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Bioaccessibility and health risk assessment of hydrophobic organic pollutants in soils from four typical industrial contaminated sites in China

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ABSTRACT

There have been reports of potential health risks for people from hydrophobic organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated hydrocarbons (PCHs), and organophosphate flame retardants (OPFRs). When a contaminated site is used for residential housing or public utility and recreation areas, the soil-bound organic pollutants might pose a threat to human health. In this study, we investigated the contamination profiles and potential risks to human health of 15 PAHs, 6 PCHs, and 12 OPFRs in soils from four contaminated sites in China. We used an in vitro method to determine the oral bioaccessibility of soil pollutants. Total PAHs were found at concentrations ranging from 26.4 ng/g to 987 ng/g. PCHs (0.27–14.3 ng/g) and OPFRs (6.30–310 ng/g) were detected, but at low levels compared to earlier reports. The levels of PAHs, PCHs, and OPFRs released from contaminated soils into simulated gastrointestinal fluids ranged from 1.74% to 91.0%, 2.51% to 39.6%, and 1.37% to 96.9%, respectively. Based on both spiked and unspiked samples, we found that the oral bioaccessibility of pollutants was correlated with their $\log K_{ow}$ and molecular weight, and the total organic carbon content and pH of soils. PAHs in 13 out of 38 contaminated soil samples posed potential high risks to children. When considering oral bioaccessibility, nine soils still posed potential risks, while the risks in the remaining soils became negligible. The contribution of this paper is that it corrects the health risk of soil-bound organic pollutants by detecting bioaccessibility in actual soils from different contaminated sites.

Introduction

The manufacturing industries of textiles, printing, metallurgy, and chemicals are all rapidly expanding with industrialization. In the course of the manufacturing process, numerous chemicals are intentionally or unintentionally released into the surrounding environment, thereby impacting the health

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of both humans and organisms inhabiting the soil and water (Arslan et al., 2017; Chen et al., 2022b, 2023; Jiang et al., 2023). It has been reported that hydrophobic organic pollutants easily bind to organic matter and can be found in contaminated soils (Li et al., 2015). These soil pollutant residues, resulting from human activities, pose potential risks to people living or working near contaminated sites (Alharbi et al., 2018; Tang et al., 2010). Soil remediation is recommended because some persistent organic pollutants degrade slowly in soils, so remediation is required to make the land safe for human and animal use (Xiang et al., 2022). Therefore, it is necessary to detect toxic pollutant levels in contaminated soils.

As representative examples of traditional hydrophobic organic pollutants, 15 polycyclic aromatic hydrocarbons (PAHs) were included on the United States Environmental Protection Agency's the priority control list as early as 1976 due to their carcinogenic, teratogenic, and mutagenic effects (Keith, 2015). PAHs have been detected in contaminated soils in various countries. Qi et al. (2020) demonstrated that PAH concentrations in industrial soils in Caserta, Italy ranged from 10 ng/g dry weight (dw) to 1491 ng/g dw. Higher soil contamination of PAHs was found in Guizhou and Shenyang, China, as well as Ulsan, South Korea, with concentrations of 196–11,592, 290–8492, and 65–12,000 ng/g dw, respectively (Chen et al., 2017; Kwon and Choi, 2014; Yang et al., 2013). A toxicological study revealed that benzo[a]pyrene (BaP) reduces cell regeneration by upregulating receptors that inhibit stem cell proliferation and differentiation (Heo et al., 2019). Additionally, BaP causes DNA methylation, damages DNA integrity and its repair process, leads to cell death and genome reordering, and thereby increases the incidence of cancer (Sadikovic and Rodenhiser, 2006). The existence of PAHs presents potential risks to human health. For example, the incremental lifetime cancer risk (*ILCR*) associated with PAHs exceeded the high potential risk range value for individuals exposed to soils within industrial zones in two distinct cities in India (Sankar et al., 2023).

In addition to PAHs, polychlorinated hydrocarbons (PCHs) are hydrophobic organic pollutants that have gained increasing attention. Hexachlorobutadiene (HCBD), pentachloroanisole (PCA), hexachlorobenzene (HCB), and pentachlorobenzene (PeCB) were added to the Stockholm Convention's list due to their persistence, bioaccumulation, and toxicity (UNEP, 2001, 2009, 2015). Tetrachlorobenzenes and trichlorobenzenes are regarded as priority pollutants by European, American, and Canadian environmental organizations (CEPA, 1993; EU, 2013; US EPA, 2014). These pollutants have been found in soils (Wang et al., 2007; Zhang et al., 2014). Among them, chlorobenzenes have a high irritant effect on the eyes, skin, and respiratory system and easily react with liver and kidney tissues (Brahushi et al., 2017). Organophosphate flame retardants (OPFRs), which are globally more frequently used, can effectively replace brominated flame retardants (Wei et al., 2015). The majority of OPFRs are typically incorporated into polymer materials through physical mixing instead of chemical bonding. This facilitates the release of contaminants into the environment via processes such as wear, volatilization, leaching, combustion, and waste disposal (Li et al., 2014). As a result, OPFRs can be ubiquitously detected in various environmental samples, including dusts (Bacaloni et al., 2007; Marklund et al., 2003) and soils (Mihajlović et al., 2011). The potential hazards of organophosphorus flame retardants, such as tris(2-chloroethyl) phosphate (TCEP), tris(2-chloropropyl) phosphate (TCPP), and tris(2,3-dichloropropyl) phosphate (TDCPP), to ecosystems and human health have been reported (Du et al., 2019; Yu et al., 2019).

Risk evaluation and site soil remediation typically rely on the total content of pollutants in soils across different countries. This approach assumes that soil pollutants are completely absorbed by humans after ingestion, inhalation, or epidermal penetration. However, due to the binding of organic compounds to soils, this assumption does not reflect reality and may overestimate risk levels (UKEA, 2002). To address this issue, the terms bioaccessibility and bioavailability are used. Bioavailability refers to the percentage of a chemical that reaches the systemic circulation in the body, while bioaccessibility is the ratio of a chemical's soluble portion that can be released from the environmental matrix into the gastrointestinal system (Collins et al., 2015; Ruby et al., 1999). Bioavailability is determined through in vivo experiments (Ruby et al., 2016), but these are unsuitable for analyzing batch samples. Conversely, analyzing bioaccessibility through in vitro experiments is suitable for processing a substantial number of samples owning to their expeditious and straightforward characteristics (Oomen et al., 2002). Numerous previously published papers have claimed that the standard solution was added to soils when measuring bioaccessibility. Furthermore, the physicochemical properties of environmental matrices (e.g., soil particle size and total organic carbon content) and target pollutants (e.g., logK_{OW}, molecular weight, and water solubility) have been reported to affect the oral bioaccessibility of target pollutants based on matrix spiking with a standard solution (Yu et al., 2013). However, these results do not provide a reliable indicator of the actual situation.

Assessing the oral bioaccessibility of soil organic pollutants, a primary pathway for human exposure, is crucial. This evaluation should be conducted in soils without the use of commercial standard solutions. The study aims to: 1) characterize contamination profiles of PAHs, PCHs, and OPFRs in soils from four typical contaminated sites in China; 2) determine the release of target pollutants from soils into simulated gastrointestinal fluids using a physiologically based extraction test (PBET), without the addition of standard solutions; 3) explore the correlation between the bioaccessibility of target pollutants and the physicochemical properties of contaminated soils and pollutants; 4) validate this correlation by introducing spiked samples with added standard solutions to soils; and 5) assess human health risks posed by the oral ingestion of toxic pollutants in soils, before and after oral bioaccessibility correction. This information underscores the importance of correcting oral bioaccessibility during risk assessment.

1. Materials and methods

1.1. *Soil sampling*

Thirty-eight soil samples were collected from four contaminated sites, including a copper-zinc smelting plant (BY, $n = 6$), an antimony mining plant (QL, $n = 12$), a petrochemical plant (DQ, $n = 12$), and an ink factory (ZS, $n = 8$) (Appendix A Table S1 and Fig. S1). The BY and QL sites represent industries related to heavy metal production, while the DQ and ZS sites represent industries involved in the manufacturing of organic chemicals. Worker living areas are present within the BY site, whereas the QL site is abandoned. Within 800 m of the DQ site, there are residential areas and two middle schools. The ZS site is located near a river and features a mixed industrial and residential area, with a developed furniture industry. It is essential to conduct a human health risk assessment for these four contaminated sites. Three subsamples within a 1.0-m diameter (0–20 cm depth) were thoroughly mixed to generate composite soil samples for each sampling site. To remove debris and pebbles, all soils were air dried, ground at room temperature, and sieved through a 10-mesh screen (Sankar et al., 2023). Soil samples were then further sieved to less than 250 µm for physical and chemical analysis of soil properties (such as pH and total organic carbon) (Xie et al., 2023) (Appendix A Text S1), determination of target pollutants, and in vitro bioaccessibility tests.

1.2. *In vitro bioaccessibility assays*

Simulated gastric and intestinal fluids were prepared using an improved physiologically based extraction test (PBET). This test closely mimics gastrointestinal conditions under fasting states and has been widely employed to simulate the leaching of organic contaminants in various matrices (Juhasz et al., 2009; Wang et al., 2013). The simulated gastrointestinal fluid was freshly prepared with ultrapure water to avoid contamination caused by bacteria. The PBET comprises gastric and intestinal phases, with the gastric phase set to 1 hr and the intestinal phase to 4 hr, aligning with the retention times of the digestive tract (Cui et al., 2016). The pH value of the gastric fluid is 1.5, which represents the fasting state (Cui et al., 2016). Based on previous works (Juhasz et al., 2009; Wang et al., 2013), 2 g of soils were added to 200 mL of simulated gastric fluid (pH = 1.5) containing 1.76 g of sodium chloride, 0.1 g of trisodium citrate dihydrate, 84 µL of DL-malic acid disodium salt, 100 µL of acetic acid, and 0.25 g of pepsin. The temperature, solid/liquid ratio, and incubation time were set at 37°C, 1:100, and 60 min, respectively, to simulate the gastric digestion process. After the gastric digestion process, the solution pH was adjusted to 7.0, and 0.4 g of pig bile and 0.12 g of pancreatin were added. The resulting solution underwent a 4 hr incubation period at an oscillator speed of 100 r/min to simulate the intestinal digestion process. The incubation flask was filled with nitrogen throughout the process. After incubation, the final mixtures were divided into three aliquots, centrifuged at 2500 r/min for 10 min, and the supernatant was collected for chemical analysis. It should be noted that four soils, namely DQ8, QL9, BY6, and ZS1, from different contaminated sites were spiked with a standard solution of PAHs, PCHs, and OPFRs at concentrations of 250, 25, and 250 ng/g, respectively. These soils were also used for in vitro oral bioaccessibility tests to compare the results obtained from soils without the addition of a standard solution. All experiments were performed in triplicate. The oral bioaccessibility (f_{Bac}, %) of each target pollutant was calculated using Eq. (1):

$$f_{\mathrm{Bac}} = C_{\mathrm{gi}}/C_{\mathrm{soil}} \times 100\% \tag{1}$$

where, C_{gi} (ng/g) and C_{soil} (ng/g) represent the concentration of a target pollutant in the simulated gastrointestinal fluids after incubation and in soils, respectively.

1.3. *Sample pretreatment and GC–MS/MS analysis*

Fifteen PAHs, six PCHs, and 12 OPFRs were selected as target analytes in this study. Information on the target analytes and suppliers of chemicals and reagents is provided in Appendix A Text S2 and Table S2. Soil samples were pretreated using accelerated solvent extraction and column clean-up, as described in previous studies (Dong et al., 2021; Xu et al., 2022). Detailed pretreatment procedures are provided in Appendix A Text S3. For samples of simulated gastrointestinal fluid, the fluid was mixed with 30 mL of dichloromethane: n-hexane (V: V = 3:1) after being spiked with 0.5 ng/g of surrogate standards. The pear-shaped flask containing the fluid and solvent was shaken vigorously for 1 min and left to stand for 5 min, after which the organic phase was collected in a new flat-bottomed flask. The extraction process was repeated three times. To remove water, 5 g of anhydrous sodium sulfate was added to the combined organic phase. After manually shaking the extracts, they were transferred to another flat-bottomed flask and concentrated to a volume of approximately 1 mL using a rotary evaporator. The final extracts underwent a purification procedure using a commercial florisil cartridge, identical to the soil samples.

The target compounds were determined using a Thermo TRACE$^{\mathrm{TM}}$ 1300 gas chromatograph coupled to a TSQ 8000 Evo mass spectrometer (Waltham, USA). A Thermo TG-5MS capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) was used for the chromatographic separation of the target analytes. Quantitative analysis was performed using the selected reaction monitoring mode. The optimized instrument operating parameters are presented in Appendix A Tables S3–S4.

1.4. *Quality control*

Unlike the simulated gastrointestinal fluid samples, which were spiked with a mixed standard solution containing 0.5 ng/g of each analyte, soil samples were spiked with a mixed standard solution containing 2.5 ng/g of each analyte for recovery tests. Each test was conducted in triplicate. Depending on the spiked samples, the method detection or quantitation limit (MDL or MQL) of each analyte was determined to be three or ten times the signal-to-noise ratio (S/N). The recoveries, MDLs, and MQLs of all target compounds in soils were 63.4%–113%, 0.16–21.5 pg/g, and 0.53–71.6 pg/g, while those of the simulated gastrointestinal fluids were 61.4%–119%, 0.05–52.2 pg/g, and 1.74–174 pg/g, respectively (Appendix A Table S5). For quality control, all sample runs included the evaluation of a standard solution, a solvent blank, and an extraction procedure blank. The findings indicate that the method employed in this study is sensitive and effective in determining the target analytes in soil and simulated gastrointestinal fluid samples.

1.5. *Health risk assessment*

To determine the amount of PAHs present in the soil of the study site, the current toxicity assessment method for PAHs primarily uses the toxic equivalence factor (*TEF*), which is based on the equivalent toxicity concentration of BaP (Gao et al., 2019). Based on the routes of oral, nasal, and dermal ingestion of soils (Cao et al., 2017), the *ILCR* of PAHs in contaminated sites was used for cancer risk assessment (US EPA, 2005). In addition, daily intake (*DI*) (US EPA, 2017) and hazard quotient (*HQ*) (Boonsaner and Hawker, 2013; Zhao et al., 2015) calculations were used to determine the human health risk assessments for PCHs and OPFRs. The oral bioaccessibility of PAHs, PCHs, and OPFRs in soils was introduced to correct the risk assessment. Detailed calculation methods are presented in Appendix A Text S4. When $ILCR \leq 10^{-6}$, the risk is negligible under the supervision of most regulations. *ILCR* between 10^{-6} and 10^{-4} indicates a potential risk, while $ILCR > 10^{-4}$ indicates a potentially high risk (Ali et al., 2017). $HQ < 1$ and $HQ \geq 1$ indicate low and high risk, respectively (Boonsaner and Hawker, 2013; Zhao et al., 2015).

1.6. *Data analysis*

Before the statistical analysis, the concentration values below the MDL were set to 0, and concentration values below the MQL but above the MDL were given a value equal to half of the corresponding MQL. The isomer ratios of Ant/(Phe + Ant), BaA/(BaA + Chr), Flt/(Flt + Pyr), and IcdP/(IcdP + BghiP) were commonly used to distinguish between petrogenic and pyrolytic sources and determine the sources of PAH pollution in the soils of the four contaminated sites (Kurwadkar et al., 2023; Pies et al., 2008).

2. Results and discussion

2.1. *Contamination levels of PAHs, PCHs, and OPFRs in contaminated soils*

Hydrophobic organic contaminants are commonly found in contaminated soils (Adeyinka et al., 2022; Lei et al., 2020; Li et al., 2022). In this study, PAHs, PCHs, and OPFRs were detected in all four contaminated sampling sites. The total concentrations ranged from 26.4–987 ng/g, 0.27–14.3 ng/g, and 6.30–310 ng/g, respectively, with mean detection frequencies of 97.9%, 80.7%, and 89.0%. The mean concentrations of PAHs in the sampling sites of copper-zinc smelting (BY), antimony mining (QL), petrochemical (DQ), and ink factory (ZS) were 276, 353, 266, and 88.6 ng/g dry weight (dw), respectively (Appendix A Table S6). The contributions of seven carcinogenic PAHs ($\Sigma_{7-\mathrm{Car}}$PAHs) accounted for 33.1% (BY), 70.5% (QL), 73.3% (DQ), and 43.6% (ZS) of the total PAHs. Among the sampling sites, QL soils had the highest contribution of $\Sigma_{7-\mathrm{Car}}$PAHs (Appendix A Fig. S2). The PAH contents investigated in this study were approximately one order of magnitude lower compared to those documented in heavy industrial zones in Ulsan, Korea (mean value = 960 ng/g) (Kwon and Choi, 2014) and Shenyang, China (mean value = 2989 ng/g) (Yang et al., 2013). Furthermore, they were notably lower than PAH levels reported in urban soils from Orlando, USA (mean value = 3227 ng/g) (Liu et al., 2019). The concentrations of PAHs in BY, DQ, and QL soils were higher than those in agricultural soils from Huanghuai Plain, China (mean value = 130 ng/g) (Yang et al., 2012) and Nanjing, China (mean value = 178 ng/g) (Yin et al., 2008), urban and rural soils from Hong Kong, China (mean value = 54.6 ng/g) (Zhang et al., 2006), and industrial areas and production sites from Caserta, Italy (mean value = 137 ng/g) (Qi et al., 2020). The main source of PAH pollution in contaminated soils is believed to be the incomplete combustion of petroleum fuel during the production process (Ambade and Sankar, 2021; Ambade et al., 2022; Han et al., 2019). Nap content accounted for 26.4% of Σ_{15}PAHs, establishing it as a significant contributor to the overall PAH composition (Appendix A Fig. S2). This result can be explained by the generation of Nap from unburned oil, oil leakage, and insufficient ignition of organic matter (Zhang et al., 2020). The PAH residues in ZS soils were similar to those found in agricultural soils (Yang et al., 2012; Yin et al., 2008), possibly due to the primary use of aromatic hydrocarbon solvents instead of petroleum fuels in printing ink (Jaen et al., 2022).

To identify the pollution sources of PAHs in the soils of the four contaminated sampling sites, we calculated the isomer ratios of Ant/(Phe + Ant), BaA/(BaA + Chr), Flt/(Flt + Pyr), and IcdP/(IcdP + BghiP) (Kurwadkar et al., 2023; Pies et al., 2008). Detailed information on the isomer ratios of PAHs corresponding to different sources in different contaminated sampling sites is provide in Appendix A Table S7. The results indicated that PAHs in BY, ZS, and DQ soils originated from combustion. Specifically, PAHs in ZS soils came from petroleum combustion, while those in DQ came from biomass and coal combustion.

Apart from PAHs, the mean concentrations of PCHs in the four contaminated sampling sites were 4.75, 0.70, 4.02, and 2.13 ng/g dw for BY, QL, DQ, and ZS, respectively (Appendix A Table S8). These values were lower than those found in sediment from the Tonghui River, China (Σ_{10}CBs mean value = 562.6 ng/g) (Zhou et al., 2009), vegetable planting soils from Hangzhou, China (mean value = 49 ng/g) (Zhang et al., 2005), and field soils from Woburn, UK (mean value = 7.65 ng/g) (Wang et al., 1995). These results indicate low PCH pollution in the investigated zones. For OPFRs, they were found in soils from the BY, QL, DQ, and ZS sampling sites, with mean concentrations of 15.8, 47.3, 95.7, and 50.5 ng/g dw, respectively (Appendix A Table S9). Soil OPFR residues in this study were higher than those found in soils used for growing vegetables in Chengdu, China (Σ_{13}OPFRs mean value = 21.4 ng/g) (Liao et al., 2020), similar to agricultural soils from Hebei, China (mean value = 80 ng/g) (Wan et al., 2016), but lower than those found in electronic waste recycling sites in Vietnam (mean value = 196 ng/g) (Matsukami et al., 2015). Except for electronic waste recycling sites, soil OPFR pollution levels in the four contaminated sampling sites can be considered moderate. Since OPFRs are often physically added to products rather than chemically combined with them, they can be released into the surrounding environment through volatilization and wear during application (Wei et al., 2015).

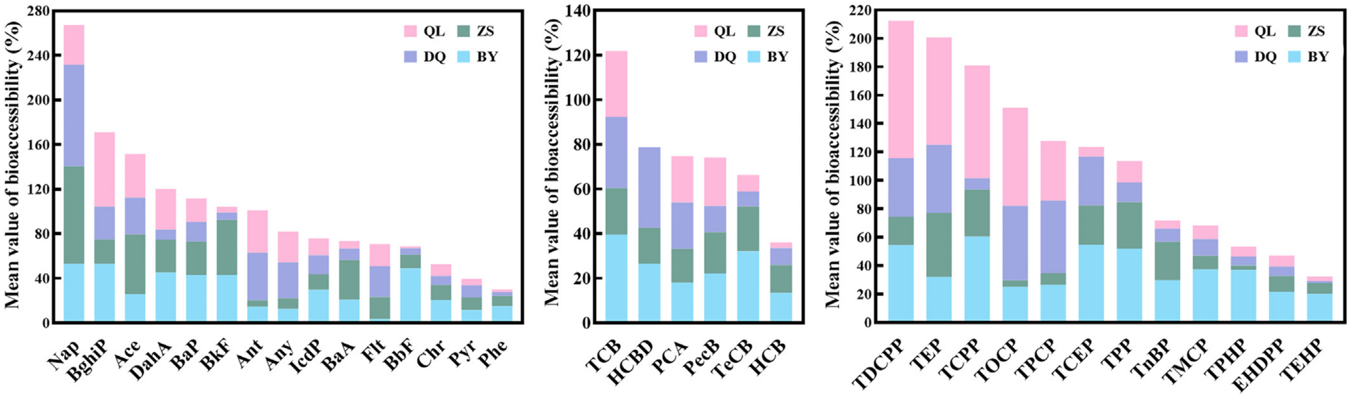

Fig. 1 – Mean bioaccessibility of each target analyte in soils from copper-zinc smelting (BY), antimony mining (QL), petrochemical (DQ), and ink factory (ZS).

2.2. *In vitro oral bioaccessibility of PAHs, PCHs, and OPFRs*

Fig. 1 illustrates the mean oral bioaccessibility of individual PAHs, PCHs, and OPFRs at each contaminated site. The ranges of PAHs, PCHs, and OPFRs released from contaminated soils into simulated gastrointestinal fluids were 1.74%–91.0%, 2.51%–39.6%, and 1.37%–96.9%, respectively. Nap (mean value = 66.9%), TCB (mean value = 30.5%), and TDCPP (mean value = 53.1%) exhibited the highest bioaccessibility capacities for PAHs, PCHs, and OPFRs, respectively, suggesting that these three chemicals could readily enter the human body.

Soil is composed of various constituents. The interactions of these components are directly impacted by the physical properties, such as texture, structure, and porosity, as well as the chemical properties like pH and ion exchange capacity of the soil. These factors subsequently influence the bioaccessibility of organic pollutants within the soil (Shen et al., 2019). As presented in Fig. 2a–b, a significant negative correlation was observed between the total organic carbon (TOC) content and the total oral bioaccessibility of PAHs in soils ($R^2 = 0.709$, $p < 0.0001$), while a significant positive correlation existed between soil pH and the total oral bioaccessibility of PAHs ($R^2 = 0.443$, $p = 0.025$). Similar findings of a negative correlation between TOC and the total oral bioaccessibility of PAHs were observed in labeled soil samples (Lu et al., 2010). PAHs, being lipophilic organic compounds, exhibit stronger binding affinity to organic carbon compared to inorganic compounds (Dean and Ma, 2007; Ghosh et al., 2000). Consequently, the binding of PAHs to soils may hinder their release during digestion, thereby affecting the percentage of PAHs dissolved in the simulated gastric and intestinal fluids. Furthermore, a negative correlation between TOC and the oral bioaccessibility of 2,3′,4,4′,5-pentachlorobiphenyl (PCB118) and non-planar 2,2′,5,5′-tetrachlorobiphenyl (PCB52) was observed in spiked soils (Pu et al., 2006). The TOC content may be influenced by fluctuations in soil pH caused by environmental factors such as precipitation. According to a previous study, the bioaccessibility of nitrated PAHs was significantly negatively correlated with soil TOC but only weakly correlated with pH (Chen et al., 2022a). This observation supports our results (Fig. 2a–b).

In the case of OPFRs, their total oral bioaccessibility decreased with increasing TOC content, although not significantly ($R^2 = 0.074$, $p = 0.368$; Appendix A Fig. S3). This could be attributed to the classification of OPFRs into three subgroups based on the difference in straight chain substituents: chlorinated OPFRs (Cl-OPFRs), alkyl OPFRs (alkyl-OPFRs), and aryl OPFRs (aryl-OPFRs). The total desorption of Cl-OPFRs ($R^2 = 0.532$, $p = 0.017$) and alkyl-OPFRs ($R^2 = 0.740$, $p = 0.001$), but not aryl-OPFRs ($R^2 = 0.044$, $p = 0.560$), from soils into simulated gastrointestinal juices exhibited a significant negative correlation with soil TOC content (Fig. 2c). Similar results were observed in a previous investigation, which indicated a negative correlation between the organic carbon content and the oral bioaccessibility of TDCPP, EHDPP, and TEHP in atmospheric fine particulate matter (Zeng et al., 2021). The effect of soil TOC content on the bioaccessibility of OPFRs may be explained by the fact that increasing organic matter content provides more adsorption sites for hydrophobic organic pollutants (Palm et al., 2002), and OPFRs in soils bind to the micropores of organic matter, thereby reducing the transoral availability of organisms.

The physicochemical properties of organic pollutants can affect their bioaccessibility. The logK_{ow} is a crucial parameter for determining the water solubility of organic pollutants. Additionally, as the number of rings in PAHs increases, their solubility in water decreases. The release of PAHs from soils into simulated gastrointestinal juices decreased with increasing logK_{ow} ($R^2 = 0.073$, $p = 0.041$) and molecular weight ($R^2 = 0.081$, $p = 0.032$) of the PAHs (Fig. 3a–b). Similar negative correlations between logK_{ow} values and bioaccessibility have been observed for other organic pollutants, including polychlorinated biphenyls and other chlorinated compounds, in various environmental matrices such as fish and dust (Drouillard and Norstrom, 2000; Kang et al., 2013; Kelly et al., 2004; Moser and McLachlan, 2001; Xing et al., 2008). The R^2 and p values for logK_{ow} in the spiked soil samples ranged from 0.307 to 0.612 and from 0.001 to 0.032, respectively (Fig. 3c), which are consistent with the findings of Tang et al. (2006), except for the QL9 sample ($R^2 = 0.178$, $p = 0.118$). The oral bioaccessibility of individual PAHs initially decreased and then increased with increasing logK_{ow} (Fig. 3d-g). This trend becomes more evident with increasing soil TOC content. In other words, as the TOC

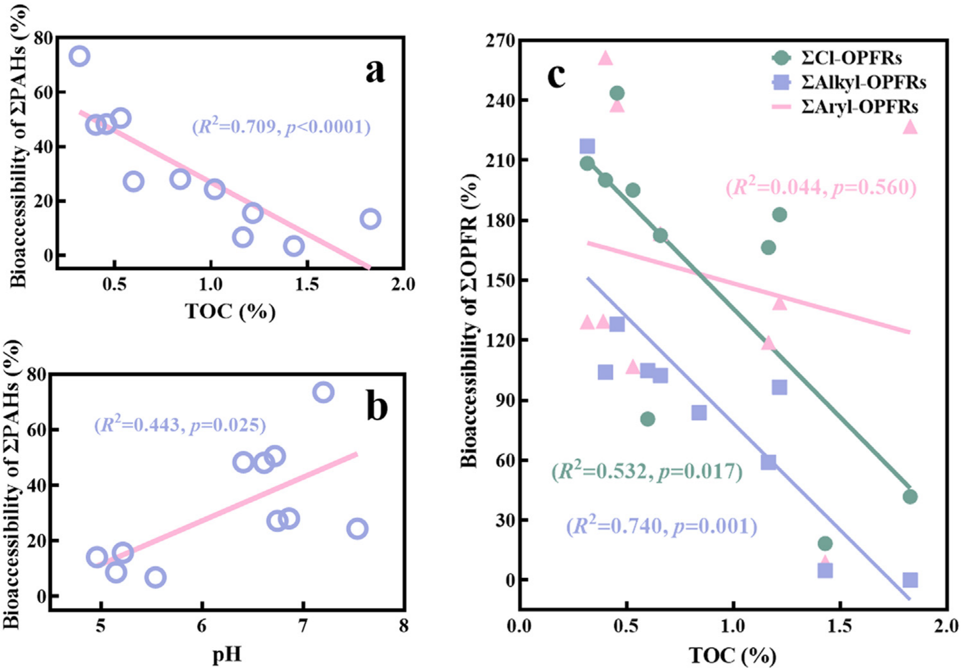

Fig. 2 – Correlation analysis between (a) the bioaccessibility of total polycyclic aromatic hydrocarbons (PAHs) and the TOC content of soils; (b) the bioaccessibility of total PAHs and the soil pH; and (c) the bioaccessibility of Cl-OPFRs, alkyl-OPFRs, and aryl-OPFRs, and the TOC content of soils.

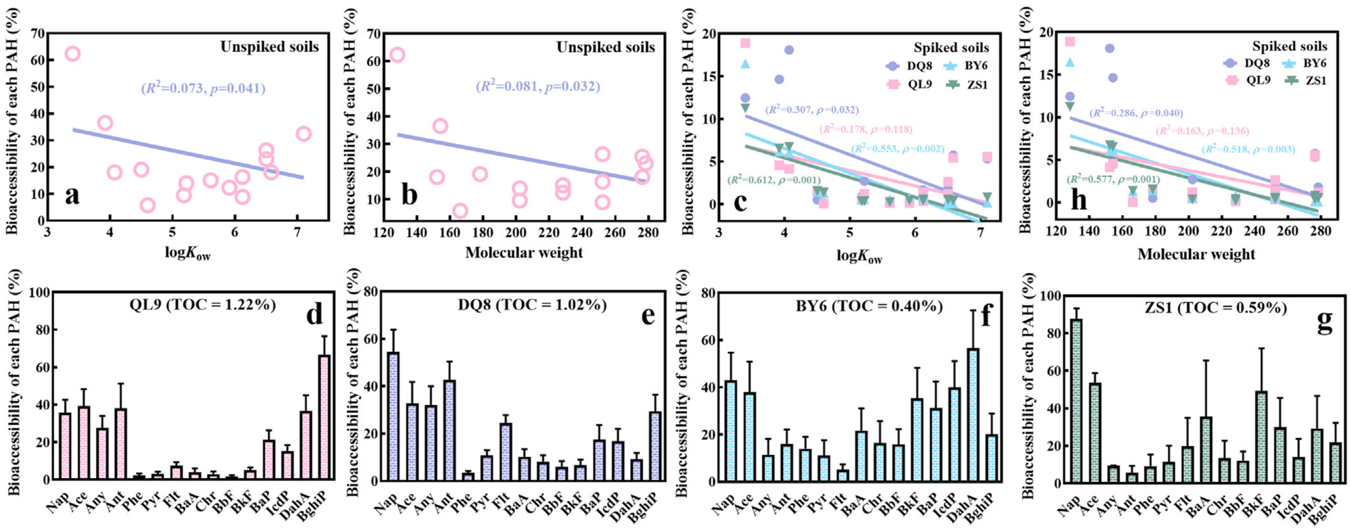

Fig. 3 – Correlation analysis between the bioaccessibility of each PAH and (a) logK_{ow}, (b) molecular weight in unspiked soil samples, and the bioaccessibility of each PAH and (c) logK_{ow}, (h) molecular weight in spiked soil samples. Bioaccessibility of each PAH in soils from (d) antimony mining (QL9), (e) petrochemical (DQ8), (f) copper-zinc smelting (BY6), and (g) ink factory (ZS1).

content increased, the bioaccessibility of Phe, Pyr, Flt, BaA, Chr, BbF, and BkF decreased. The low R^2 and high p value for the QL9 sample (TOC = 1.22%) may be attributed to this cause. In a previous study, both negative and positive correlations were identified between the TOC content and oral bioaccessibility of PAHs, categorized by logK_{ow} values as < 6.0 and > 6.0, respectively. The high TOC content was elucidated by the authors as a driver for increased solubility of the PAHs (logK_{ow} > 6.0) within bile extracts (Kang et al., 2013; Tang et al., 2006). The R^2 and p values for molecular weight in the spiked soil samples ranged from 0.163 to 0.577 and from 0.001 to 0.136, respectively (Fig. 3h). These findings demonstrate the consistency between the correlation observed in the spiked samples and the unspiked samples.

For PCHs, their oral bioaccessibility in soils exhibited a negative correlation with logK_{ow} (R^2 = 0.367, p = 0.002) and molec-

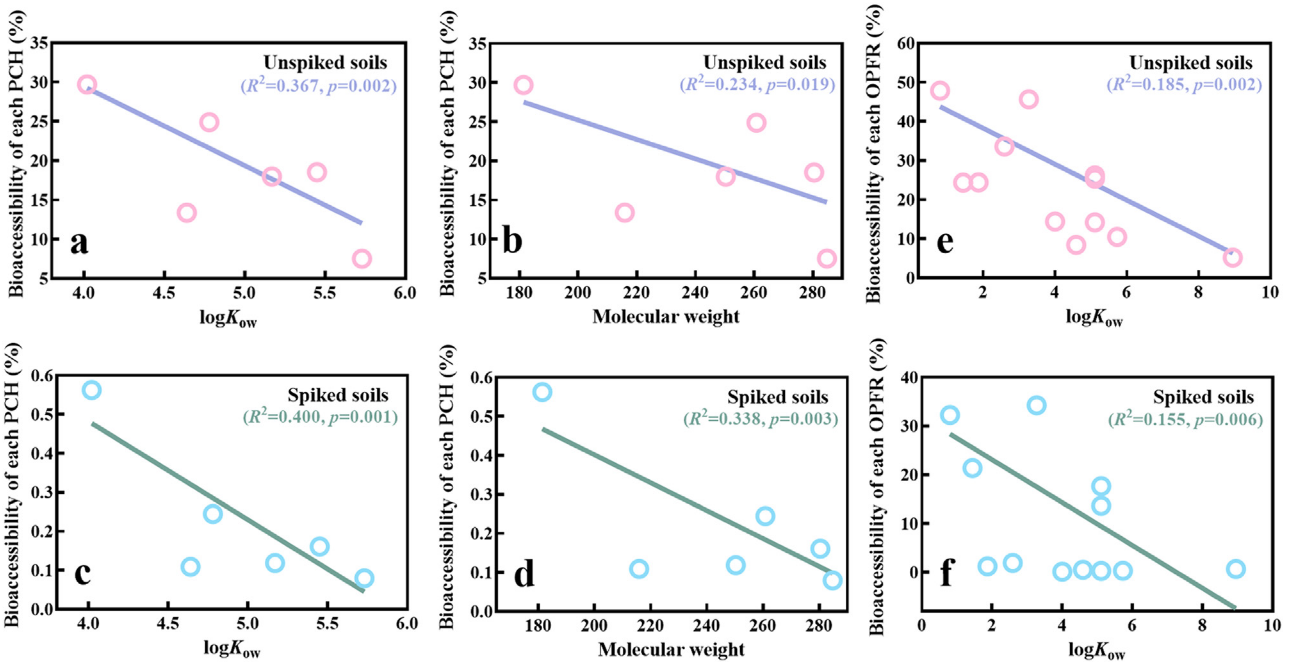

Fig. 4 – Correlation analysis between the bioaccessibility of each polychlorinated hydrocarbon (PCH) and (a) logK_{ow}, (b) molecular weight in unspiked soil samples; the bioaccessibility of each PCH and (c) logK_{ow}, (d) molecular weight in spiked soil samples; and the bioaccessibility of each organophosphate flame retardant (OPFR) and logK_{ow} in (e) unspiked and (f) spiked soil samples.

ular weight ($R^2 = 0.234$, $p = 0.019$) (Fig. 4a–b). A more pronounced relationship was observed in the spiked soils (logK_{ow}: $R^2 = 0.400$, $p = 0.001$; molecular weight: $R^2 = 0.338$, $p = 0.003$) (Fig. 4c–d), which is in line with the findings of a negative correlation between oral bioaccessibility and K_{ow} for organochlorine pesticides in food (Wang et al., 2021). Furthermore, the desorption of OPFRs from unspiked ($R^2 = 0.185$, $p = 0.002$) and spiked soils ($R^2 = 0.155$, $p = 0.006$) into a simulated human gastrointestinal environment decreased as the logK_{ow} of OPFRs increased (Fig. 4e–f). A similar relationship was observed in a previously published report for each individual OPFR, including TCEP, TCPP, and TDCPP, in dust (Quintana et al., 2017). Although both correlations were significant, the correlation observed in spiked soils was stronger than in unspiked soils. Our results using unspiked samples validate the reliability of the results obtained from spiked samples, as factors influencing the bioaccessibility of organic pollutants in soils are commonly determined using spiked samples (Juhasz et al., 2016; Umeh et al., 2019; Zhang et al., 2015). When incorporating bioaccessibility into risk assessment, it is advisable to derive bioaccessibility values from in vitro studies utilizing unspiked samples.

2.3. *Risk assessment of PAHs, PCHs, and OPFRs in contaminated soils*

Residues of organic pollutants in soils can potentially pose risks to humans. Accurate risk assessment of PAHs in terms of toxic equivalent quotient (*TEQ*) with respect to BaP (TEQ_{BaP}) can be conducted. The total *TEQ* levels for all 15 PAHs ($\Sigma_{15}TEQ_{BaP}$) ranged between 3.85–74.4, 1.32–31.1, 0.47–112, and 21.9–159, while those for 7 carcinogenic PAHs ($\Sigma_{7\text{-car}}TEQ_{BaP}$) varied between 3.80–72.9, 1.28–30.6, 0.40–111, and 21.7–158 ng *TEQ*/g in BY, ZS, DQ, and QL soils, respectively (Appendix A Table S10). The ratio of $\Sigma_{7\text{-car}}TEQ_{BaP}$ to $\Sigma_{15}TEQ_{BaP}$ in sampling sites of copper-zinc smelting, ink factory, petrochemical, and antimony mining was 98.1%–98.8%, 95.4%–99.2%, 57.2%–99.8%, and 99.2%–99.7%, respectively. These findings suggest that seven types of PAHs with potential human carcinogenicity play a vital role in determining the carcinogenic effect in the four contaminated areas. Ten PAHs are regulated by a soil protection law issued by the Dutch Ministry of Housing, Spatial Planning, and the Environment (Wu et al., 2019). In BY, DQ, and QL soils, there were one, six, and six sampling sites, respectively, with $\Sigma_{10\text{-Dutch}}TEQ_{BaP}$ values exceeding the Dutch soil intervention value ($\Sigma_{10\text{-Dutch}}TEQ_{BaP}$) of 33 µg/kg (Appendix A Table S11). This result implies potential adverse effects on individuals living or working near these 13 PAH-contaminated soils.

The organic pollutant content in soils does not accurately reflect the level of contamination that people ingest orally (Forsberg et al., 2021). The degree of oral bioaccessibility, determined through a batch in vitro experiment using actual soils without spiking, can be rapidly and accurately used to correct risk assessment. After correction by oral bioaccessibility, the $\Sigma_{10\text{-Dutch}}TEQ_{BaP}$ values in the four contaminated sites were lower than the Dutch soil standard value (Fig. 5a). Potential risks become negligible risks to human health when considering the degree of oral bioaccessibility. To determine the age-specific effects of PAH exposure in humans, an assessment of total incremental lifetime cancer risk (*ILCR*) through three exposure pathways was conducted. The *ILCR* values for

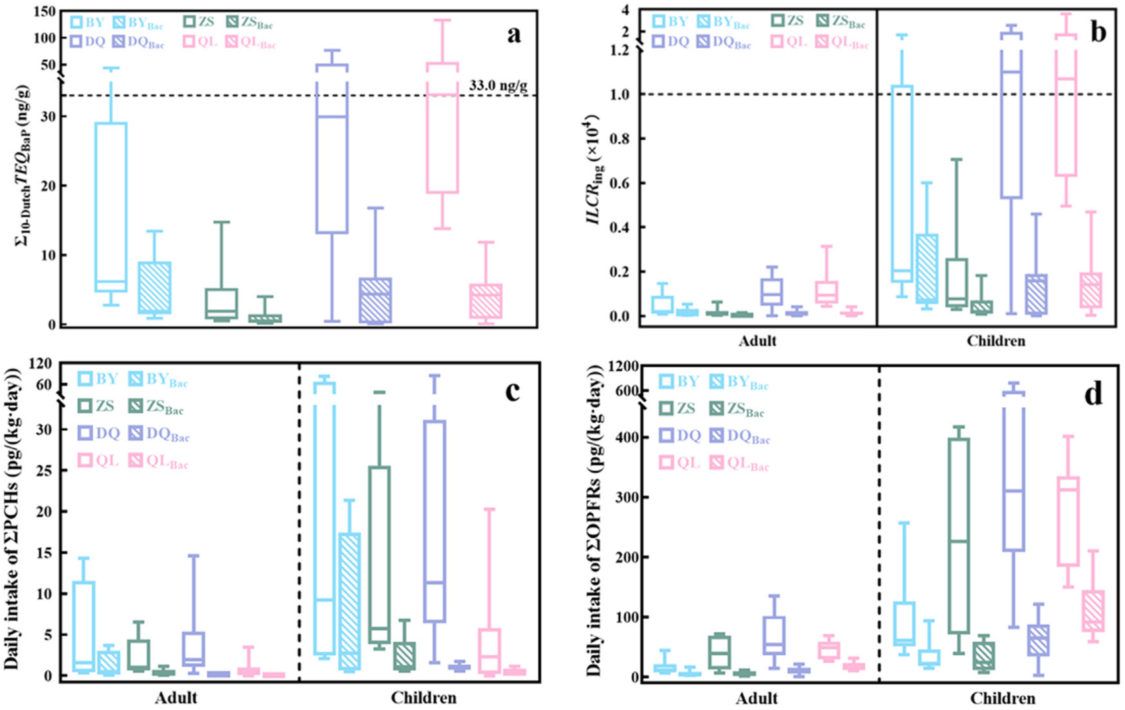

Fig. 5 – (a) Levels of toxic equivalent quotient with respect to BaP (TEQ_{BaP}) for ten PAHs associated with a soil protection law issued by the Dutch Ministry. The Dashed line represents the Dutch soil intervention value ($\Sigma_{10\text{-Dutch}}TEQ_{BaP}$) of 33 µg/kg; (b) Values of incremental lifetime cancer risk (*ILCR*) associated with oral exposure to PAHs in adults and children, (c) Daily intake of total PCHs; and (d) Daily intake of total OPFRs in adults and children at sampling sites of copper-zinc smelting (BY), antimony mining (QL), petrochemical (DQ), and ink factory (ZS) before and after oral bioaccessibility correction.

ingestion, inhalation, and dermal pathways were found to be in the order of 10^{-4}–10^{-8}, 10^{-8}–10^{-11}, and 10^{-4}–10^{-6}, respectively (Appendix A Table S12). The findings of a previous study revealed that the *ILCR* associated with PAHs surpassed the threshold for high potential risk in adults and children exposed to soils within industrial zones in two different cities in India (Sankar et al., 2023). The *ILCR* values for children were higher than those for adults, and the decrease in *ILCR* values for children after adjusting for bioaccessibility was larger than that for adults (Appendix A Table S13). Regarding children's health, the number of sampling sites in BY, ZS, and DQ with potential risks decreased from four to one, from four to one, and from four to three, respectively, when taking oral bioaccessibility into account. Potential high risks of PAHs were found in one, six, and six soils from BY, DQ and QL sampling sites. After oral bioaccessibility correction ($ILCR_{Bac}$), one BY, five DQ, and three QL soils still posed potential risks, while the risks in the remaining soils became negligible (Fig. 5b). In addition to children's health, the adult *ILCR* values showed potential risks in one, six, and six soil samples from BY, DQ, and QL areas, respectively. However, the potential risks in these sites reduced to negligible after considering oral bioaccessibility (Fig. 5b). Similar changes in PAH-related risks were observed in particulate matter with aerodynamic diameters less than 10 µm (PM_{10}) before and after oral bioaccessibility adjustment (Sadikovic and Rodenhiser, 2006). Using total concentrations rather than bioaccessible concentrations may have led to an overestimation of cancer risk.

Daily intakes of soil PCHs and OPFRs were measured for adults and children. Using bioaccessible concentrations instead of total concentrations resulted in a significant reduction in daily intakes (Fig. 5c–d). Based on available reference dose data, the hazard quotients (*HQ*s) of two PCHs and five OPFRs were calculated for risk assessment. The results indicated that the *HQ* values for PCHs and OPFRs in soils were all below one ($HQ < 1$) (Appendix A Table S14), indicating that the exposure scenarios presented in this study are unlikely to cause serious health concerns based on our current understanding of toxic effects. The effect of oral bioaccessibility correction will be more pronounced for sites with moderate or severe levels of pollution, resulting in a decrease in the cost of land restoration after correction. In other words, oral bioaccessibility must be taken into account when assessing the risk that organic pollutants in contaminated soils pose to human health, particularly at sites with high contamination levels.

A limitation inherent in this study pertains to the absence of bioavailability data for the target pollutants in the soil samples. In contrast to bioaccessibility, bioavailability has the potential to more accurately reflect the circumstances surrounding the transfer of pollutants from soils into the human circulatory system. Nonetheless, bioaccessibility tests offer a convenient and cost-effective means for processing a substantial number of samples. It is imperative to elucidate the relationship between the bioaccessibility and bioavailability of PAHs across diverse soil properties. This elucidation is crucial for deriving bioavailability insights by means of analyzing bioaccessibility data.

3. Conclusions

In this study, we investigated contamination profiles and human health risks associated with three types of hydrophobic organic pollutants in soils from four contaminated sites in China. We observed higher concentrations of PAH concentrations in BY, QL, and DQ compared to ZS. The primary source of PAH pollution in the studied soils was combustion (e.g., petroleum, biomass, and coal). PCHs and OPFRs were also detected, but at low concentrations than previously reported. Nap, TCB, and TDCPP exhibited the highest oral bioaccessibility capacities among PCHs, OPFRs, and PAHs, respectively. We found a significant negative correlation between the total oral bioaccessibility of PAHs, Cl-OPFRs, and alkyl-OPFRs in soils, and the TOC content. Additionally, there was a significant positive correlation between soil pH and the total oral bioaccessibility of PAHs. The oral bioaccessibility of PAHs, PCHs, and OPFRs decreased significantly as the pollutant logK_{ow} increased, indicating its importance as a variable. Moreover, the oral bioaccessibility of PAHs and PCHs exhibited an inverse correlation with their molecular weight. To enhance the accuracy of our findings, we considered both spiked and unspiked samples in establishing these relationships. Considering oral bioaccessibility, fewer soils were found to pose potential risks to children, even though some contaminated soils contained high levels of PAHs. Our results underscore the significance of assessing oral bioaccessibility when evaluating the health risk posed by hydrophobic organic pollutants in contaminated soils. Incorporating oral bioaccessibility into risk assessment can greatly aid in the development of local soil environmental criteria.

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

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2023.12.003.

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