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Bioaccessibility and Toxicity Assessment of Polycyclic Aromatic Hydrocarbons in Two Contaminated Sites

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous soil contaminants, and their bioaccessibility determines their environmental risks in contaminated land. In the present study, the residual concentrations of PAHs in the soils of two industrial sites were determined, and their bioaccessibility was estimated by the hydroxypropyl-β-cyclodextrin extraction (HPCD) extraction method. The results showed heavy PAH contamination at both site S1 (0.38–3342.5 mg kg^{-1}) and site S2 (0.2–138.18 mg kg^{-1}), of which high molecular weight (HMW) PAHs (4-, 5-, and 6-ring compounds) accounted for approximately 80%. The average bioaccessibility of PAHs at sites S1 and S2 was 52.02% and 29.28%, respectively. The bioaccessibility of certain PAH compounds decreased with increasing ring number of the molecule. Lower PAH bioaccessibility was detected in loamy and silty soil textures than in sandy soil. Moreover, among the soil properties, the dissolved organic matter, total organic carbon, total potassium, and total manganese concentrations had significant effects on the bioaccessibility of PAHs. The toxicity analysis showed that the composition and bioaccessibility of PAHs could affect their potential toxicity in soil. We suggest that bioaccessibility should be taken into consideration when assessing the toxicity of PAHs in soil, and more attention should be given to low-ring PAHs with high bioaccessibility.

Keywords Hydroxypropyl-β-cyclodextrin extraction · Molecular weight · PAH-contaminated sites · Dissolved organic carbon · Toxic equivalent

Polycyclic aromatic hydrocarbons (PAHs), a series of hydrophobic aromatic compounds composed of two or more benzene rings, are carcinogenic, teratogenic and mutagenic (Cvancarova et al. 2013). Sixteen PAHs have been listed as priority pollutants by the U.S. Environmental Protection Agency (EPA) (Zelinkova and Wenzl 2015). Generally, PAHs are the products of pyrolysis or rearrangement of molecules during incomplete combustion of organic matter under oxygen-deficient conditions (Dat and Chang 2017). In addition to some natural sources such as biological releases, natural fires and volcanic eruptions (Tsibart and Gennadiev 2013), many anthropogenic sources including the chemical industry, transportation, and domestic pollution have resulted in the current worldwide distribution of PAHs (Dat and Chang 2017; Duran and Cravo-Laureau 2016; Gao et al. 2018; Wilcke 2007). The produced PAHs are semivolatile, lipophilic, and persistent and easily accumulate in the environment, posing great risks to organisms including human beings.

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Soil is a major sink of PAHs in terrestrial ecosystems and serves as an important medium for the volatilization, deposition and degradation of PAHs in the environment. The average concentration of PAHs in topsoil in China was found to be approximately 730 ng g^{-1} (Zhang and Chen 2017). The sources of PAHs in the soil are mainly from coal combustion, vehicular emissions, sewage disposal, and petroleum spills (Han et al. 2014). Therefore, PAHs are frequently detectable in soils located in areas with high urbanization and industrialization (Zhang et al. 2017). For example, the PAH content detected in 40 soil sampling points collected from a coke factory in Shandong Province, China, exceeded the heavy contamination standard (Han et al. 2014). Idowu et al. (2020) reported that the content of PAHs in the soils of a renowned industrial heritage city in Australia ranged from 2.51 to 392.93 mg kg^{-1}, hundreds of times higher than the local standards. In addition, the total PAH contents in the soil near a cement factory in Beijing reached 1134.3 μg kg^{-1}, 3.37 times higher than the local background value (Wang et al. 2018), leading to high health risks for children and adults near the cement factory. Moreover, the PAHs in soil can be revolatilized into the atmosphere (Jia et al. 2019), transported by the soil–plant system (Zhang et al. 2015), and leached into the deep soil profile or even groundwater (Widdowson et al. 2003), leading to serious ecological and environmental issues. Therefore, the contamination of PAHs in the environment is of great concern.

Once organic contaminants enter the soil, they gradually exhibit diverse speciation, such as dissolved in soil solution, adsorbed on soil organic matter and minerals, or bound to the soil solid phase to form unextractable residues (Sabate et al. 2006). Since not all forms of contaminants pose threats to organisms, it is necessary to take into account the bioaccessibility of contaminants, which is described as the process of association and dissociation between the bound contaminant and released contaminant, and both of them transport to a biological membrane and finally across it (Semple et al. 2004). Considering the bioaccessibility of pollutants is conducive to predicting more realistic exposure limits and providing more justifiable and prospective risk assessment (Ortega-Calvo et al. 2015). The evaluation methods and influencing factors of PAH bioaccessibility in soil have received extensive attention, among which chemical extraction is still the most commonly used indirect in vitro method to determine the bioaccessibility of PAHs in soils (Gao et al. 2019; Tao et al. 2006). It is worth mentioning that modified cyclodextrin with a cyclic structure has been broadly utilized to evaluate PAH bioaccessibility (Humel et al. 2020; Leech et al. 2020; Qin et al. 2020). Reid et al. (2000) showed that the optimized hydroxypropyl-β-cyclodextrin (HPCD) extraction method could best predict the available microbial concentrations of soil-associated phenanthrene. A better correlation between HPCD-extracted PAHs and earthworm-accumulated PAHs than other chemical extraction methods in soil was also observed by Zhang et al. (2017). Moreover, studies have revealed that PAH bioaccessibility is affected by PAH properties, soil properties and environmental factors (Duan et al. 2014), such as the molecular weight of PAHs (Cheng et al. 2021; Li et al. 2013), cocontaminants (Lin et al. 2008), soil composition (Portet-Koltalo et al. 2020), and soil organic matter (SOM) (Moeckel et al. 2014). However, the influence and degree of influence of various factors have been inconsistent in diverse studies, and the change in PAH bioaccessibility in different soil profiles of contaminated sites is still lacking sufficient research.

In the present study, we intended to investigate the influencing factors that affect the bioaccessibility of PAHs in contaminated sites. Soil samples, including different profile depths, were collected from two industrial sites in China. HPCD extraction was chosen as the PAH bioaccessibility assessment method. The relationship between PAH bioaccessibility and soil properties was analyzed. Therefore, this study sheds light on the risk assessment of organic contaminants in soil.

Materials and Methods

The PAH-contaminated soils were sampled from a coal gasification plant site in Nanjing (S1) and a steel plant site in Chongqing (S2), China. According to the size of the contaminated sites, 5 and 15 sampling points in S1 and S2 were sampled by Geoprobe (TecopSA TEC15DP, AMK, Spain) and a self-contained pump drilling rig (GK200-1, YiXin Machinery Corp., China), respectively. The soils in S1 were sampled at a depth of 6 m, while the soils in S2 were sampled at a depth of 11 m with the horizon as a base depth. Finally, a total of 34 and 53 soil samples were collected at S1 and S2, respectively. All the soil samples were air-dried at room temperature. After removing stones and root residues, all soil samples were ground evenly to pass through a 0.25 mm sieve, and their physicochemical properties were characterized, as shown in the supplemental material (Table S1 and Fig. S1).

In this study, 16 priority PAHs proposed by the U.S. EPA were determined through the accelerated solvent extraction method (ASE 200, Dionex, USA). The ASE program was conducted under the following conditions (Zhang et al. 2016): hexane/acetone (1:1, v/v) as the solvent, a temperature and pressure of 100°C and 10.34 MPa, respectively, and static extraction for 5 min. Then, the extract obtained from ASE was concentrated to 2 mL by a rotary evaporator, transferred to a silica gel column packed with Florisil, silica gel and anhydrous Na_2SO_4, and eluted with 15 mL of *n*-hexane/dichloromethane solution (9:1, v/v). Then, the eluate was concentrated and dissolved in 2 mL of acetonitrile, and the mixture was passed through a 0.22 μm polytetrafluoroethylene filter membrane. The final extract was determined by gas chromatography–mass spectrometry (Agilent 7890A/5975C, Santa Clara, CA) (Ni et al. 2018). The instrument limit of detection (LOD) and of quantification (LOQ) was 0.03–0.15 μg kg^{-1} and 0.10–0.55 μg kg^{-1}, respectively.

The specific steps of HPCD extraction are as follows. One gram of soil sample was placed into a 50 mL glass centrifuge tube, and 20 mL of 50 mmol L^{-1} HPCD solution was added. The extraction was carried out with oscillation (200 r min^{-1}) for 20 h at room temperature. Then, the mixture was centrifuged at high speed for 10 min (2000 r min^{-1}) after static placement for 30 min. Next, the supernatant was discarded, and 20 mL of deionized water was added to the bottom soil, which was centrifuged again at high speed. The deposited soil was retained, and an appropriate amount of diatomite was added to the bottom soil sample, which was evenly stirred and loaded into the ASE extraction column. The sample was then extracted and determined following the same steps as for total PAH extraction. Finally, the PAH content extracted by HPCD was calculated by the subtraction method and regarded as the bioaccessible PAH content.

The potential toxic effects of PAHs were evaluated based on toxic equivalent (TEQ) analysis. In this study, the TEQ was computed according to the method from Richter-Brockmann and Achten (2018). The specific calculation is shown in Eq. (1).

$$\mathrm{TEQ} = \sum \mathrm{C}_{(\mathrm{bio})\mathrm{i}} \times \mathrm{TEF}_{\mathrm{i}} \tag{1}$$

where $C_{(bio)i}$ is the (bioaccessible) concentration of individual PAHs and TEF_i is the corresponding toxic equivalent factor, representing the potential toxicity relative to that of benzo[a] pyrene (Nisbet and Lagoy 1992). The TEF values of 16 PAHs are presented in Table S2. Furthermore, to compare the toxicity intensity of PAH in soils of different sites, the toxic concentration ratio ($R_{t/c}$) based on the TEQ was calculated as Eq. (2).

$$(\mathrm{Bio\text{-}})\mathrm{R}_{\mathrm{t/c}} = \mathrm{C}_{(\mathrm{bio\text{-}})\mathrm{TEQ}} / \mathrm{C}_{\mathrm{total}} \tag{2}$$

where $C_{(bio-)\,TEQ}$ is the (bioaccessible) TEQ concentration of PAHs in soil and C_{total} is the total PAH concentration in soil.

Stepwise linear regression (LR) analysis with soil properties as independent variables and PAH bioaccessibility as the dependent variable was carried out using the software Statistical Product and Service Solutions (SPSS). The F test was used for the linear regression model, and the t test was used for the regression coefficient significance test. The Kruskal–Wallis test and Mann–Whitney test were used to assess the difference between different sites. The content data of each PAH in the soil at different depths are expressed as the mean ± SD. Differences at $p < 0.05$ were regarded as statistically significant.

Results and Discussion

The residue concentrations of PAHs in soils are shown in Fig. 1. A total of fifteen kinds of PAHs were detected at site S1. The content of individual PAHs ranged from 0.41 to 668.85 mg kg^{-1}, and the mean value of individual PAHs was 3.08–47.81 mg kg^{-1}. Twelve kinds of PAHs were detected at site S2, with the concentrations ranging from 0.25 to 21.4 mg kg^{-1}, and the mean content of individual PAHs ranged from 0.77 to 3.24 mg kg^{-1}. In addition, PAHs were barely detectable in soils deeper than 6 m at site S2. Overall, the PAH contents at site S1 were significantly higher than those at site S2 ($p < 0.05$). As shown in Fig. 1c, 4-ring PAHs

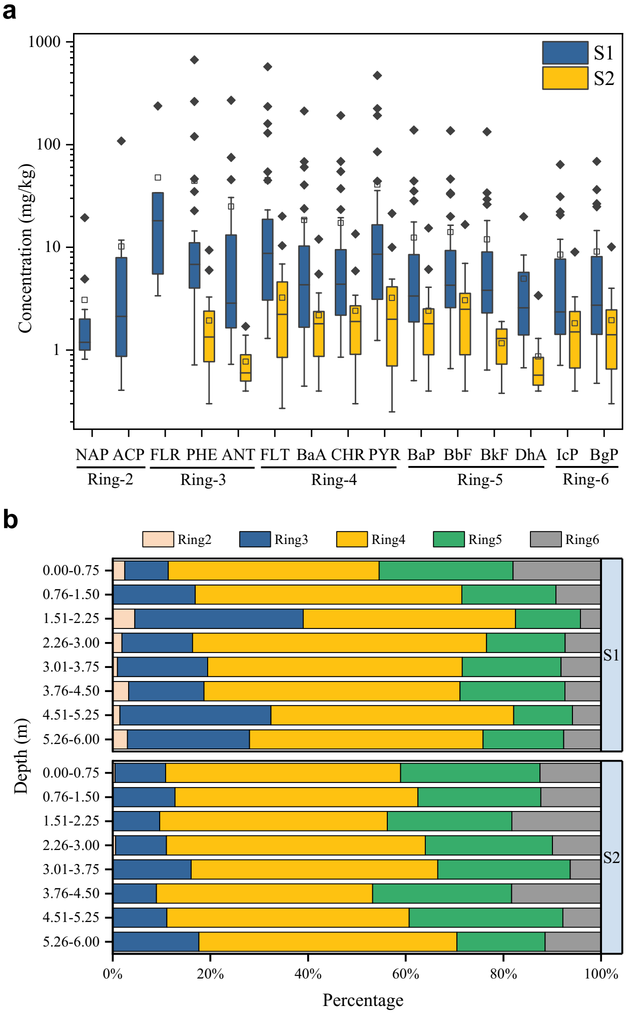

Fig. 1 The contents of polycyclic aromatic hydrocarbons (PAHs) at sites S1 and S2 (**a**) and the distribution of PAHs with different ring numbers in the soil profile (**b**)

were the dominant fraction at both sites (33.6%–60.9%), followed by 3-ring PAHs at site S1 and 5-ring PAHs at site S2, regardless of soil profile depth. Two-ring PAHs showed the lowest proportion and were almost undetectable at site S2. The high-ring PAHs (4-, 5-, and 6-ring PAHs) at the two sites accounted for approximately 80% of all PAH contents.

Compared with those found in existing studies, the total PAH contents at sites S1 and S2 were all relatively high (Wang et al. 2017), indicating that the risks of PAH contamination in the coal gasification plant and steel plant were high. PAHs naturally exist in coal due to diagenesis. The total amount of PAHs extracted from coal may range from tens to several thousand milligrams per kilogram (Hindersmann and Achten 2018); hence, the combustion of coal and coke has been an important source of PAHs in the environment and at industrial sites. Moreover, one study showed that PAHs in coal-rich soil were deficient in microbial degradation (Achten et al. 2011).

The composition of PAHs with different ring numbers in soils differed substantially (Hindersmann and Achten 2018; Karaca 2016; Siemering and Thiboldeaux 2021). Studies have shown that 4-ring PAHs are dominant in heavy traffic and industrial areas (Karaca 2016). High-ring (5- and 6-ring) and 2-ring PAHs are distributed in the soil near petrochemical complexes (Nadal et al. 2004), while 3- and 4-ring PAHs are mainly concentrated near chemical companies. In this study, The S1 and S2 sampling sites were located at the former sites of the coal gasification plant and steel plant, respectively. After the plant stopped operating, the plant-derived LMW PAHs in the soil were relatively quickly degraded due to their comparably higher water solubility, while the HMW PAHs persisted in the soil for a long time (Li et al. 2012). In addition, our diagnostic ratio results further corroborate that the dominant source of PAH in two sites was the combustion of coal and other fuels (Fig. S3), and there was source of traffic emission because the two sites were located in urban areas (Wu et al. 2021).

The bioaccessibility of PAHs (bioacc-PAHs) with different ring numbers is shown in Fig. 2. The bioaccessibility of PAHs extracted by HPCD at site S1 ranged from 1.18% to 92.93%, with an average of 52.02%, while those at site S2 ranged from 0.84% to 77.86%, with an average of 29.28%. In general, the bioacc-PAHs at site S1 were significantly higher than that at site S2, and the average bioacc-PAHs for 3-ring PAHs were the highest in soils at both sites. The bioacc-PAHs of 5- and 6-ring at site S1 were significantly lower than that of the 3- and 4-ring PAHs. Although there was no significant difference among the bioacc-PAHs with different ring numbers at site S2, the average bioacc-PAHs for 6-ring (20.81%) at site S2 was apparently lower than that of 3–5 ring (29.21%–31.96%). This result is consistent with that reported by other studies. For example, Crampon et al. (2016) and Oleszczuk et al. (2017) both demonstrated a decline in bioacc-PAHs with increasing number of aromatic rings in soils. The amounts of PAHs retained by humin in soils increased with increasing number of aromatic rings, leading to decreased bioaccessibility (Han et al. 2020). Three-ring PAHs had the highest bioaccessibility for grains, i.e., the highest likelihood to be taken up, whereas the 5- and 6-ring PAHs had the lowest likelihood (Tian et al. 2018). Such a tendency could be explained by the increased K_{ow} of PAHs with high molecular weight (Oleszczuk et al. 2017); a higher K_{ow} value represents stronger hydrophobicity and lipophilicity (Yu et al. 2018), leading to lower contents of water-soluble PAHs and poor migration ability of PAHs from soil particles to the soil solution. Therefore, PAHs with more aromatic rings and larger K_{ow} values were more difficult to extract and more recalcitrant in soils than those with fewer aromatic rings (Cheng et al. 2021).

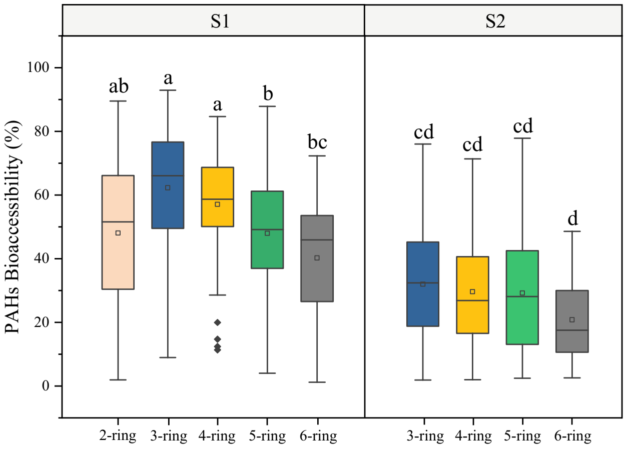

Fig. 2 The bioaccessibility of polycyclic aromatic hydrocarbons with different ring numbers. Boxes sharing the same letter are not significantly different based on the Kruskal–Wallis test

As shown in Fig. S2, the bioacc-PAHs varied greatly at different soil profile depths. A slight increasing trend with increasing depth was found in the bioacc-PAHs of the 3-, 4- and 6-ring PAHs at site S1, while at site S2, higher bioacc-PAHs were found in the mid-deep soil layers (1.51–2.25 m, 3.76–4.50 m) than in the deep layers (5.26–6.00 m) and upper soil layers (0–0.75 m), which could be attributed to the changes in soil properties. In general, the soil organic matter content reaches its highest value in the soil surface layer and decreases significantly with increasing depth, which affects the adsorption and desorption processes in the soil to a great extent (Gao et al. 2013). Several studies have also obtained similar results that the sorption of organic pollutants in deep soil is lower than that in surface soil (Knight et al. 2019; Gao et al. 2013; Si et al. 2009), which could explain the high bioaccessibility of contaminants in deep soil layers.

The organic matter content and mineral content of soils with different textures are very distinct, greatly influencing the morphological distribution and toxicity of organic pollutants in soil (Princz et al. 2018). There were four soil textures, i.e., sandy loam, loamy sand, silt loam and loam, in our studied sites (Fig. 3). In both sites, there was almost no significant difference in bioacc-PAHs among different soil textures. However, it is worth noting that the bioacc-PAH in silt loam soil in site S1 was significantly lower than that of loamy sand soil, and the bioacc-PAH of loam soil in site S2 was significantly lower than that of sand loamy soil, which may be due to the fact that silt loam and loam are exactly the two of the four studied soils with higher silt particle (2–0.02 mm) proportion. Wilcke et al. (1996) reported that PAHs in soil were adsorbed the most on silt particles and the least on sand particles, resulting in the low bioaccessibility of PAHs in silt soils. Ritore et al. (2022) observed a decline trend in the removal efficiency of hydrophobic organic contaminants (HOCs) in the soil with the transformation of soil texture from sandy to silt loam and clay soil. Therefore, the abundant aromatic ring structures in the organic matter of silt particles leads to the adsorption and binding of HOCs in soil, thus decreasing their bioaccessibility (Wilcke et al. 1996).

The correlations between the bioaccessibility of PAHs and soil properties were analyzed. As shown in Table S4, the total bioacc-PAHs had a positive LR coefficient (0.478) with soil dissolved organic carbon (DOC) and a negative coefficient (− 0.247) with total organic carbon (TOC). Compared to those on insoluble organic matter, PAHs adsorbed on dissolved organic matter (DOM) have higher mobility and bioaccessibility. The former matter can immobilize PAHs, while the latter can solubilize PAHs in the soil, which has been suggested by numerous studies (Li et al. 2022; Tao et al. 2006; Yu et al. 2018). Therefore, the decreasing DOC value in the soil samples found in this study led to a reduction in the bioaccessibility of PAHs.

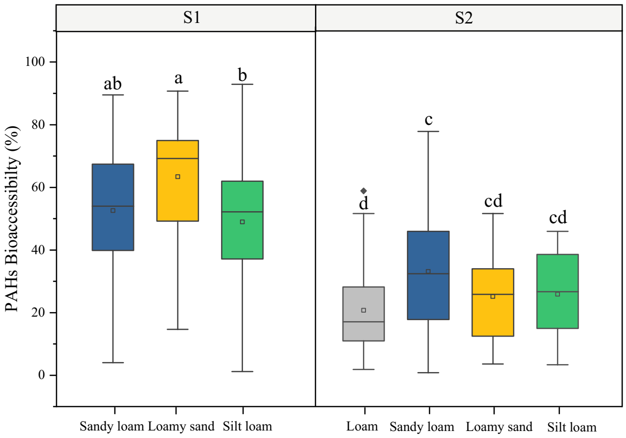

Fig. 3 The bioaccessibility of polycyclic aromatic hydrocarbons in different soil textures. Boxes sharing the same letter are not significantly different based on the Kruskal–Wallis test

There were significant positive LR coefficients between 3, 4, and 6-ring bioacc-PAHs and pH. Studies have shown that pH affects bioacc-PAHs by influencing the content or morphological changes of DOM and SOM in soil (Yu et al. 2018). Under different pH conditions, SOM exists in diverse physical forms and has different adsorption capacities for PAHs (Yu et al. 2018). In addition, Yu et al. (2016) concluded that higher pH values promoted an increased DOM content in soils, thereby inhibiting the proportion of PAHs sequestered by the soil solid phase and improving their bioaccessibility. The cation exchange capacity (CEC) had a significant influence only on 6-ring PAHs. It was reported that an increased CEC in soil would deepen the sequestration degree of PAHs (Chung and Alexander 2002). Soil salinity showed subtractive LR coefficients with 3-ring and total bioacc-PAHs, which was consistent with the results obtained by Anderson (2013) that saline soil could retain PAHs in soil to a certain extent.

The total potassium, total iron and total manganese contents all had significant negative effects on the bioacc-PAHs (Table S4). Previous studies have shown that the presence of metal ions can enhance the adsorption capacity of soil for PAHs with poor desorption reversibility, thereby reducing its bioavailability (Luo et al. 2010; Saeedi et al. 2018). On the one hand, metal ions interact with solid organic matter in the soil, such as by forming complexes with polar functional groups of organic matter, modifying its structure and improving its adsorption capacity for PAHs (Saison et al. 2004). The higher the soil organic carbon content is, the stronger the enhancement of the adsorption affinity by metal cation modification (Liang et al. 2016). On the other hand, quantum mechanics have proven that the cationic–π interaction between metal ions and PAHs may improve the adsorption of PAHs in SOC (Liang et al. 2016).

The proportion of soil silt and clay had no significant effect on the total bioacc-PAHs but had different effects on the 2-ring, 4-ring and 5-ring PAHs (Table S4). Numerous studies have indicated the negative effects of the clay proportion in soil on the extractability of PAHs. However, its impact was limited, such as decreasing only the low molecular weight bioacc-PAHs (Portet-Koltalo et al. 2020) or having only a negative correlation in the soil in particular research areas (Pu et al. 2004). Theoretically, clay is rich in pores with a size less than 20 nm or even smaller and has a large surface area, which is difficult to invade by soil (micro)organisms or plant roots, making it an excellent place for pollutant storage (Whittaker et al. 2019). Moreover, with high surface areas, enhanced sorption to contaminants through weak physical interactions was verified in clay soil (Pu et al. 2004).

The TEQ concentration based on total and bioaccessible PAH contents in 78 soil samples from the two sites was calculated (Table S3). The total TEQ concentration ranged from 0.0004 to 263.24 mg kg^{-1} at site S1 and 0.0002 to 10.11 mg kg^{-1} at site S2, with mean values that were 7.5 times higher at site S1 than at S2. The bioaccessible TEQ concentration ranged from 0 to 90.22 mg kg^{-1} at site S1 and 0 to 13.34 mg kg^{-1} at site S2, with mean values that were 9.2 times higher at site S1 than at S2. Due to the high PAH contents at site S1 (Fig. 1a), the total TEQ and bioaccessible TEQ were all higher at site S1 than at site S2. Therefore, a toxic concentration ratio ($R_{t/c}$) was calculated to normalize the PAH concentrations. It was shown that the $R_{t/c}$ (C_{TEQ}/C_{total}) at site S2 was significantly higher than that at site S1 ($p < 0.01$) (Fig. 4), which can be attributed to the fact that the proportion of HMW PAHs with high toxicity at site S2 was about 10% higher than that at site S1(Fig. 1b). This result indicates that higher PAH toxicity would be achieved at site S2 rather than S1 when the contaminated sites show the similar total PAH contents. However, the Bio-$R_{t/c}$ ($C_{bio\text{-}TEQ}/C_{total}$) based on the bioaccessible TEQ was significantly higher at site S1 than at site S2 ($p < 0.01$). This opposite result means that higher bioaccessible toxicity would be present at site S1 than S2 under the condition of similar total PAH contents, even though the proportion of HMW PAHs was larger at site S2 than S1. Therefore, the proportion of HMW PAHs and the bioaccessibility of PAHs both dominate the toxicity of PAHs in contaminated soils. Since PAHs are likely sequestered by soil organic matter and minerals in soil (Umeh et al. 2019), blocking contact with organisms, we suggested that to avoid overestimating the toxicity of PAH in soil, it is necessary to take bioaccessibility into account.

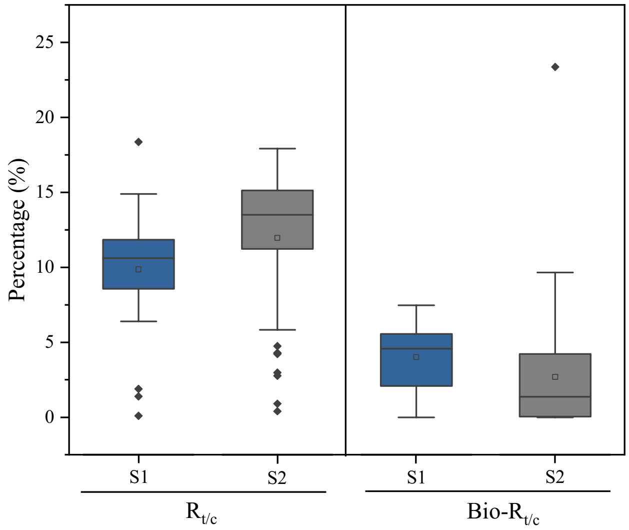

Fig. 4 The ratio of toxic equivalent concentration to total polycyclic aromatic hydrocarbons (PAHs) concentration ($R_{t/c}$), and the ratio of bioaccessiable toxic equivalent concentration to total PAHs concentration (Bio-$R_{t/c}$) in site S1 and S2

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00128-022-03530-6.

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Declarations

Conflict of 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.

Human and Animal Rights and Informed consent Our study did not involve human participants, their data or biological material.

References

Achten C, Cheng SB, Straub KL et al (2011) The lack of microbial degradation of polycyclic aromatic hydrocarbons from coal-rich soils. Environ Pollut 159:623–629

Anderson CJ (2013) Degradation and composition of polycyclic aromatic hydrocarbons (PAHs) following oil exposure in experimental salt marshes. Water Air Soil Pollut 224:1608

Cheng Y, Sun H, Yang ET et al (2021) Distribution and bioaccessibility of polycyclic aromatic hydrocarbons in industrially contaminated site soils as affected by thermal treatment. J Hazard Mater 411:125129

Chung N, Alexander M (2002) Effect of soil properties on bioavailability and extractability of phenanthrene and atrazine sequestered in soil. Chemosphere 48:109–115

Crampon M, Bodilis J, Le Derf F et al (2016) Alternative techniques to HPCD to evaluate the bioaccessible fraction of soil-associated PAHs and correlation to biodegradation efficiency. J Hazard Mater 314:220–229

Cvancarova M, Kresinova Z, Cajthaml T (2013) Influence of the bioaccessible fraction of polycyclic aromatic hydrocarbons on the ecotoxicity of historically contaminated soils. J Hazard Mater 254:116–124

Dat ND, Chang MB (2017) Review on characteristics of PAHs in atmosphere, anthropogenic sources and control technologies. Sci Total Environ 609:682–693

Duan LC, Palanisami T, Liu YJ et al (2014) Effects of ageing and soil properties on the oral bioavailability of benzo[a]pyrene using a swine model. Environ Int 70:192–202

Duran R, Cravo-Laureau C (2016) Role of environmental factors and microorganisms in determining the fate of polycyclic aromatic hydrocarbons in the marine environment. Fems Microbiol Rev 40:814–830

Gao GY, Fu BJ, Zhan HB et al (2013) Contaminant transport in soil with depth-dependent reaction coefficients and time-dependent boundary conditions. Water Res 47:2507–2522

Gao P, Li HB, Wilson CP et al (2018) Source identification of PAHs in soils based on stable carbon isotopic signatures. Crit Rev Environ Sci Technol 48:923–948

Gao P, da Silva EB, Townsend T et al (2019) Emerging PAHs in urban soils: concentrations, bioaccessibility, and spatial distribution. Sci Total Environ 670:800–805

Han XM, Liu YR, Zheng YM et al (2014) Response of bacterial pdo1, nah, and C12O genes to aged soil PAH pollution in a coke factory area. Environ Sci Pollut Res 21:9754–9763

Han D, Jiang L, Zhong MS et al (2020) Desorption and bioaccessibility of high-molecular-weight PAHs in aged field soil and humin-like fraction from a coke plant. Environ Earth Sci 79:243

Hindersmann B, Achten C (2018) Urban soils impacted by tailings from coal mining: PAH source identification by 59 PAHs, BPCA and alkylated PAHs. Environ Pollut 242:1217–1225

Humel S, Schritter J, Sumetzberger-Hasinger M et al (2020) Atmospheric carbonation reduces bioaccessibility of PAHs in industrially contaminated soil. J Hazard Mater 383:121092

Idowu O, Semple KT, Ramadass K et al (2020) Analysis of polycyclic aromatic hydrocarbons (PAHs) and their polar derivatives in soils of an industrial heritage city of Australia. Sci Total Environ 699:134303

Jia JP, Bi CJ, Zhang JF et al (2019) Atmospheric deposition and vegetable uptake of polycyclic aromatic hydrocarbons (PAHs) based on experimental and computational simulations. Atmos Environ 204:135–141

Karaca G (2016) Spatial distribution of polycyclic aromatic hydrocarbon (PAH) concentrations in soils from Bursa, Turkey. Arch Environ Contam Toxicol 70:406–417

Knight ER, Janik LJ, Navarro DA et al (2019) Predicting partitioning of radiolabelled C-14-PFOA in a range of soils using diffuse reflectance infrared spectroscopy. Sci Total Environ 686:505–513

Leech C, Tighe MK, Pereg L et al (2020) Bioaccessibility constrains the co-composting bioremediation of field aged PAH contaminated soils. Int Biodeterior Biodegrad 149:104922

Li F, Guo S, Hartog N (2012) Electrokinetics-enhanced biodegradation of heavy polycyclic aromatic hydrocarbons in soil around iron and steel industries. Electrochim Acta 85:228–234

Li XJ, Shuang SQ, Li XY et al (2013) The effect of concentrations and properties of phenanthrene, pyrene, and benzo(a)pyrene on desorption in contaminated soil aged for 1 year. J Soils Sediments 13:375–382

Li Z, Zhang W, Shan B (2022) Effects of organic matter on polycyclic aromatic hydrocarbons in riverine sediments affected by human activities. Sci Total Environ 815:152570

Liang X, Zhu LZ, Zhuang SL (2016) Sorption of polycyclic aromatic hydrocarbons to soils enhanced by heavy metals: perspective of molecular interactions. J Soils Sediments 16:1509–1518

Lin Q, Shen KL, Zhao HM et al (2008) Growth response of *Zea mays* L. in pyrene-copper co-contaminated soil and the fate of pollutants. J Hazard Mater 150:515–521

Luo L, Zhang S, Christie P (2010) New insights into the influence of heavy metals on phenanthrene sorption in soils. Environ Sci Technol 44:7846–7851

Moeckel C, Monteith DT, Llewellyn NR et al (2014) Relationship between the concentrations of dissolved organic matter and polycyclic aromatic hydrocarbons in a typical UK upland stream. Environ Sci Technol 48:130–138

Nadal M, Schuhmacher M, Domingo JL (2004) Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. Environ Pollut 132:1–11

Ni N, Shi RY, Liu ZT et al (2018) Effects of biochars on the bioaccessibility of phenanthrene/pyrene/zinc/lead and microbial community structure in a soil under aerobic and anaerobic conditions. J Environ Sci 63:296–306

Nisbet I, Lagoy P (1992) Toxic equivalency factors (TEFs) for polycyclic aromatic-hydrocarbons (PAHs). Regul Toxicol Pharmacol 16:290–300

Oleszczuk P, Godlewska P, Reible DD et al (2017) Bioaccessibility of polycyclic aromatic hydrocarbons in activated carbon or biochar amended vegetated (Salix viminalis) soil. Environ Pollut 227:406–413

Ortega-Calvo JJ, Harmsen J, Parsons JR et al (2015) From bioavailability science to regulation of organic chemicals. Environ Sci Technol 49:10255–10264

Portet-Koltalo F, Gardes T, Debret M et al (2020) Bioaccessibility of polycyclic aromatic compounds (PAHs, PCBs) and trace elements: influencing factors and determination in a river sediment core. J Hazard Mater 384:121499

Princz J, Jatar M, Lemieux H et al (2018) Perfluorooctane sulfonate in surface soils: effects on reproduction in the collembolan, *folsomia candida*, and the *oribatid mite*, oppia nitens. Chemosphere 208:757–763

Pu XZ, Lee LS, Galinsky RE et al (2004) Evaluation of a rat model versus a physiologically based extraction test for assessing phenanthrene bioavailability from soils. Toxicol Sci 79:10–17

Qin SB, Qi SH, Li XS et al (2020) Magnetic solid-phase extraction as a novel method for the prediction of the bioaccessibility of polycyclic aromatic hydrocarbons. Sci Total Environ 728:138789

Reid BJ, Stokes JD, Jones KC et al (2000) Nonexhaustive cyclodextrin-based extraction technique for the evaluation of PAH bioavailability. Environ Sci Technol 34:3174–3179

Richter-Brockmann S, Achten C (2018) Analysis and toxicity of 59 PAH in petrogenic and pyrogenic environmental samples including dibenzopyrenes, 7H-benzo[c] fluorene, 5-methylchrysene and 1-methylpyrene. Chemosphere 200:495–503

Ritore E, Coquelet B, Arnaiz C et al (2022) Guidelines for surfactant selection to treat petroleum hydrocarbon-contaminated soils. Environ Sci Pollut Res 29:7639–7651

Sabate J, Vinas M, Solanas AM (2006) Bioavailability assessment and environmental fate of polycyclic aromatic hydrocarbons in biostimulated creosote-contaminated soil. Chemosphere 63:1648–1659

Saeedi M, Li LY, Grace JR (2018) Effect of organic matter and selected heavy metals on sorption of acenaphthene, fluorene and fluoranthene onto various clays and clay minerals. Environ Earth Sci 77:305

Saison C, Perrin-Ganier C, Amellal S et al (2004) Effect of metals on the adsorption and extractability of C-14-phenanthrene in soils. Chemosphere 55:477–485

Semple KT, Doick KJ, Jones KC et al (2004) Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. Environ Sci Technol 38:228–231

Si YB, Takagi K, Iwasaki A et al (2009) Adsorption, desorption and dissipation of metolachlor in surface and subsurface soils. Pest Manag Sci 65:956–962

Siemering GS, Thiboldeaux R (2021) Background concentration, risk assessment and regulatory threshold development: polycyclic aromatic hydrocarbons (PAH) in Milwaukee. Wisconsin Surf Soils Environ Pollut 268:115772

Tao S, Xu FL, Liu WX et al (2006) A chemical extraction method for mimicking bioavailability of polycyclic aromatic hydrocarbons to wheat grown in soils containing various amounts of organic matter. Environ Sci Technol 40:2219–2224

Tian K, Bao HY, Zhang XC et al (2018) Residuals, bioaccessibility and health risk assessment of PAHs in winter wheat grains from areas influenced by coal combustion in China. Sci Total Environ 618:777–784

Tsibart AS, Gennadiev AN (2013) Polycyclic aromatic hydrocarbons in soils: sources, behavior, and indication significance (a review). Eurasian Soil Sci 46:728–741

Umeh AC, Duan L, Naidu R et al (2019) In vitro gastrointestinal mobilization and oral bioaccessibility of PAHs in contrasting soils and associated cancer risks: focus on PAH nonextractable residues. Environ Int 133:105186

Wang RW, Sun RW, Liu GJ et al (2017) A review of the biogeochemical controls on the occurrence and distribution of polycyclic aromatic compounds (PACs) in coals. Earth-Sci Rev 171:400–418

Wang C, Yang ZZ, Zhang YH et al (2018) PAHs and heavy metals in the surrounding soil of a cement plant co-processing hazardous waste. Chemosphere 210:247–256

Whittaker ML, Lammers LN, Carrero S et al (2019) Ion exchange selectivity in clay is controlled by nanoscale chemical-mechanical coupling. Proc Natl Acad Sci USA 116:22052–22057

Widdowson MA, Shearer S, Andersen RG et al (2003) Remediation of polycyclic aromatic hydrocarbon compounds in groundwater using poplar trees. Environ Sci Technol 39:1598–1605

Wilcke W (2007) Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil. Geoderma 141:157–166

Wilcke W, Zech W, Kobza J (1996) PAH-pools in soils along a PAH-deposition gradient. Environ Pollut 92:307–313

Wu Y, Salamova A, Venier M (2021) Using diagnostic ratios to characterize sources of polycyclic aromatic hydrocarbons in the Great Lakes atmosphere. Sci Total Environ 761:143240

Yu L, Vázquez-Cuevas G, Duan L et al (2016) Buffered cyclodextrin extraction of ^{14}C-phenanthrene from black carbon amended soil. Environ Technol Innov 6:177–184

Yu LB, Duan LC, Naidu R et al (2018) Abiotic factors controlling bioavailability and bioaccessibility of polycyclic aromatic hydrocarbons in soil: putting together a bigger picture. Sci Total Environ 613:1140–1153

Zelinkova Z, Wenzl T (2015) The occurrence of 16 EPA PAHs in food—a review. Polycycl Aromat Compd 35:248–284

Zhang P, Chen YG (2017) Polycyclic aromatic hydrocarbons contamination in surface soil of China: a review. Sci Total Environ 605:1011–1020

Zhang J, Fan SK, Du XM et al (2015) Accumulation, allocation, and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in soil-brassica chinensis system. PLoS ONE 10:e0115863

Zhang YN, Yang XL, Gu CG et al (2016) A novel bioaccessibility prediction method for PAHs in soil: composite extraction with hydroxypropyl-beta-cyclodextrin and extracellular polymer substances. Sci Total Environ 569:997–1003

Zhang YN, Yang XL, Gu CG et al (2017) Prediction of polycyclic aromatic hydrocarbon bioaccessibility to earthworms in spiked soils by composite extraction with hydroxypropy1-beta-cyclodextrin and organic acids. Pedosphere 27:502–510