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Application of the PDMS Passive Sampling Method to Assess Bioavailability and Health Risks Associated with PAH-Contaminated Soil

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Abstract: Integrating bioavailability into risk assessments is an effective way to objectively assess human health risks. In this study, the bioavailability of 16 polycyclic aromatic hydrocarbons (PAHs) in contaminated soil from a coking plant was evaluated using the polydimethylsiloxane (PDMS) passive sampling method. The results showed that the bioavailability factor (*BAF*) of each PAH, predicted using PDMS fibers, ranged from 0.46% to 9.74%. The PDMS passive sampling method was more stable in testing the bioavailability of PAHs with more than 4 benzene rings; a preliminary relationship was established between the *BAF* and the log value of the octanol–water partition coefficient ($\log K_{ow}$). After considering their bioavailability, the carcinogenic risks (*CR*s) and non-carcinogenic hazard quotients (*HQ*s) associated with the 16 PAHs were reduced by 1 to 2 orders of magnitude. Only the health risks associated with benzo(a)pyrene and dibenzo(a,h)anthracene exceeded the acceptable level. The PDMS passive sampling method provides a useful tool for estimating oral bioavailability, and incorporating its results into human exposure testing can help to refine the health risk assessment of contaminants through oral ingestion.

Keywords: passive sampling method; PDMS fiber; PAHs contaminated soil; bioavailability; health risk assessment

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) comprise a group of persistent organic pollutants that have been widely detected in the environment [1]. Sixteen PAH compounds have been identified as priority pollutants by the United States Environmental Protection Agency (USEPA) because of their toxicity, mutagenicity, and (potential) carcinogenicity [2,3]. Soil is a major sink for PAHs, and high PAH concentrations have been found in industrial contaminated sites such as coking plants [4,5], steel plants [6–8], and coal gas plants [9]. Jennings et al. [10] found that the RGVs for seven carcinogenic or mutagenic PAHs varied over 6.3–7.2 orders of magnitude worldwide under different land uses. The soil regulatory guidance values (RGVs) for benzo(a)pyrene under sensitive land use in different counties ranged from 0.11 to 1 mg/kg due to differences in regulations, theoretical basis, and soil properties [11]. Human exposure to PAHs is mainly through three pathways including oral ingestion, skin contact, and inhalation, with the oral ingestion pathway being the most important [12,13]. However, many studies evaluating the health risk exposure to PAHs through oral ingestion are based on the total amount of contaminants analyzed by exhaustive chemical extraction [8,14–17]. In other words, it conservatively assumes that 100% of the contaminants in soil can be digested and absorbed after oral intake, subsequently reaching the target organs through the blood circulation system and causing harm to human health. However, soils are subject to long-term aging in the environment,

and as aging time increases, contaminants that have been adsorbed in soil natural organic matter will gradually diffuse into organic matter with strong adsorption capacity, such as black carbon particles, or enter the soil micropore structure and become locked, resulting in a decrease in the bioavailable fraction [18,19]. Studies show that when considering bioavailability, risk assessment methods based on total concentration can overestimate the actual risk by 1–10,000 times [20,21]. Therefore, incorporating bioavailability into risk assessment is essential for scientifically and rationally assessing the risks caused by site contamination.

Contaminant bioavailability can be described in absolute and relative terms [12]. Absolute bioavailability (*ABA*) is defined as the fraction of an administered dose that reaches the central (blood) compartment from the gastrointestinal tract [22]. Relative bioavailability (*RBA*) refers to the comparative bioavailability of different forms of a substance or for different exposure media containing the substance [22]. Bioavailability can be determined using in vivo methods, mainly in rats or pigs, by measuring parent substances or metabolites in blood, urine, or feces [19,23–26]. The *ABA* and *RBA* of benzo(a)pyrene assessed by Duan et al. [23] using rat blood as the metabolic endpoint ranged from 8.9% to 21.3% and from 24.2% to 46.1%, respectively. The *RBA* of PAHs measured by Kogantia et al. [26] using 1-hydroxypyrene, a metabolite of PAHs in mouse urine, as a biomarker ranged from 9% to 75%. As the concentration of contaminants in blood and urine is usually very low, only higher concentrations of contaminants in soil can be detected in blood and urine, so the accuracy of the method cannot be guaranteed for low concentrations in contaminated soil [19]. The *RBA* of benzo(a)pyrene measured by Grøn et al. [24] based on pig feces (36% to 55%) was higher than that tested in mouse urine (7.3% to 31%), mainly due to the fact that fecal excretion-based methods do not take into account other loss mechanisms in vivo, such as hepatic–intestinal recirculation of contaminants and the influence of microbial metabolism in the intestinal lumen, often leading to a significant overestimation of bioavailability [25].Therefore, there is a high degree of uncertainty in the results of in vivo methods due to the physicochemical properties of contaminants, animal type, metabolic endpoint, etc. In addition, in vivo methods are difficult to implement on a large scale due to being time-consuming and costly. In vitro methods based on gastrointestinal simulation have attracted wide attention because of their convenient operation, low cost, and lack of ethical restrictions [12,13,19,27,28]. This method tests for bioaccessibility, which is the fraction that is soluble in the gastrointestinal environment and is available for absorption, which is theoretically greater than or equal to RBA [22]. Several in vitro methods have been applied for bioaccessibility measurement, including the physiologically based extraction test (PBETs) [19], unified bioaccessibility method (UBM) [29], Deutsches Institut für Normung (DIN) [30], fed organic estimation human simulation test (FOREhST) [25], simulator of the human intestinal microbial ecosystem (SHIME) [31], etc. Influenced by the digestion conditions (such as components, pH, and solid-liquid ratio), digestion time, shaking method, and food, the results of different in vitro methods are quite different [27,32–34].

The concept of environmental passive sampling was first introduced in the 1980s, and application at real sites began in the 1990s [35]. Different from the active sampling method to measure the total dissolved concentrations (freely dissolved and colloidally bound states) or total concentrations (total dissolved and particulate states), the passive sampling method allows measurement of the concentrations of freely dissolved pollutants (C_{free}) [36]. This method is based on the equilibrium distribution theory [20] and characterizes the bioavailability of pollutants by measuring the freely dissolved concentration of the pollutant in environmental media. Passive sampling materials are usually composed of high-molecular-weight polymers, such as polydimethylsiloxane (PDMS), polyethylene (PE), and polyoxymethylene (POM), since these have strong adsorption capacity for hydrophobic organic compounds. PDMS has good affinity for hydrophobic organic matter (HOC) due to its special straight-chain structure, which leads to a high diffusion rate of pollutants in PDMS, in addition to being chemically stable and solvent-resistant, making PDMS an ideal material for passive sampling [37,38]. PDMS passive sampling methods have been used for

the determination of the freely dissolved concentrations of hydrophobic organic compunds such as PAHs, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDE), and DDT in water [38,39], sediment [40,41], and soil [41,42]. Maruya et al. [43] used a PDMS-coated solid phase microextraction device (SPME) to test the C_{free} of 12 HOCs in sediments at the laboratory and site scales, concluding that the SPME passive sampler could serve as a proxy for bioaccumulation. Van der Wal et al. [41] found that the bioavailable concentrations of organic chlorinated pesticides (OCPs) and PCBs in soil measured using SPME were twice as high as the concentrations measured in earthworms, and the values were well correlated. Van der Heijden et al. [20] further verified that the in situ SPME passive sampling method (*is*SPME) accurately predicted the bioavailability of PAHs in sediment and the ratio of bioavailable concentration to the measured concentration. To the best of our knowledge, research on the use of PDMS for bioavailability in contaminated sites in China is very limited, and there is also no definitive method for applying PDMS test results to human health risk assessment, which is not conducive to the application of this method in contaminated sites.

This study focused on testing contaminated soil from a coking plant associated with an iron and steel enterprise in Beijing, China. The specific objectives of this study were to: (1) analyze the bioavailability of 16 PAHs in coke-contaminated soil using the PDMS passive sampling method, and evaluate the applicability of this method to different PAHs; (2) propose a computational approach for calculating the bioavailability factor (*BAF*) based on the freely dissolved concentrations measured by PDMS passive sampler and those predicted by the three-phase equilibrium theoretical model; and (3) assess the health risks associated with oral ingestion of PAHs in soils based on bioavailability. The computational approach proposed in this study combines PDMS passive sampling results with human health risk assessment, which can also help refine health risk assessment and address the issue of over-remediation.

2. Materials and Methods

2.1. Sample Collection and Analysis

2.1.1. Sample Collection and Processing

The soil was collected from the chemical production area of a coking plant associated with a large iron and steel enterprise, and the soil sampling protocol followed the requirements of the technical guidelines [44]. The sampling depth was 0–1 m below the ground surface, and the soil lithology was sandy silt. The soil was naturally air-dried in a ventilated and dark laboratory, passed through a 60 mesh sieve after removing gravel, residual roots, and other unwanted materials, and then sealed in brown glass bottles and stored in a refrigerator at 4 °C [45].

2.1.2. Total PAHs and Soil Properties

Two replicated soil samples were analyzed for total PAH content. A 10 g soil sample was well mixed with 5 g florisil and placed into an accelerated solvent extraction (ASE) extraction tank. PAHs in the concentrated extractions were analyzed using a gas chromatograph with a mass selection detector (7890 A/5975 C, Agilent Technologies, Wilmington, DE, USA), using the standard USEPA 8270 D method [46]. The PAHs were separated using a 30 m high-resolution glass capillary column DB-5MS (0.25 mm in diameter), coated with a 0.25 μm film (J&W Scientific, Agilent Technologies). The temperature of the oven was initially held at 45 °C for 2 min, and was then increased to 265 °C at 20 °C·min^{-1}, 285 °C at 6 °C·min^{-1}, and 320 °C at 10 °C·min^{-1} for 4 min. Calibration was performed using an internal standard method with a certified PAH mixture (TCL PAHs Mix-Ref 4–8905-U, Supelco, Bellefonte, CA, USA). The relative standard deviations (*RSD*s) of the two replicated samples ranged from 2.83% to 20.54%; the results from a spiked blank recovery ranged from 87.56% to 113.45%, within the control range of 60–140% [47].

The physical and chemical properties of the soil are shown in Table 1. The soil particle density (ρ_s) was measured according to the industrial standard LY/T 1224-1999 [48]. The

soil bulk density (ρ_b) was measured according to the industrial standard LY/T 1211.4-2006 [49]. The soil moisture content (P_w)was measured according to the industrial standard LY/T 1213-1999 [50]. The soil organic matter content (f_{om}) was measured according to the industrial standard NY/T 1121.6-2006 [51]. The soil organic carbon content (f_{oc}), soil total porosity (θ_T), volume ratio of water in the soil pore (θ_w), and volume ratio of air in the soil pore (θa) was calculated followed the methods in the technical guideline HJ 25.3-2019 [52].

Table 1. Physical and chemical properties of the soil.

Parameter	ρ_s g/cm^3	ρ_b g/cm^3	P_{ws} kg-Water/kg-Soil	f_{om} g/kg	f_{oc} Dimensionless	θ_T Dimensionless	θ_w Dimensionless	θ_a Dimensionless
Value	2.98	1.7	0.15	39.1	0.023	0.43	0.26	0.17

2.1.3. PAH Bioavailability

This experiment was conducted in triplicate for one soil. Concentrations of PAHs in soil pore water were measured according to a slightly modified version of the methodology described by Jonker et al. [21]. The disposable PDMS-coated fiber (Poly Technologies, Inc., Phoenix, AZ, USA) was used as a passive sampler (glass core diameter of 110 µm, 28.5 µm thick coating, density of 0.135 µL/cm). Prior to use, the fiber was cut into pieces 5 cm in length, which were soaked in methanol solution for 24 h, washed with Millipore ultrapure water 3 times, and then dried and sealed in plastic bags for later use. Amber-colored 20 mL vials were filled with 5 g soil; 15 mL of Millipore water, containing 0.01 M calcium chloride and 25 mg/L sodium azide; and two 5 cm PDMS fibers. Shaking during exposure was performed on a "rock and roller" shaker for 30 days, with a rolling speed of 30 rpm at 37 °C. After 30 days of exposure, the two fibers were collected from each vial, wiped with wetted tissue to remove any attached particles, cut into pieces 1 cm in length, and placed in amber-colored HPLC vial filled with 200 µL (in a 250 µL insert) of acetonitrile. Finally, the internal standard (2 µL of 100 ppm decafluorobiphenyl) was added, and the vials were vortexed at 3000 rpm for 1 min and stored at −20 °C. Prior to analysis, the vials were defrosted, vortexed again, and left at room temperature for 1 day.

The PAHs in the fiber extracts were determined using a high-performance liquid chromatography (HPLC) system. A Supelcosil (Supelco, Bellefonte, CA, USA) LC-PAH column (100 mm in length, 4.6 mm in diameter, 3 µm in particle size) was used for separation at 26 °C. All analyses were performed at a 1000 µL/min flow rate with a 20 µL injection. The mixture was separated using gradient elution, eluting with 40% water for 2 min, and then gradually increasing the proportion of acetonitrile to 100% within 9.5 min. The mixture was held for 7.5 min, and then returned to the original solvent composition for 6 min. The *RSD*s of the triplicate samples ranged from 9.42% to 26.57%; the recovery of a spiked blank ranged from 91.54% to 102.34%, which was within the control range of 60–140% [47].

The bioavailability factor (*BAF*) is defined as the ratio of the freely dissolved PAHs concentration in soil pore water, measured by the PDMS fibers, to the theoretical concentration calculated by the traditional three-phase equilibrium model (Equation (1)). The freely dissolved PAH concentration is calculated using Equations (2) and (3), and the theoretical freely dissolved PAH concentration in soil pore water is calculated using the three-phase equilibrium model, as in Equation (4).

$$BAF = \frac{C_{free}}{C_w} \times 100\% \quad (1)$$

$$C_{free} = \frac{C_{PDMS}}{K_{PDMS-w}} \quad (2)$$

$$C_{PDMS} = \frac{C_L \times V_L}{\rho_{PDMS} \times L_{PDMS}} \quad (3)$$

$$C_w = C_s \times \frac{\rho_b}{\theta_w + H \times \theta_a + \rho_b \times K_{oc} \times f_{oc}} \quad (4)$$

In these expressions, *BAF* is the bioavailability factor and is dimensionless; C_{free} is the concentration of freely dissolved PAHs in soil pore water, measured by the PDMS fiber and expressed in μg/L. C_{PDMS} is the PAH concentration in the PDMS fiber, expressed as μg/L. K_{PDMS} is the partition coefficient of PAHs in the PDMS fiber and water, expressed as L-water/L-PDMS (Table A1 in Appendix A). C_L is the PAH concentration in the vortexed extract, expressed in μg/L. V_L is the volume of vortexed extract, which is 200 μg/L. ρ_{PDMS} is the density of the PDMS fiber, which is 0.135 μL/cm. L_{PDMS} is the length of the PDMS fiber, which is 10 cm. C_w is the theoretical freely dissolved PAHs concentration in soil pore water, expressed in mg/L. C_s is the total PAH concentration analyzed using exhaustive chemical extraction, expressed in mg/kg. ρ_b is the soil dry bulk density, expressed in kg/L (Table 1). θ_w is the volume ratio of water in the soil pore and is dimensionless (Table 1). θ_a is the volume ratio of air in the soil pore, which is dimensionless (Table 1). f_{oc} is the soil organic carbon content, which is also dimensionless (Table 1). H is Henry's constant for contaminants, which is also dimensionless (Table A1). K_{oc} is the organic carbon-water partition coefficient for contaminants, expressed as cm^3-water/g-carbon (Table A1).

2.2. Human Health Risk Assessment

The human health risk assessment was conducted according to the technical guideline HJ 25.3-2019 [52]. PAHs are semi-volatile organic pollutants, for which the oral ingestion pathway contributes the most to human health risks [53]. Therefore, this study only focused on the health risks of PAHs through oral ingestion. The carcinogenic risk (CR_o) and non-carcinogenic hazard quotient (HQ_o) for the oral ingestion pathway are calculated as follows:

$$CR_o = C_s \times \left(\frac{OSIR_c \times ED_c \times EF_c}{BW_c \times AT_{ca}} + \frac{OSIR_a \times ED_a \times EF_a}{BW_a \times AT_{ca}}\right) \times BAF \times SF_o \times 10^{-6} \quad (5)$$

$$HQ_o = C_s \times \frac{OSIR_c \times ED_c \times EF_c}{BW_c \times AT_{nc}} \times BAF \times \frac{1}{RfD_o \times SAF} \times 10^{-6} \quad (6)$$

In these expressions, CR_o is the carcinogenic risk associated with the oral ingestion pathway, and HQ_o is a non-carcinogenic hazard quotient associated with the oral ingestion pathway; both are dimensionless. $OSIR_c$ and $OSIR_a$ are the daily soil intake values estimated for children and adults, respectively, expressed as $mg \cdot d^{-1}$. ED_c and ED_a are the exposure durations for children and adults, respectively, expressed in years. EF_c and EF_a are the exposure frequencies for children and adults, respectively, expressed as days per year ($d \cdot a^{-1}$). BW_c and BW_a are the bodyweights of children and adults, respectively, expressed in kg. AT_{ca} and AT_{nc} are the average time of carcinogenic and non-carcinogenic effects, respectively, expressed as days. *BAF* is the bioavailability factor, which is dimensionless. SF_o is the carcinogenic slope factor for oral intake, expressed as $(mg \cdot kg^{-1} \cdot d^{-1})^{-1}$. RfD_o is the non-carcinogenic reference dose for oral intake, expressed as $mg \cdot kg^{-1} \cdot d^{-1}$. *SAF* is the reference dose distribution coefficient of soil exposure, which is dimensionless. Based on the bioavailability test results, only PAHs with more than 4 benzene rings were assessed for risk. The values of the above parameters referred to the recommended values in the technical guideline HJ 25.3-2019 [52] and the TRRP Protective Concentration Levels [54], as shown in Table A2.

3. Results and Discussion

3.1. Total PAHs in Soil

Table 2 shows that the ΣPAH value of the two replicated soil samples was 747.76 mg/kg; PAHs were mainly composed of 3-, 4-, and 5-ring PAHs, accounting for 31.97%, 28.15%, and 25.41% of the total concentration, respectively. Naphthalene,

benzo(a)anthracene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, and dibenzo(a,h)anthracene exceeded the screening levels by multiples of 0.64, 6.81, 11.96, 184.91, 0.45, and 59.64, respectively. Heavy PAH contamination in soils is generally found around coking plants. For example, Meng et al. [55] found that the maximum ΣPAH value in the coking area of an iron and steel plant in Beijing was 11,266.81 mg/kg and was dominated by 2–3-ring PAHs. The contamination was mainly due to leaks of tar, bitumen, and deep-processed products. Guo et al. [56] studied the pollution characteristics of a coking plant in Hebei Province and found that benzo(k)fluoranthene, benzo(a)pyrene, indeno(1, 2, 3-cd)pyrene, and dibenzo(a, h)anthracene in shallow soil exceeded the screening levels by 5.24–44.47 times. Jia et al. [4] found a similar result in a coking plant in Beijing; the maximum ΣPAH value in soil was 143,363.7 mg/kg, with 2–3-ring PAHs accounting for 85% of total PAHs. Li et al. [57] found that the coking and chemical production areas of a large coking plant were significantly contaminated by PAHs, with a maximum ΣPAH value of 47,912.23 mg/kg, which was mainly concentrated in the 0–3 m soil layer. The PAHs came from tar leakage during the coking production process.

Table 2. Initial content of PAHs in soil (mg/kg).

Number of Rings	Contaminants	Content	Proportion		Screening Value	Exceeding Multiple
2-ring	Naphthalene	41.10	5.50%	5.50%	25 ①	0.64
3-ring	Acenaphthene	10.75	1.44%	31.97%	2189 ②	-
	Acenaphthylene	106.00	14.18%		2120 ③	-
	Fluorene	13.85	1.85%		1459 ②	-
	Phenanthrene	21.75	2.91%		1060 ②	-
	Anthracene	86.75	11.60%		10,000 ②	-
4-ring	Fluoranthene	81.25	10.87%	28.15%	1459 ②	-
	Pyrene	46.60	6.23%		1094 ②	-
	Benzo(a)anthracene	42.95	5.74%		5.5 ①	6.81
	Chrysene	39.70	5.31%		490 ①	-
5-ring	Benzo(b)fluoranthene	71.30	9.54%	25.41%	5.5 ①	11.96
	Benzo(k)fluoranthene	16.45	2.20%		55 ①	-
	Benzo(a)pyrene	102.25	13.67%		0.55 ①	184.91
6-ring	Indeno(1,2,3-cd)pyrene	7.97	1.07%	8.97%	5.5 ①	0.45
	Dibenzo(a,h)anthracene	33.35	4.46%		0.55 ①	59.64
	Benzo(g,h,i)perylene	25.75	3.44%		1060 ②	-
-	∑PAHs	747.76	-	-	-	-

Notes: ① Screening value of Class I land in the Soil Environmental Quality Risk Control Standard for Contamination of Development Land (GB36600-2018); ② screening value of Class I land in the Screening Value of Soil Pollution Risk of Construction Land (DB13/T 5216-2020) [58]; ③ screening value of Class I land in the Risk Screening Values and Intervention Values for Soil Contamination of Development Land (DB4403-2020) [59].

Compared with other coking plants, high PAH levels in soil were also detected in this study; they were mainly generated by tar leakage during the recovery process associated with chemical production. However, the naphthalene level was relatively low, which may have been due to the direct exposure of the surface soil to ambient air. Low-ring naphthalene was attenuated by volatilization and degradation.

3.2. PAH Bioavailability in Soil

3.2.1. C_{free} in PDMS Fiber

Table 3 shows that the *RSD*s of the PAH concentrations in the vortexed extract of three replicated samples ranged from 9.42% to 26.57%. The average concentrations ($C_{L\text{-average}}$) of the different PAHs in the vortexed extract ranged from 5.63×10^{-3} to 6.81×10^{-1} μg/mL.

Table 3. PAH concentrations in the vortexed extract.

Number of Rings	Contaminants	C_{L1} μg/mL	C_{L2} μg/mL	C_{L3} μg/mL	$C_{L\text{-average}}$ μg/mL	RSD_s
2-ring	Naphthalene	ND	ND	ND	ND	-
3-ring	Acenaphthene	ND	ND	ND	ND	-
	Acenaphthylene	ND	ND	ND	ND	-
	Fluorene	ND	ND	ND	ND	-
	Phenanthrene	2.64×10^{-2}	2.18×10^{-2}	3.02×10^{-2}	2.61×10^{-2}	16.10%
	Anthracene	5.58×10^{-2}	4.05×10^{-2}	5.42×10^{-2}	5.02×10^{-2}	16.76%
4-ring	Fluoranthene	7.71×10^{-1}	4.73×10^{-1}	7.99×10^{-1}	6.81×10^{-1}	26.57%
	Pyrene	5.07×10^{-1}	3.20×10^{-1}	4.67×10^{-1}	4.31×10^{-1}	22.87%
	Benzo(a)anthracene	1.87×10^{-1}	2.42×10^{-1}	2.37×10^{-1}	2.22×10^{-1}	13.59%
	Chrysene	2.16×10^{-1}	2.68×10^{-1}	2.60×10^{-1}	2.48×10^{-1}	11.18%
5-ring	Benzo (b)fluoranthene	1.84×10^{-1}	2.16×10^{-1}	2.19×10^{-1}	2.06×10^{-1}	9.42%
	Benzo (k)fluoranthene	5.08×10^{-2}	6.31×10^{-2}	6.30×10^{-2}	5.90×10^{-2}	11.99%
	Benzo (a)pyrene	1.28×10^{-1}	1.67×10^{-1}	1.59×10^{-1}	1.51×10^{-1}	13.51%
6-ring	Indeno(1,2,3-cd)pyrene	4.60×10^{-3}	5.50×10^{-3}	6.80×10^{-3}	5.63×10^{-3}	19.63%
	Dibenzo(a,h)anthracene	4.04×10^{-2}	5.65×10^{-2}	5.65×10^{-2}	5.11×10^{-2}	18.18%
	Benzo (g,h,i) perylene	4.86×10^{-2}	6.25×10^{-2}	6.00×10^{-2}	5.70×10^{-2}	12.99%

As shown in Figure 1, the C_{free} was not detected for low-ring naphthalene, acenaphthene, acenaphthylene, and fluorene, mainly because these PAHs are relatively volatile, easily photolyzed and biodegraded, and not easily adsorbed by PDMS fibers. Li et al. [60] concluded that the accumulation of low-ring PAHs in earthworms was small and poorly reproducible due to their volatility, which was consistent with our study. The C_{free} of other PAHs ranged from 2.51×10^{-6} to 6.34×10^{-3} μg/mL. In general, the freely dissolved PAHs in soil pore water mainly consisted of 4-ring PAHs, accounting for 83.81% of the total freely dissolved content; these were followed by 3-ring PAHs at 12.96%, 5-ring PAHs at 2.91%, and 6-ring PAHs at 0.32%.

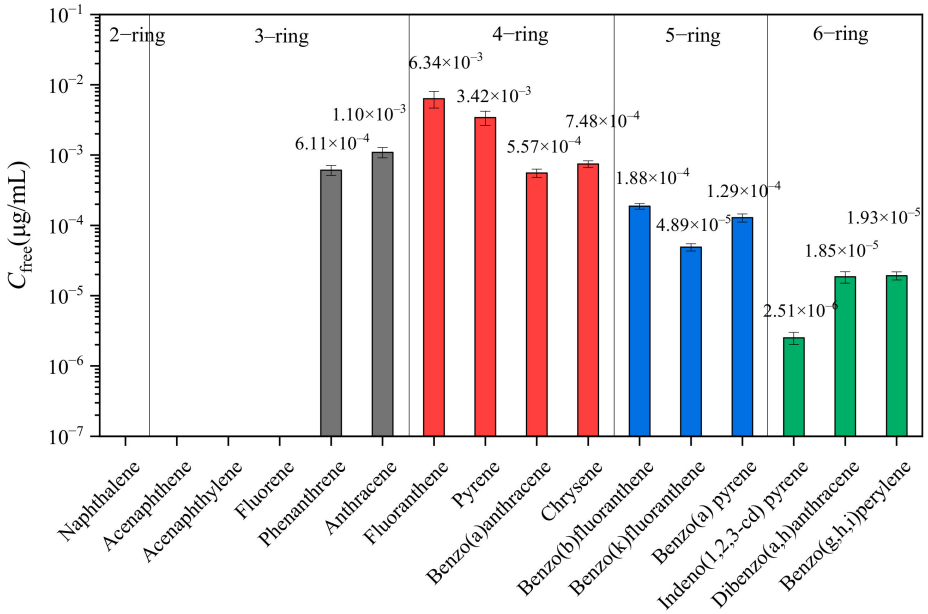

Figure 1. C_{free} measured by PDMS fiber.

Several factors, such as soil characteristics and chemical properties of contaminants, affect the distribution of contaminants in environmental media [41,60,61]. As shown in Figure 2a, the C_{free} of each PAH was positively correlated with C_s. This indicated that a

higher total concentration of soil pollutants was associated with a higher concentration that could be desorbed and dissolved in water. The octanol–water partition coefficient (K_{ow}) is a very important parameter for predicting the distribution of a substance in various environmental compartments [62]. With the increase of K_{ow}, the water solubility of a substance decreases as it adsorb more readily to organic matter in soils or sediments, which leads to a decrease in oral bioavailability [35,63]. The *K*ow values of PAHs in this study were obtained from other studies [54,64] (Table A1), and the C_{free} of each PAH was negatively correlated with the K_{ow} (Figure 2b). This is mainly because the high-ring PAHs have relatively high K_{ow} values and are difficult to desorb from soil after they have combined with soil organic matter [35]. As a result, they experience less adsorption by PDMS fibers. Similarly, Tao et al. [65] found that the highly hydrophobic PAHs bound strongly to soil organic carbon through strong π-π bonds and hydrophobicity, resulting in low mobility in the digestate.

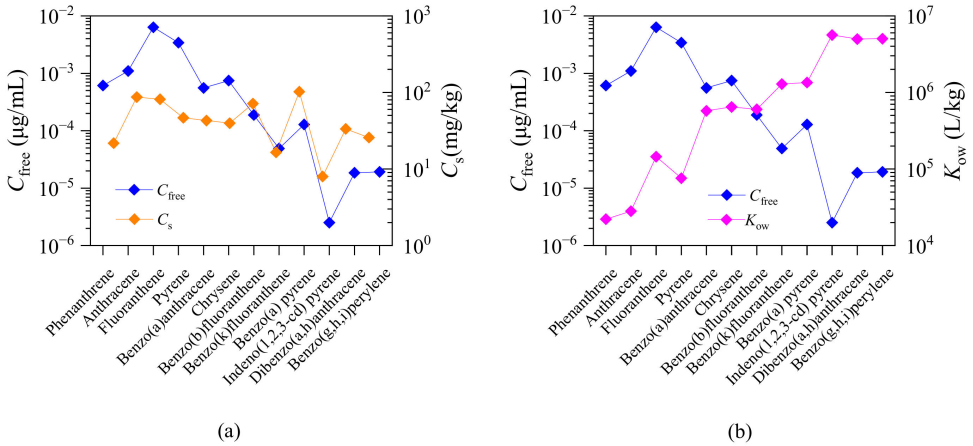

Figure 2. The relationship between C_{free}, K_{ow}, and C_s. (**a**) Relationship between C_{free} and C_s (**b**) Relationship between C_{free} and K_{ow}.

3.2.2. Comparison of C_{free} and C_w

Figure 3a shows that the theoretically calculated C_w of PAHs was 1.82×10^{-4}–1.18 μg/mL, which was 1–2 orders of magnitude higher than the measured value using the PDMS fiber (2.51×10^{-6}–6.34×10^{-3} μg/mL). Van der Heijden et al. [20] verified that the in situ passive sampling method *is*SPME accurately predicted PAH bioavailability in sediment during field tests. The ratio of the bioavailable concentration predicted by *is*SPME to the measured concentration in earthworms was close to 1, while the bioavailable concentration predicted by the traditional three-phase equilibrium model overestimated the measured concentration in earthworms by 10–100 times. Those results were generally consistent with the results of our study. Jonker et al. [21] studied the bioavailability of PAH-contaminated soil in a gas plant, and found that PAH bioavailability predicted using a PDMS-coated SPME was one order of magnitude higher than the measured bioaccumulation in earthworms. However, compared with the traditional method based on total concentration, which yields a 10–10,000 time overestimate, the SPME passive sampling method remains an effective way to improve risk predictions. In addition, there was a significant linear positive correlation ($R^2 = 0.9729$) between the logC_{free} and logC_w for PAHs with more than 4 rings (Figure 3b), indicating that the PDMS passive sampling method was more stable in testing the bioavailability of PAHs with more than 4 rings.

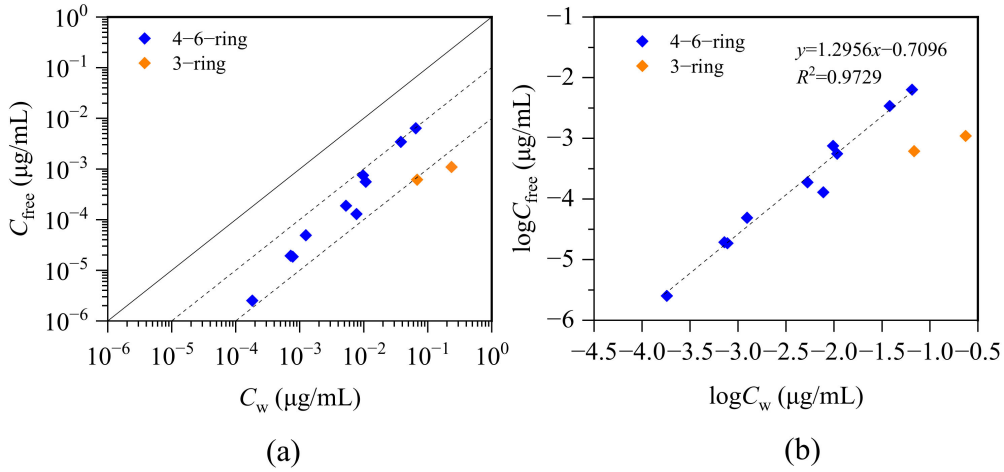

Figure 3. The relationship between C_{free} and C_w. (**a**) Relationship between logC_{free} and logC_w (**b**) Relationship between C_{free} and C_w.

3.2.3. Bioavailability Factor

Table A3 and Figure 4 show that the *BAF*s of PAHs predicted using the PDMS fibers ranged from 0.46% to 9.74%. Phenanthrene and anthracene, each with 3 rings, were not easily adsorbed by the PDMS fibers due to their relatively high volatility, resulting in low *BAF* values. The *BAF*s of PAHs with more than 4 rings decreased as the ring number increased. The *BAF*s of PAHs with more than 4 rings were negatively correlated with logK_{ow} (R^2 = 0.7719). As the logK_{ow} of PAHs increased from 4.88 to 6.75, the *BAF* decreased from 9.74% to 1.38%. Khan et al. [66] also found that the bioaccessibility of individual PAHs in soils decreased with increasing ring number, possibly due to the decrease in water solubility and increase in K_{ow} of individual PAHs with increasing ring number. A similar result was seen in a study of PBDEs conducted by Yu et al. [67], which found an inverse correlation between logK_{ow} and bioavailability (based on in vivo experiments in mice) (R^2 = 0.636) and a parabolic relationship with bioaccessibility (based on in vitro gastrointestinal simulation) (R^2 = 0.757). This difference suggested that factors other than hydrophobicity might also have an impact on bioaccessibility.

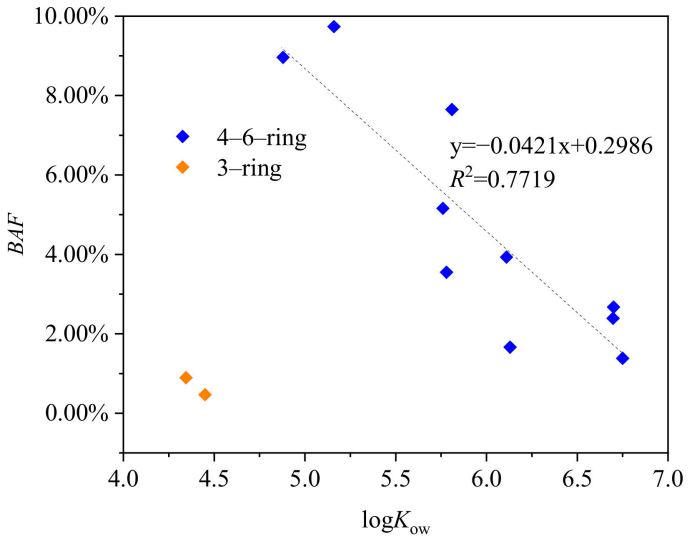

Figure 4. Relationship between BAF and logK_{ow}.

The regression equation in Figure 4 showed that the relationship between *BAF* and logK_{ow} was preliminarily established (Equation (7)), and the bioavailability of PAHs could be predicted using K_{ow}.

$$BAF = -0.0421 \log K_{ow} + 0.2986 \quad (7)$$

3.3. Human Health Risk

Figure 5 shows that the *CRs* of oral ingestion for the PAHs based on total concentration ranged from 3.88×10^{-9} to 1.31×10^{-4}. The risks associated with benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(b)fluoranthene, benzo(a)anthracene, and indeno(1,2,3-cd) pyrene exceeded the acceptable carcinogenic risk level of 10^{-6}. After considering bioavailability, only benzo(a)pyrene and dibenzo(a,h)anthracene had unacceptable *CRs* of 1.02×10^{-6} and 2.17×10^{-6}, respectively. Figure 6 shows that the non-carcinogenic *HQs* of oral ingestion for the PAHs based on the total concentration ranged from 2.78×10^{-3} to 1.10×10^{-1}, and only benzo(a)pyrene had a *HQ* that exceeded the acceptable level of 1. After considering bioavailability, the non-carcinogenic *HQs* of all PAHs were at acceptable levels. Inclusion of bioavailability reduced the *CRs* and non-carcinogenic *HQs* of PAHs by 1–2 orders of magnitude. The degree of reduction was higher for 5–6 ring PAHs (25.45–72.46 times) than for 4-ring PAHs (10.27–19.38 times), and was most pronounced for benzo(a)pyrene and dibenzo(a,h)anthracene, at 60.24 and 72.46 times, respectively. The oral bioaccessibility of PAHs in coke-contaminated soil measured by Fan et al. [53] by in vitro methods ranged from 1.2% to 18.0%, and the corresponding exposure and carcinogenic risk of PAHs were reduced by 1 to 2 orders of magnitude. Juhasz et al. [68] revealed the use of a PBET–silicone cord enabled the prediction of bioaccessibility (5.6%), which reduced the cancer risk for incidental soil ingestion from 1.3×10^{-3} to 7.5×10^{-5}. A study by Tarafdar et al. [69] revealed that health risks were overestimated by a factor of 2.87 to 2.89 when bioaccesibility was not considered. Although these studies were mainly based on bioaccesibility using in vitro methods, their conclusions were generally consistent with ours. Additionally, the degree of reduction was generally lower than that of bioavailability, mainly due to the fact that the in vitro approach provides a conservative estimate of bioavailability since it determines the desorbable fraction, which is generally agreed to be greater than the absorbable fraction [68]. These results confirmed that the risk assessment method based on total concentration may significantly overestimate the actual risk associated with site contamination.

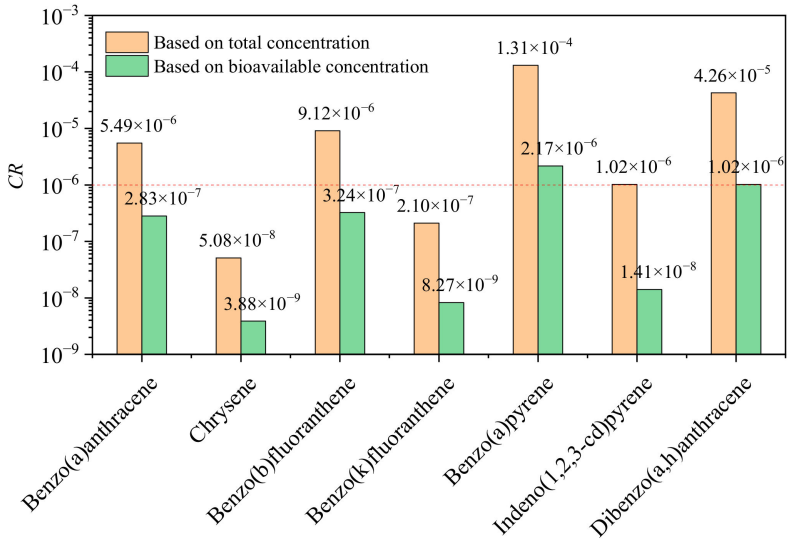

Figure 5. *CR* of each PAH based on total concentration and bioavailable concentration.

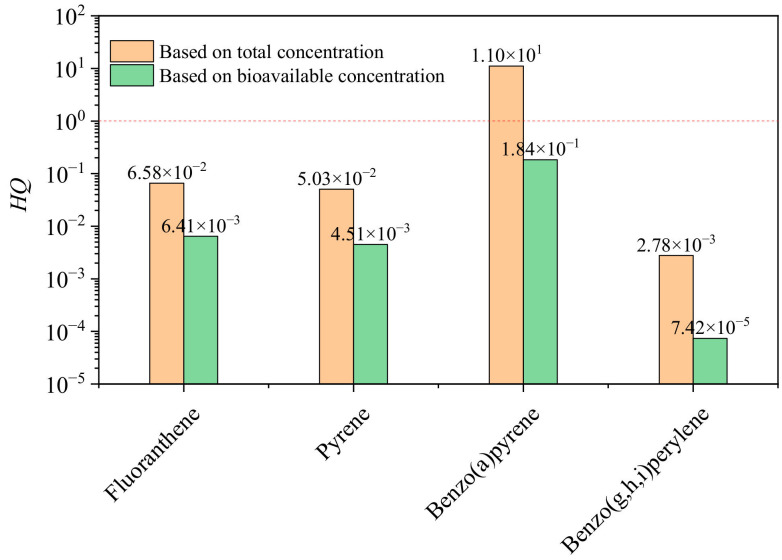

Figure 6. Non-carcinogenic *HQ* of each PAH based on total concentration and bioavailable concentration.

4. Conclusions

The C_{free} measured using the PDMS fiber was 1 to 2 orders of magnitude lower than the theoretical value calculated based on total concentration, which was positively correlated with C_s and negatively correlated with K_{ow}. The PDMS passive sampling method was more stable in testing the bioavailability of PAHs with more than 4 rings. The *BAF*s of PAHs predicted using PDMS fibers ranged from 0.46%–9.74%, and a preliminary relationship was established between the *BAF* and logK_{ow} of PAHs having more than 4 rings. Inclusion of bioavailability reduced the *CR*s and non-carcinogenic *HQ*s of all PAHs by 1 to 2 orders of magnitude. The degree of reduction was higher for 5–6 ring PAHs (25.45–72.46 times) than for 4-ring PAHs (10.27–19.38 times), and was most pronounced for benzo(a)pyrene and dibenzo(a,h)anthracene, at 60.24 and 72.46 times, respectively. This study concludes that incorporating bioavailability into risk assessments is an effective way to address the problem that traditional risk assessment based on total concentration overestimates the actual risk. This may ultimately help to avoid over-remediating contaminated sites. This study focused on studying heavily contaminated sandy silt soils for PAH bioavailability. To fully assess the reliability and applicability of the PDMS passive sampling method, more studies are needed on different soil types and pollution levels in the future.

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Appendix A

Table A1. Values associated with the physical and chemical properties of pollutants.

Contaminants	$K_{PDMS\text{-}Water}$ [19] mL-Water/mL-PDMS	K_{oc} [54,64] L/kg	logK_{ow} [54,64] L/kg	H [54,64] Dimensionless
Naphthalene	7.24×10^2	1.54×10^3	3.30	1.80×10^{-2}
Acenaphthylene	5.62×10^2	6.92×10^3	3.94	4.74×10^{-3}
Acenaphthene	2.51×10^3	5.03×10^3	3.92	7.52×10^{-3}
Fluorene	3.63×10^3	9.16×10^3	4.18	3.93×10^{-3}
Phenanthrene	6.31×10^3	1.41×10^4	4.35	5.40×10^{-3}
Anthracene	6.76×10^3	1.64×10^4	4.45	2.27×10^{-3}
Fluoranthene	1.58×10^4	5.55×10^4	5.16	3.62×10^{-4}
Pyrene	1.86×10^4	5.43×10^4	4.88	4.91×10^{-4}
Benzo(a)anthracene	5.89×10^4	1.77×10^5	5.76	4.91×10^{-4}
Chrysene	4.90×10^4	1.81×10^5	5.81	2.14×10^{-4}
Benzo(b)fluoranthene	1.62×10^5	5.99×10^5	5.78	2.69×10^{-5}
Benzo(k)fluoranthene	1.78×10^5	5.87×10^5	6.11	2.39×10^{-5}
Benzo(a)pyrene	1.74×10^5	5.87×10^5	6.13	1.87×10^{-5}
Dibenzo(a,h)anthracene	3.31×10^5	1.95×10^6	6.75	1.42×10^{-5}
Benzo(g,h,i)perylene	4.07×10^5	1.91×10^6	6.70	5.76×10^{-6}
Indeno(1,2,3-cd)pyrene	4.37×10^5	1.58×10^6	6.70	5.82×10^{-6}

Table A2. Risk assessment parameter values.

Symbol	Unit	Value	Symbol	Unit	Value
$OSIR_c$	$mg \cdot d^{-1}$	200	$OSIR_a$	$mg \cdot d^{-1}$	100
ED_c	a	6	ED_a	a	24
EF_c	$d \cdot a^{-1}$	350	EF_a	$d \cdot a^{-1}$	350
BW_c	kg	19.2	BW_a	kg	61.8
AT_{ca}	d	27740	AT_{nc}	d	2190
SAF	dimensionless	0.5	BAF	dimensionless	measured
SF_o	$(mg \cdot kg^{-1} \cdot d^{-1})^{-1}$	Benzo(a)anthracene: 1.0×10^{-1} Chrysene:1.0×10^{-3} Benzo(b)fluoranthene: 1.0×10^{-1} Benzo(k)fluoranthene: 1.0×10^{-2} Benzo(a)pyrene: 1 Dibenzo(a,h)anthracene: 1 Indeno(1,2,3-cd)pyrene: 1.0×10^{-1}	RfD_o	$mg \cdot kg^{-1} \cdot d^{-1}$	Fluoranthene: 4.0×10^{-2} Pyrene: 3.0×10^{-2} Benzo(a)pyrene: 3.0×10^{-4} Benzo(g,h,i)Perylene: 3.0×10^{-1}

Table A3. Bioavailability factors measured using PDMS.

Number of Rings	Contaminants	C_{free} µg/mL	C_w µg/mL	*BAF*
2-ring	Naphthalene	-	1.18	-
3-ring	Acenaphthylene	-	6.90×10^{-2}	-
	Acenaphthene	-	9.36×10^{-1}	-
	Fluorene	-	6.72×10^{-2}	-
	Phenanthrene	6.11×10^{-4}	6.84×10^{-2}	0.89%
	Anthracene	1.10×10^{-3}	2.36×10^{-1}	0.46%
4-ring	Fluoranthene	6.34×10^{-3}	6.51×10^{-2}	9.74%
	Pyrene	3.42×10^{-3}	3.81×10^{-2}	8.96%
	Benzo(a)anthracene	5.57×10^{-4}	1.08×10^{-2}	5.16%
	Chrysene	7.48×10^{-4}	9.77×10^{-3}	7.65%
5-ring	Benzo(b)fluoranthene	1.88×10^{-4}	5.29×10^{-3}	3.55%
	Benzo(k)fluoranthene	4.89×10^{-5}	1.24×10^{-3}	3.93%
	Benzo(a)pyrene	1.29×10^{-4}	7.74×10^{-3}	1.66%
6-ring	Dibenzo(a,h)anthracene	2.51×10^{-6}	1.82×10^{-4}	1.38%
	Benzo(g,h,i)perylene	1.85×10^{-5}	7.75×10^{-4}	2.39%
	Indeno(1,2,3-cd)pyrene	1.93×10^{-5}	7.22×10^{-4}	2.67%

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