration curve, and the standard deviation of the response was determined based on the standard deviation of the y-intercepts of the regression lines. The DL and QL for the 16 PAHs ranged from 0.5 to 1.2 and 1.6–3.8 ng g^{-1}, respectively. The average surrogate standard recoveries (Acenaphthene-d_{10}, Chrysene-d_{12}, Perylene-d_{12}, Phenanthrene-d_{10}) of Soxhlet-extracted samples were 60%, 94%, 105%, and 118%, respectively, while those of PDMS-extracted samples were 75%, 90%, 98%, and 94%, respectively.

3. Results and discussion

3.1. *PAH concentration and profiles*

The concentrations of the 16 PAHs measured in the dust and soil samples are presented in Fig. 1. The median total concentration of 16 PAHs were approximately five times higher in dust from covered playground than in soil from uncovered playground, with ranges of 173.6–919.4 μg kg^{-1} dw (median 582.6 μg kg^{-1} dw) and 68.2–168.5 μg kg^{-1} dw (median 119.2 μg kg^{-1} dw), respectively (Table S4). The PAHs concentration in playground dust and soil in this study were comparable with those in soil (13.2–145.5 μg kg^{-1} dw, median 31.8 μg kg^{-1} dw) from Gwangju, Republic of Korea, but lower than those in soil

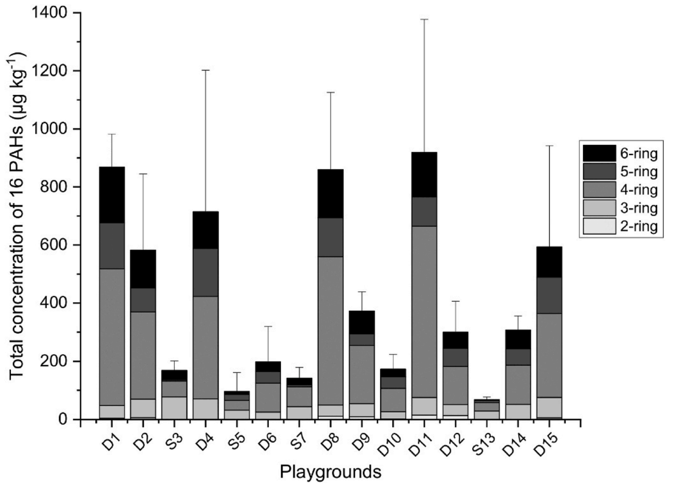

Fig. 1. Total concentrations of 16 PAHs in surface dust and soil of the 11 rubber-surfaced and 4 soil playgrounds (S3, S5, S7, S13) in Seoul. The whiskers on the bars represent the standard deviations of triplicates.

(2820–6460 μg kg^{-1} dw, median 4205 μg kg^{-1} dw) and dust (4910−57,930 μg kg^{-1} dw, median 12,554 μg kg^{-1} dw) from Seoul (Tarafdar et al., 2019). Playgrounds 1, 2, and 8, located near main roads and parking lots, had higher total PAH concentrations in the dust samples. Contrastingly, playgrounds 6 and 10 had the lowest total PAH concentrations. Playground 6 is located far from main roads and surrounded by buildings, whereas playground 10 is next to a stream and an alley. The total PAH concentration in the soil followed the same pattern as that in dust. Playgrounds 3, 5, and 7 are near main roads and a parking garage, while playground 13 is near an alley within a housing complex. Thus, it can be predicted that vehicles contributed to abundant PAHs in urban dust and soil particles.

The profiles of the individual PAHs in the surface dust and soil are listed in Table S4. The top three PAH congeners found in all dust and soil samples were FLU, PYR, and PHE, which accounted for 48% and 63.5% of the dust and soil samples of all PAH concentrations, respectively. This is consistent with the results of previous studies showing that these three compounds accounted for more than 35% of the total PAH content in Huanggang, Central China (Liu et al., 2019) and four major cities in Nepal (Birgunj, Kathmandu, Pokhara, and Biratnagar) (Yadav et al., 2018). CHR was identified as the most abundant PAH measured in dust, accounting for 28.2% of the 16 PAHs, while PHE was the most abundant PAH in soil, accounting for 29.1% of the 16 PAHs. This suggests that CHR and PHE may be relatively stable, thereby accumulating dominantly in dust and soil. Eight relatively more carcinogenic PAHs (HCar-PAHs), including CHR, BaA, BbF, BkF, BaP, IcdP, DahA, and BghiP, were detected at higher levels in dust than in surface soil. The total concentration of HCar-PAHs in dust and soil ranged from 71.5 to 388.4 μg kg^{-1} dw (median 221 μg kg^{-1} dw) and 9.6–37.3 μg kg^{-1} dw (median 33.7 μg kg^{-1} dw), respectively, and occupied lower than 50% of the concentration of 16 PAHs. BaP concentration in the dust and soil ranged from 4.9 to 61.2 μg kg^{-1} dw (median 18.7 μg kg^{-1} dw) and n.d.–1.85 μg kg^{-1} dw (median n.d.), respectively.

Considering the number of aromatic rings, 4-ring PAHs were the most dominant, followed by 6-ring and 5-ring PAHs, accounting for 48%, 17%, and 15% of the 16 PAHs, respectively. The contents of high molecular weight PAHs (HMW-PAHs) containing 4−6-ring PAHs ranged from 39 to 844 μg kg^{-1} dw (median 255.5 μg kg^{-1} dw), accounting for 53.8–94.5% of the total PAHs. Contrastingly, the contents of low molecular weight PAHs (LMW-PAHs) ranged from 25.7 to 77.9 μg kg^{-1} dw (median 51.7 μg kg^{-1} dw), accounting for 5.5–46.2% of total PAHs. The predominance of HMW-PAHs over LMW-PAHs strongly implies the dominance of pyrogenic sources over petrogenic sources (Viñas et al., 2009; Zakaria et al., 2002) and is a common feature of urban soils from different cities. This finding is consistent with those of previous studies of PAHs in playground soil from Bratislava, Slovakia (Hiller et al., 2015), urban soil from Nepal (Yadav et al., 2018), and street dust from Ezhou, China (Zhang et al., 2016). The elevated HMW-PAH content in dust and soil could be caused by higher stability of HMW-PAHs (Chung et al., 2007), while the low level of LMW-PAHs might be due to degradation and volatilization (Marquez-Bravo et al., 2016; Morillo et al., 2007). However, exceptionally high levels of PHE measured in soil were likely because PHE is the most thermodynamically stable compound among the 3-ring parent PAHs (Vane et al., 2014).

TOC has been found to be a principal factor controlling the sorption of hydrophobic organic chemicals in soils and sediments, with higher concentrations accompanied by high TOC (Nam et al., 2008). Generally, dust from covered playgrounds had higher TOC than soil from uncovered playgrounds. Correlations of contents of LMW-PAHs, HMW-PAHs, and 16 PAHs with TOC levels of surface dust and soil were examined (Figure S2, Supplementary Material), showing that TOC was not correlated with each PAH group. This trend is similar to that observed for street dust from Dalian (Wang et al., 2009). TOC has less influence on PAH distribution in dust than in soil (Hiller et al., 2015; Wang et al., 2009; Zhang et al., 2016). This may be attributed to different physical and chemical properties of dust and soil. Dust is described as a complex and heterogeneous mixture of atmospheric aerosols, asphalt particles, tire particles, sand, and other minerals (Takada et al., 1990), while soil organic matter mainly contains humic substances (Senesi, 1992).

3.2. Diagnostic ratio (DRs) and principal component analysis (PCA)

A quantitative understanding of PAH sources plays a significant role in assessing and reducing the environmental risk caused by PAHs. PAH sources directly impact the congener profile (Akyüz and Çabuk, 2010; Tarafdar et al., 2018). The diagnostic ratio is a conventional technique to identify the PAH sources present in different environmental media (Devi et al., 2016). Understanding the origins (i.e., petrogenic or pyrolytic/combustion) of PAHs in multi-environmental matrices is important for evaluating the fate and transport processes. The ratios of the selected individual PAH compounds used to categorize the PAH sources were interpreted in Table S3.

The diagnostic ratio analysis generally suggests that fuel combustion and petrogenic origin were likely the main sources of PAHs in dust and soil samples from children's playgrounds in Seoul (Fig. 2). Most of the dust samples had FLA/(FLA + PYR) values < 0.40, and IcdP/(IcdP + BghiP) values ranging from 0.20 to 0.50. According to the interpretation of the DRs (Table S3), these values suggested a mixed petroleum combustion and petrogenic origin of the PAHs in urban playground dust. On the contrary, the scattered BaA/(BaA + CHR) ratios and ANT/(ANT + PHE) ratios (Fig. 2b) indicated that the source of PAHs in dust also included coal combustion, in addition to petroleum combustion and petrogenic origin. Only FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) ratios were calculated for soil samples, because the individual PAH concentrations in the other ratios were close to or lower than the detection limits. The FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) values are the most appropriate for identifying PAH sources in soils (Tobiszewski and Namieśnik, 2012), as individual pairs of PAHs included in the ratios exhibit similar behavior in terms of their chemical stability in air and soil (Yunker and Macdonald, 2003). The FLA/(FLA + PYR) values ranging from 0.40 to 0.50 and the IcdP/(IcdP + BghiP) values ranging from 0.20 to 0.50 show a mixed petroleum combustion and fossil fuel combustion origin of PAHs in urban soils.

In some cases, the values of the four ratios are not always in agreement, therefore resulting to different sources of the PAHs. The total index (Orecchio et al., 2010) was calculated as the sum of single ratios normalized to the limit value.

$$\textit{Total intex} = \frac{\mathrm{ANT}/(\mathrm{ANT}+\mathrm{Phe})}{0.1} + \frac{\mathrm{FLA}/(\mathrm{FLA}+\mathrm{PYR})}{0.4} + \frac{\mathrm{BaA}/(\mathrm{BaA}+\mathrm{CHR})}{0.2} + \frac{\mathrm{IcdP}/(\mathrm{IcdP}+\mathrm{BghiP})}{0.5} \tag{3}$$

PAHs originating from combustion have a total index >4, whereas a total index <4 indicates products prevalently originating from petroleum. The value of the total index for all dust and soil samples varied between 1.39 and 5.31, supporting the results of the DR analysis that PAHs likely originated from a mixed combustion and petroleum products.

The diagnostic ratios can only be used to qualitatively identify PAH sources. However, principal component analysis (PCA) can be used to semi-quantitatively describe the contribution of main PAH sources (Wang et al., 2012). The four factors having eigenvalue higher than one accounted for 84% of the total variance. Due to the weak correlation of PC3 and PC4 (6.98% and 6.35% of the total variance, respectively), PC3 and PC4 were not discussed in this study. PC1 explained 56% of the variance, and PC2 accounted for 14% of the data variability (Fig. 3). The score plot for the samples (Fig. 3) indicated that the soil samples had similar sources while the dust samples were scattered, suggesting that they had different PAH sources. PC1 was heavily weighted by three-to-six-ring PAHs- PHEN, FLA, BaA, BghiP, BaP, BbF, and IcdP, indicating the characteristics of carcinogenic and high molecular weight of PAHs. According to the literature (Wang et al., 2012; Zhang et al.,

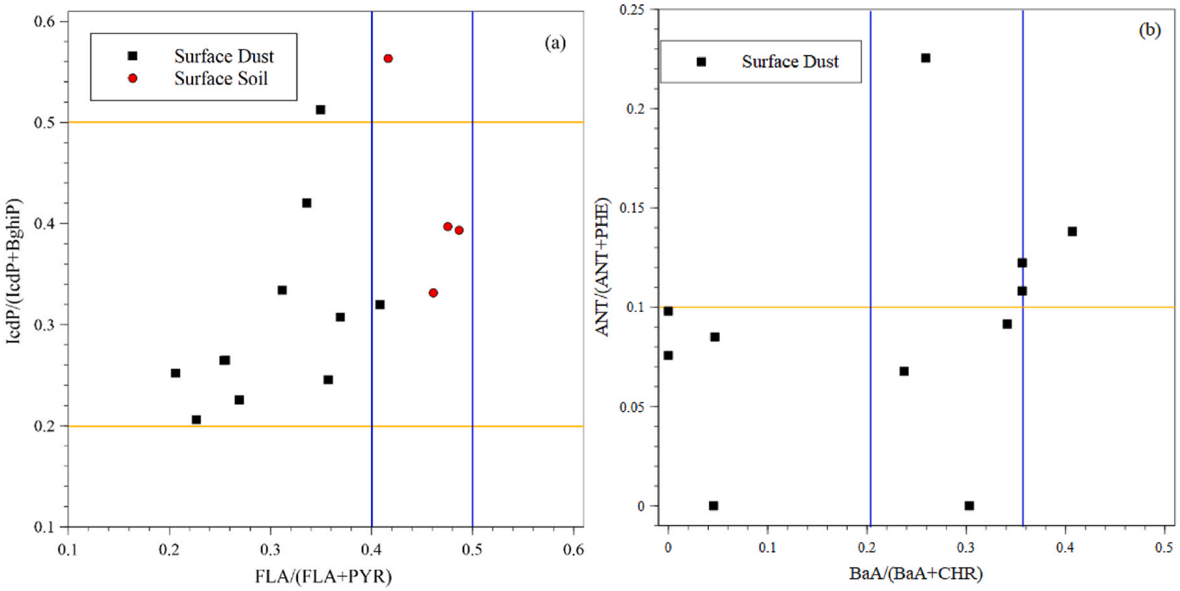

Fig. 2. Compositional relationship between (a) FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) and (b) BaA/(BaA + CHR) and ANT/(ANT + Phe) in playground surface dust and soil.

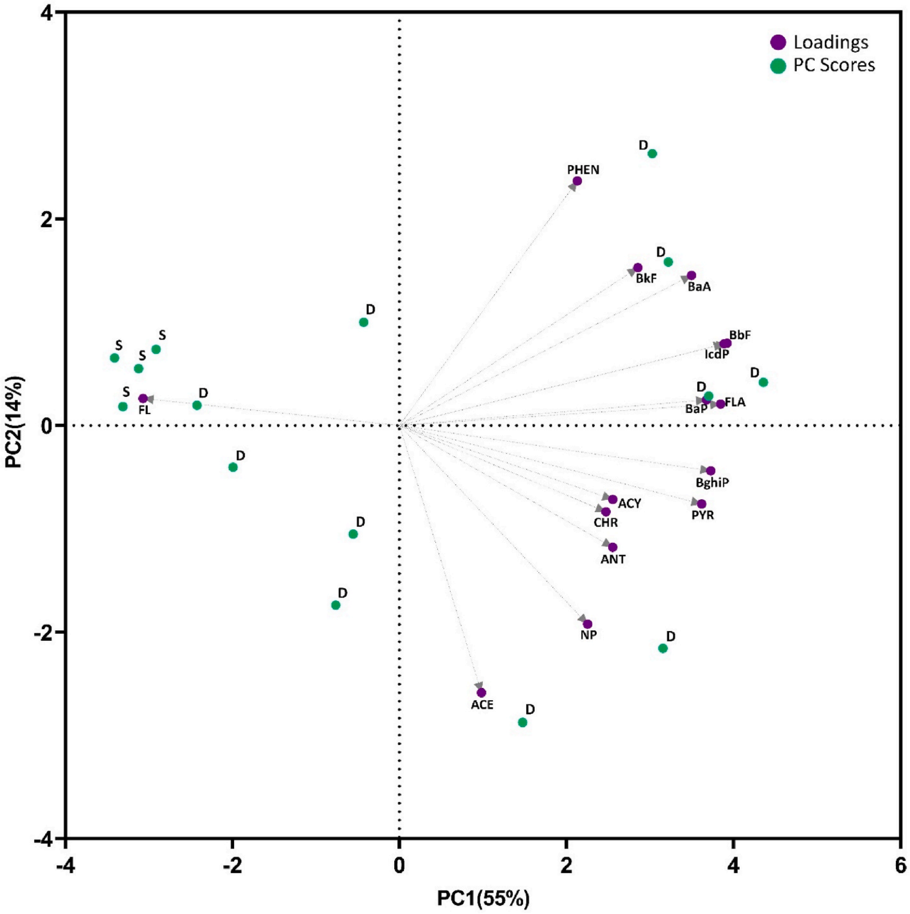

Fig. 3. Principal components of 16 PAHs in playground surface dust and soil. S and D refer uncovered playground surface soil samples and poured rubber-surfaced playground dust, respectively.

2009), BbF, BaP, BghiP, and IndP have been suggested to indicate vehicle emission while PHEN, FLA, and BaA were related with the emission characteristics of PAHs from coal combustion. PC2 was dominated by NAP, ACE, ANT, DahA and PHEN, indicating that PC2 is characterized by low molecular weight PAHs. These two-to-three-ring PAHs suggested the emission characteristics of PAH composition

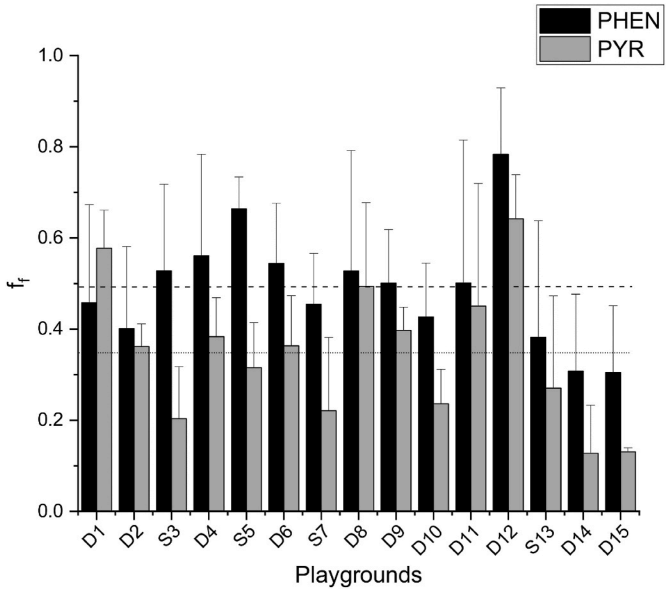

Fig. 4. Fugacity fraction (f_f) values of PHE and PYR for winter. The whiskers on the bars represent the range of the f_f values; the respective dash and dot line represent the mean f_f values of PHEN and PYR.

related to coal combustion. Taking the PCA and DR results together, vehicle emission and coal combustion were likely the major sources for total PAHs (see Fig. 4).

3.3. Soil-air gas exchange

Measured C_{free} of $\sum$ 16 PAHs in dust and soil samples varied from 0.017 to 0.12 μg $L^{-1}{}_{free}$ (median 0.053 μg $L^{-1}{}_{free}$) (Table S5). The dust samples from covered playgrounds were predicted to have lower C_{free} than soil. The higher TOC in dust could increase PAH accumulation and prevent PAHs leaching from dust particles, especially HMW-PAHs, owing to their greater hydrophobicity. LMW-PAHs (2–3-ring PAHs) occupied 29.6–98.0% of the $C_{free,}$ with PHE having the highest C_{free} value. PYR and PHE occurred in all samples and had the highest C_{free} among the HMW-PAHs. Five- and six-ring PAHs were barely present in all samples, and benzo[a]pyrene only occurred at the D4, S5, and D8 sites.

The fugacity of the compounds in the compartment was compared to determine whether the compartments were in equilibrium. The fugacity fraction (f_f) is a convenient and conventional way of expressing the relative fugacity of two environmental compartments (Harner et al., 2001; Meijer et al., 2003; Wang et al., 2011). A fugacity fraction of approximately 0.50 indicates equilibrium, >0.50 indicates net volatilization from soil into air, and <0.5 indicates net deposition from air to soil. However, owing to uncertainties and the propagation of errors in the calculation, f_f values between 0.3 and 0.7 are not considered to differ significantly from equilibrium; $f_f > 0.7$ indicates that the soil is a source with net volatilization from soil to air, and $f_f < 0.3$ indicates that the soil is a sink with net deposition from air to soil (Harner et al., 2001; Meijer et al., 2003; Wang et al., 2011).

$$f_f = f_s / (f_s + f_g) \tag{4}$$

The prevailing PHE and PYR were chosen as representative PAHs for LMW-PAHs and HMW-PAHs, respectively. The f_g values of PHE and PYR were calculated using the atmospheric gas-phase concentrations reported by Thang et al. (2020), and f_s values of PHE and PYR were calculated from their dust and soil freely dissolved concentrations measured in this study (Table S5). Atmospheric gas-phase concentration data was collected from one of the sampling stations in Thang et al. (2020). The sampling station U18 in Seongbuk district, Seoul, Republic of Korea was chosen since its location was within 5 km distance from the sampling playgrounds in this study, suggesting the minimally spatial variability. Despite the two years apart in terms of sampling between the two studies, data from samples taken in the winter was chosen to minimize the potential influence of seasonal variability.

The f_f values for PHE and PYR are shown in Fig. 3, ranging from 0.12 to 0.89 (median 0.54) and n.d. to 0.72 (median 0.32), respectively. Generally, the f_f values of PHE and PYR in most playgrounds were within the certainty range, implying that the dust, soil, and ambient air were close to the phase equilibrium. The f_f values for PHE were higher than those for PYR, except in D1. The mean f_f values increased with decreasing molecular weight of the individual PAHs, indicating that dust and soil acted as a sink for HMW-PAHs rather than LMW-PAHs, consistent with the results of previous studies (Bozlaker et al., 2008; Wang et al., 2011). LMW-PAHs are more mobile and subject to soil-air transfer because of their higher volatility and lower retention in dust and soil (Cousins et al., 1999; Hippelein and Mclachlan, 1998). The HMW-PAHs appeared to accumulate for longer periods in dust and soil, after deposition. Thus, surface dust and soil was a source of some LMW-PAHs to the atmosphere and a long-term sink for HMW-PAHs.

Atmospheric deposition is a major source of PAHs in dust and soil (Bozlaker et al., 2008). The predominance of PYR and PHE in Seoul air (Thang et al., 2020) could explain the dominance of these compounds in playground dust and soil particles. We initially hypothesized that PAHs could be transferred from the “cushion layer” to the “wear layer” of the rubber surface and the “wear layer” to the dust. This phenomenon could disturb the pre-existing equilibrium between the playground dust and gas phase, making dust a source of PAHs in the atmosphere. However, the equilibrium of PHE and PYR between dust, soil, and air demonstrated that the source of PAHs in dust and soil particles is unlikely to originate from the playground covers but mainly because of atmospheric depositions; however, f_s and f_g values were derived from two independent studies.

The total and freely dissolved concentrations of PAHs extracted from the rubber mulch were determined. The results showed that the concentration of 16 PAHs in rubber mulch ranged from 33.2 to 62.5 μg g^{-1} dw (median 45.4 μg g^{-1} dw) (Table S4). FLA, PYR, and PHE were the most abundant congeners, consistent with previous reports (Celeiro et al., 2014; Llompart et al., 2013). PAHs from the rubber mulch were undetected in the aqueous phase profiles, which can be explained by the strong sorption of PAHs to carbon content in rubber. The results show that PAHs in dust particles on playground surfaces rarely originate from the “cushion layer” as hypothesized but mainly from atmospheric PAHs. Taking the DRs, PCA, and soil-air gas exchange analysis together, atmospheric deposition is likely the major source for total PAHs; therefore, minimizing vehicular exhaust may reduce the health risks.

The results showed that the strong sorption of PAHs to TOC fraction in dust/soil and in the rubber surfacing can lower the environmental risk of PAHs but extend their presence. Despite this, regulatory guidelines for PAHs contaminated soil often rely on the total soil concentrations (Ehlers and Luthy, 2003; Brand et al., 2013), overestimating risk by not sufficiently accounting for (bio)availability. This study suggested that the fugacity analysis can provide complementary information for initial screening purposes on risks related to PAHs. The health risk of PAHs can be estimated by total soil concentration, while the fugacity analysis can suggest the source of contamination. Information provided from the two analyses can minimize the false positive identification of the contamination source to help policymakers target the right source of contaminants in dust and soil adhered to consumer products. In this study, the fugacity analysis suggested that the poured rubber surface is considered as a suitable material for the children’s playground in terms of the PAHs contamination.

4. Conclusion

The median total PAH concentrations from dust on poured rubber-surface playgrounds were approximately five times greater than those from soil on natural soil playgrounds in Seoul. The composition profile of PAHs in dust and soil with a predominance of 4-, 5-, and 6-ring PAHs indicated that combustion processes were the most important source of these compounds. The TOC concentration had no significant influence on the total PAH accumulation in the dust and soil particles. Diagnostic ratios and PCA analysis showed that playground PAHs originated from a mixed coal combustion and vehicular emission. The freely dissolved concentration suggested that TOC could inhibit the leaching of PAHs, especially HMW-PAHs from dust and soil particles. Measuring soil-air fugacity fractions of PHE and PYR, and total freely dissolved concentrations of PAHs in rubber mulch affirmed that atmospheric deposition was largely the source of PAHs in dust and soil particles. The strong sorption of PAHs to the carbon content in rubber is attributed to the undetected PAHs in the aqueous phase profiles. Therefore, the “cushion layer” of the playground surface was not the main source of childhood cancer risk. There is also a possibility that PAHs can directly leach from the playground to children, through direct dermal contact with the covered surface. This could be an important research area to further assess childhood cancer risk associated to PAHs in playgrounds.

Credit author statement

Thanh Dat Pham: Conceptualization, Methodology, Investigation, Validation, Writing – original draft preparation. Abhrajyoti Tarafdar: Conceptualization, Methodology, Writing – review & editing. Pil-Gon Kim: Conceptualization, Methodology, Writing – review & editing. Jung-Hwan Kwon: Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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