Abiotic factors controlling bioavailability and bioaccessibility of polycyclic aromatic hydrocarbons in soil: putting together a bigger picture

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Abstract

The bioavailability and bioaccessibility of polycyclic aromatic hydrocarbons (PAHs) in soil underpin the risk assessment of contaminated land with these contaminants. Despite a significant volume of research conducted in the past few decades, comprehensive understanding of the factors controlling the behaviour of soil PAHs and a set of descriptive soil parameters to explain variations in PAH bioavailability and bioaccessibility are still lacking. This review focuses on the role of source materials on bioavailability and bioaccessibility of soil PAHs, which is often overlooked, along with other abiotic factors including contaminant concentration and mixture, soil composition and properties, as well as environmental factors. It also takes into consideration the implications of different types of risk assessment (ecological and human health) on bioavailability and bioaccessibility of PAHs in soil. We recommend that future research should (1) account for the effects of source materials on bioavailability and bioaccessibility of soil PAHs; (2) adopt non-disruptive methods to analyse soil components controlling PAH sequestration; (3) integrate both natural organic matter (NOM) and xenobiotic organic matter (XOM) in evaluation of the influences of soil organic matter (SOM) on the behaviour of PAHs; and (4) consider the dissimilar desorption scenarios in ecological risk assessment and human health risk assessment while assessing PAH bioavailability and bioaccessibility.

Keywords — PAHs, source material, bioavailability, bioaccessibility, risk assessment, soil organic matter

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrophobic organic contaminants (HOCs) that are ubiquitous in soils, persistent and impact on human and environmental health (Sims and Overcash, 1983; Mersch-Sundermann *et al.*, 1992; Juhasz and Naidu, 2000; Semple *et al.*, 2003; Duan *et al.*, 2015b). They can be released to soils from a range of anthropogenic activities such as combustion of fossil fuels and biomass, coking, oil refining, wood preservation, and manufactured gas production (Ruby *et al.*, 2016). Due to the widespread occurrences of both point and diffusive sources (Nam *et al.*, 2008; Nam *et al.*, 2009), large quantities of soils are contaminated by PAHs.

The remediation of PAH-contaminated land starts with robust and quantitative risk assessments. Risk assessment nowadays has moved towards a bioavailability-based practice to account for the sequestration of organic contaminants in soils over time (i.e. ageing) which reduces their bioavailability and associated risks (Alexander, 2000; Semple *et al.*, 2007; Duan *et al.*, 2014; Duan *et al.*, 2015b; Naidu *et al.*, 2015). It is widely accepted that bioavailability and bioaccessibility of organic contaminants are determined by their sorption and desorption in soils which are controlled by abiotic factors including soil characteristics, physio-chemical properties of the contaminants, as well as environmental factors (Fig. 1) (Nam *et al.*, 1998; Chung and Alexander, 2002; Ehlers and Loibner, 2006; Ruby *et al.*, 2016). With increasing number of aromatic rings, PAHs demonstrate increasing hydrophobicity and lipophilicity. Toxicity of different PAH congeners also varies. In a majority of studies, representative PAHs such as phenanthrene, pyrene, and benzo(a)pyrene are targeted (Table 2, 3) due to their abundance in PAH-contaminated soils or carcinogenicity. Behaviour or levels of PAHs could also be reported as a total of 16 US EPA listed PAHs or carcinogenic PAHs (Table 2, 3) Unlike organic contaminants such as pesticides and polychlorinated

biphenyls (PCBs), which are intentionally produced and applied in the form of 'pure' chemicals, PAHs are generated unintentionally and are released to soil in a range of source materials (Duan *et al.*, 2015b; Ruby *et al.*, 2016). This results in significant challenges to the application of existing knowledge of bioavailability and bioaccessibility to PAH-contaminated soils, as source materials could significantly influence the behaviour of PAHs (Fig. 1) (Roberts *et al.*, 2016; Ruby *et al.*, 2016; Xia *et al.*, 2016).

To achieve reliable risk assessment of contaminated land with PAHs, the effects of source materials on their bioavailability and bioaccessibility must be accounted for (Fig. 1). Therefore, this review has a particular focus on the effects of PAH source materials, along with the influences of other abiotic factors, on bioavailability and bioaccessibility of soil PAHs. It aims to: (1) provide a summary of the interactions between PAHs and different types of source materials and (2) the influences of PAH concentration as well as co-contaminants present in these materials on PAH behaviour; (3) evaluate current knowledge of the effects of soil composition/properties on PAH bioavailability and bioaccessibility; and (4) consider the implications of different types of risk assessment (ecological and human health) on current knowledge of factors controlling bioavailability and bioaccessibility. Based on this, the gaps in current knowledge are identified and the future direction of research is suggested. However, this article does not serve the purpose of a literature review that describes chemistry and processes of PAH-soil interactions in details, as such knowledge has been well documented in published papers. Instead, we emphasise on the discussion of aspects that are not well understood, such as effects of PAH source materials, and the evaluation of existing knowledge, such as the methodologies used to assess effects of soil composition and properties. Those readers interested in a review of chemistry of

89 PAH-soil interactions are directed to (Luthy *et al.*, 1997; Reid *et al.*, 2000; Semple *et al.*, 2003;
90 Cornelissen *et al.*, 2005; Naidu *et al.*, 2008a; Wilson and Naidu, 2008; Duan *et al.*, 2015b).
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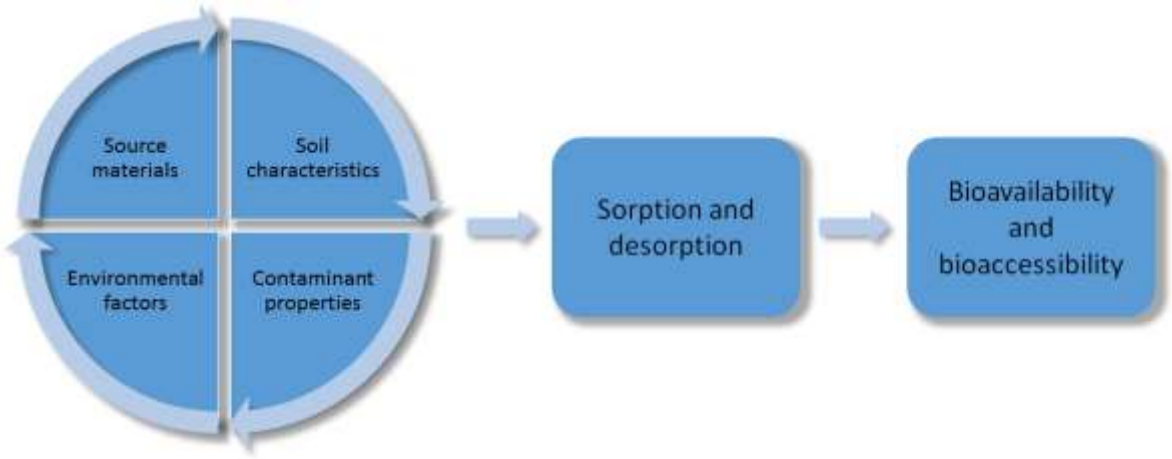


92
93 Fig. 1. Abiotic factors controlling sorption and desorption of organic contaminants in soil and their
94 bioavailability and bioaccessibility. For contaminants like PAHs, the effects of their source materials
95 should be accounted for. All these abiotic factors assert their influences as a result of interactions
96 rather than individually.

97 **2. A brief summary of approaches to identification and analysis of controlling factors**

98 Several variables can be manipulated to identify and evaluate the effects of
99 particular factors on the bioavailability and bioaccessibility of organic contaminants in soil.
100 To study the influences of soil properties, bulk soils with varying characteristics, soil
101 fractions (e.g. humic fractions and particle size fractions), amended or modified soils, as well
102 as model solids, could be selected (Fig. 2). To investigate the effects of concentration,
103 contaminant mixture, and source materials, the selected soils or model solids could be
104 spiked with a single or multiple contaminants delivered in volatile solvents or in certain
105 source materials at a range of concentrations. In addition, samples of field-contaminated
106 soils could also be used (Fig. 2). To investigate the effects of environmental factors, wet-dry
107 and freeze-thaw cycles as well as different ageing time could be applied to ageing processes,

while varying temperatures, pH, and soil-water ratios may be applied during desorption experiments (Fig. 2).

Three streams of methods could be used to analyse contaminated soils or solids: equilibrium assays, kinetics assays, and bioavailability or bioaccessibility assays (Fig. 2). Equilibrium assays usually investigate sorption isotherms of organic contaminants in soils or solids that are often described by the Freundlich model, given by

$$C_S = K_F \times C_W^n \qquad (1)$$

where K_F is the Freundlich constant indicating affinity of the sorbent to solute, and n is a measure of sorption linearity (Schwarzenbach *et al.*, 2005). Kinetic assays investigate the time-course changes in contaminant distribution between soil and aqueous phases during sorption or desorption. Many studies have employed two- or three-compartmental first-order models to describe desorption of HOCs from soil or sediment:

$$S_t/S_0 = F_{rap} \times \exp(-k_{rap} \times t) + F_{slow} \times \exp(-k_{slow} \times t) \qquad (2)$$

$$S_t/S_0 = F_{rap} \times \exp(-k_{rap} \times t) + F_{slow} \times \exp(-k_{slow} \times t) + F_{very\ slow} \times \exp(-k_{very\ slow} \times t) \qquad (3)$$

where S_0 and S_t are the amount of sorbed contaminant at the start of desorption and at time t, while F_{rap}, F_{slow}, $F_{very\ slow}$ are the rapidly, slowly and very slowly desorbing fractions, respectively. Rate constants are designated as k_{rap}, k_{slow}, and $k_{very\ slow}$ in accordance to F_{rap}, F_{slow}, and $F_{very\ slow}$. By comparing or correlating model parameters from equilibrium or kinetic assays (e.g. in equations 1, 2, and 3), or results from chemical or biological assays, the factors controlling PAH bioavailability and bioaccessibility can be analysed (Fig. 2).

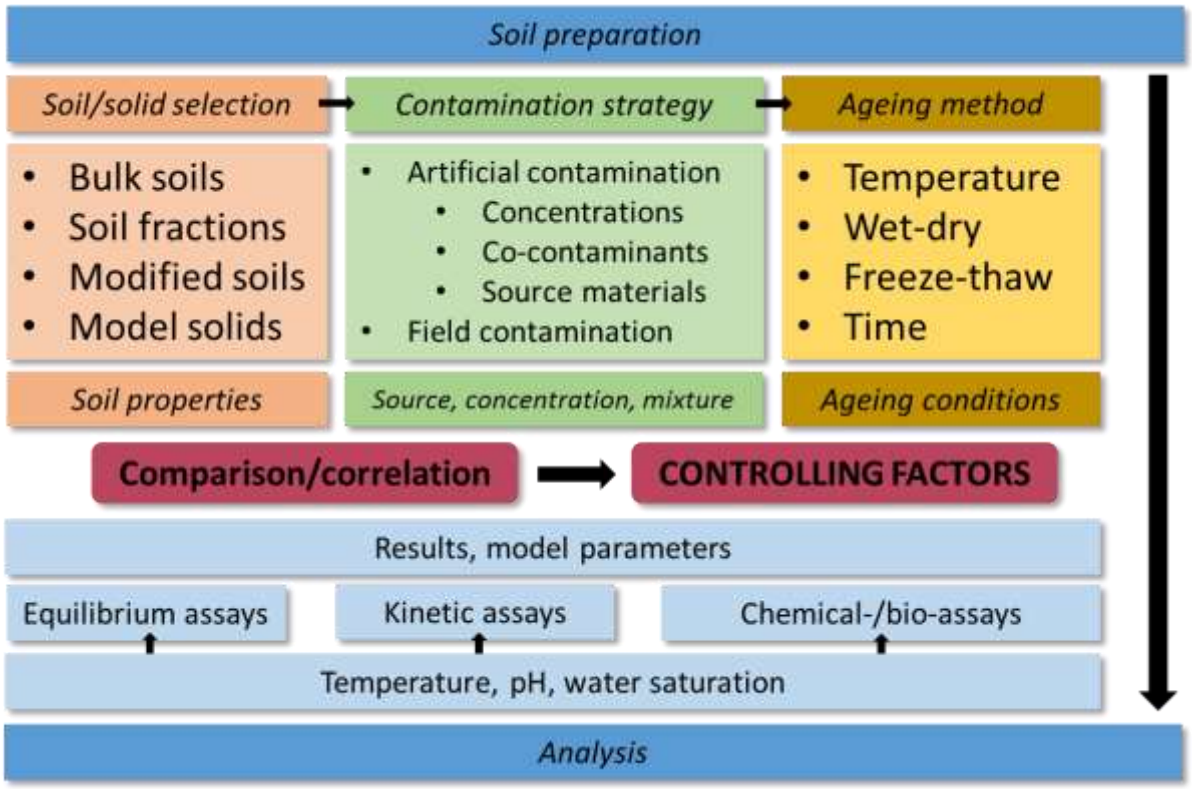


Fig. 2. A schematic of approaches to identification and analysis of the factors controlling sorption-desorption processes and the bioavailability/bioaccessibility of organic contaminants in soils.

3. Effects of PAH source materials

As already noted, the effects of source materials should not be overlooked when considering the factors controlling bioavailability and bioaccessibility of PAHs in soil. Source materials are those carrying PAHs when they are released to the environment, which are products of either pyrogenic or petrogenic processes (Ruby *et al.*, 2016). Most of these materials are either non-aqueous phase liquids (NAPLs), such as tar and oil, or solids, such as soot and char. A semi-solid state also exists as NAPLs age and solidify in soils, often designated as pitch in many studies (Table 1). Source materials contain a range of contaminants both organic and inorganic (Table 1), and are considered both as sorbents (Boyd and Sun, 1990; Luthy *et al.*, 1993; Luthy *et al.*, 1997) and as sources of PAHs (Benhabib *et al.*, 2006; Roberts *et al.*, 2016; Xia *et al.*, 2016). As carbonaceous materials,

these NAPLs, solids, and semi-solids all have high affinity to PAHs. For example, PAHs were found associated predominantly with source materials including coal tar pitch, coke, and coal in manufactured gas plant (MGP) impacted sediments (Khalil *et al.*, 2006) and with NAPL phases in petroleum and creosote contaminated soils (Zemanek *et al.*, 1997). Even at low levels these materials could dominate the sorption of PAHs (Jonker and Koelmans, 2002b; Cornelissen *et al.*, 2005; Khalil *et al.*, 2006), while at 'hot spots' of PAH contamination (e.g. manufactured gas plants) high levels of source NAPLs present as xenobiotic organic matter (XOM) could make up the most of SOM (Bayard *et al.*, 2000).

Solid source materials

Sorption of PAHs to solid source materials was suggested to be exceptionally strong (Cornelissen *et al.*, 2005; Rhodes *et al.*, 2008; Semple *et al.*, 2013). Solid-liquid partition coefficient (K_d) values for soot and charcoal samples range from 10^4 to 10^9, which is up to 1000 times higher than natural organic matter (NOM) in soils (Jonker and Koelmans, 2002b). The Freundlich isotherms of PAH sorption to soot and charcoal also demonstrated high sorptive capacity (Log K_F = 5.5 – 5.6) (Bucheli and Gustafsson, 2000; Karapanagioti *et al.*, 2000; Kleineidam *et al.*, 2002) and non-linearity ($n < 1$) (Cornelissen and Gustafsson, 2005). This indicates a site-specific adsorption mechanism involved in PAH association with these solids. After being produced in incomplete combustion, PAHs could strongly adsorb to surfaces or micropores of these source materials (Xing *et al.*, 1996; Luthy *et al.*, 1997; Xing and Pignatello, 1997; Ghosh *et al.*, 2000; Jonker and Koelmans, 2002a). The forces involved in such strong sorption include dipole-dipole interactions, π-π interactions, hydrogen bonding, and steric hindrance (Zhu *et al.*, 2004). With the strong sorption, the release of PAHs from solid source materials is highly inhibited, leading to significantly reduced bioavailability (Rust *et al.*, 2004; Thorsen *et al.*, 2004; Jonker *et al.*, 2005). However, when

adsorption sites on these materials are saturated, the release of PAHs can be enhanced (Hong *et al.*, 2003; Cornelissen and Gustafsson, 2004; Cornelissen *et al.*, 2005). Consequently, competitive desorption of PAHs by other contaminants and NOM could lead to increased desorption of PAHs and bioavailability/bioaccessibility (Wang *et al.*, 2006; Singh and Kookana, 2009). The sorptive capacity of materials like soot and char is determined by the properties and abundance of sorption sites, which is influenced by the feedstock of these materials and combustion conditions (Semple *et al.*, 2013). It is also noteworthy that interactions between solid source materials of PAHs and soil could lead to decreased sorptive capacity. Artificial ageing induced on biochar, a material which shares similarities with soot and char, led to reduced K_F values of Freundlich isotherms (Hale *et al.*, 2011). Such ageing effects should be examined on solid source materials of PAHs as after ageing the release of PAHs could be enhanced.

179 Table 1. PAH source materials: type, production, and compositions.

Material type	PAH source material	Process/activity [a]	Composition	Reference
NAPL	coal tar, oil tar	MGP[b], coking, aluminium production, asphalt sealing	PAHs, BTEX[c], TPHs[d], substituted- and heterocyclic-PAHs, heavy metals, cyanides	(USEPA, 1988; Zimmerman, 1997; MacLeod *et al.*, 2001; ATSDR, 2002; Brown *et al.*, 2006; Roberts *et al.*, 2016)
	creosote oil	wood preservation, foundry	PAHs, substituted-PAHs, phenols, biphenyls, carbazole, acridine	
	fuel oil, crude oil, diesel	oil refinery, foundry	TPHs, PAHs	
semi-solid	pitch	MGP, aluminium production, foundry, skeet shooting	PAHs, BTEX, TPHs, substituted- and heterocyclic-PAHs, heavy metals, cyanides	
solid	coal	MGP, coking	PAHs, dioxins and furans, Ni, Zn, Cu, Co, Cr	(Wornat *et al.*, 1987; Mastral and Callen, 2000; Hajaligol *et al.*, 2001; Jonker and Koelmans, 2002b, a; Koppolu *et al.*, 2003; Freddo *et al.*, 2012; Semple *et al.*, 2013)
	char	MGP, landfill, biomass combustion		
	soot	MGP, coking, foundry, oil refinery, landfill, biomass and fuel combustion		
	coke	Coking		

180 [a] Adapted from (Ruby *et al.*, 2016); [b] MGP = manufactured gas plant; [c] BTEX = benzene, toluene, ethylbenzene, xylene; [d] TPHs = total petroleum

Non-aqueous phase liquids (NAPLs) and semi-solid source materials

NAPLs and semi-solids also demonstrate high affinity for PAH. Partition coefficient (K_d) values of PAHs in coal tar pitch ranged from 10^4 up to 10^8 (Khalil *et al.*, 2006; Ghosh and Hawthorne, 2010; Xia *et al.*, 2016), while K_d values of PAHs in coal tar could be 6 times higher than those in NOM (Bayard *et al.*, 2000). Fuel oil-water partition coefficients for PAHs were reported to be 10^5 to 10^9, which was even higher than soot (Jonker *et al.*, 2003; Jonker and Barendregt, 2006; Xia *et al.*, 2016). Such large sorptive capacity often leads to slow release kinetics of PAHs from these NAPLs and semi-solids (Yeom *et al.*, 1996; Williamson *et al.*, 1998; Stroo *et al.*, 2000; Eberhardt and Grathwohl, 2002; Benhabib *et al.*, 2006). However, the bioavailability of PAHs in these materials could still be high. The benzo[a]pyrene (BaP) oral bioavailability in soils contaminated with fuel oil was found to be higher than soil spiked with pure BaP (Roberts *et al.*, 2016), although the soil organic carbon-water partitioning coefficient (K_{OC}) for BaP in fuel oil-amended soil was higher than the original soil (Xia *et al.*, 2016). PAHs associated with coal tar pitch were also found to be more bioavailable than those sorbed to charcoal (Ghosh *et al.*, 2003). Clearly, the association of PAHs with source materials in the forms of NAPLs and semi-solids may not be as strong and irreversible as that with solid source materials.

Interaction between NAPLs/semi-solids and PAHs has been suggested to be a partitioning process (Luthy *et al.*, 1997). In general, three steps are involved in the release process: diffusion within the source material, dissolution at the material-water interfaces, and diffusion to the bulk aqueous phase (Lee *et al.*, 1998). In some studies PAH source materials such as coal tar and coal tar pitch were considered as ideal solutions and the dissolution of PAHs from these source materials is governed by Raoult's law, which assumes the equilibrium concentration of a constituent chemical is a function of its water solubility

and mole fraction in the source material (Ramaswami and Luthy, 1997). In this case, diffusion of PAHs into aqueous phase is the rate-limiting step. Models incorporating Raoult's law have provided good prediction of PAH release from coal tar and coal tar pitch to the aqueous phase (Lee *et al.*, 1992; Eberhardt and Grathwohl, 2002; Khalil *et al.*, 2006).

Other studies demonstrated non-ideal dissolution characteristics of PAHs from coal tar in terms of changing surface characteristics and internal diffusion of solutes. Accelerated naphthalene biodegradation was observed in coal tar dispersed in porous silica particles (~250 µm diameter) compared to bulk coal tar due to increased surface area (Ghoshal *et al.*, 1996). Film formation at coal tar-water interfaces after ageing was observed and suggested to be responsible for the significant deviation of PAH dissolution from ideal behaviour (Luthy *et al.*, 1993; Mahjoub *et al.*, 2000). In these cases the dissolution of PAHs at the water-NAPL interface is the rate-limiting step. Dissimilar release rates of different PAHs from NAPLs due to their water solubility and diffusivity within NAPLs was suggested to cause compositional changes in NAPLs and affect the subsequent release of remaining PAHs (Lee *et al.*, 1998). It was observed that the release of naphthalene, phenanthrene, and pyrene from NAPLs created depleted zones in viscous NAPLs and resulted in longer diffusion paths in the NAPLs that led to limited release of remaining PAHs (Ortiz *et al.*, 1999). Condensation of high molecular weight PAHs was also observed after abiotic oxidation of coal tar (Hanser *et al.*, 2015). Depletion of PAHs in coal tar-based skeet was reported to lead to an exponential increase in the distribution coefficient of PAHs between water and the source material-amended soil (Xia *et al.*, 2016). The promotion of PAH diffusion in aged coal tar by surfactants was reported to enhance PAH release to soil (Yeom *et al.*, 1996; Adrion *et al.*, 2016). These observations suggested that internal diffusion of PAHs in NAPLs can also be a rate-limiting step.

It is important to point out that tar and pitch as source materials of PAHs are not only comprised of liquid but also solid phase. Quinoline insoluble (QI) particles that strongly influence the properties of these materials were found in many tar and pitch samples showed soot-like morphology in scanning electron microscope (SEM) examination (Khalil *et al.*, 2006). Apparently partitioning is not the only mechanism governing the sorption of PAHs to tar and pitch, as site-specific adsorption can play a role in the presence of soot-like QI materials. This was confirmed by Wehrer et al. (2013) who identified steric hindrance and retarded surface diffusion as the rate-limiting factors in PAH release from aged coal tar using various desorption models (Wehrer *et al.*, 2013). Elucidation of the mechanisms involved in PAH release from NAPLs and semi-solids could be a challenging task given the reports of both ideal and non-ideal behaviour and dual-mode sorption mechanism of PAHs in these materials. Investigations on the time-dependent changes in NAPL properties and corresponding changes in PAH release could be a viable approach. Adopting such an approach could also identify the roles played by internal diffusivity, interface properties, as well as QI materials during PAH desorption. Moreover, the properties of both NAPLs and soil matrices could be significantly changed after NAPLs are released to soil and lead to different behaviours of PAHs than in pure NAPLs or in natural soils (Lee *et al.*, 1998). Further investigations are needed to elucidate how the entrapment of NAPLs in soil matrices affects the ageing of NAPLs and the release of PAHs.

In many circumstances source materials in the forms of NAPLs, semi-solids, and solids are all present in PAH-contaminated soils (Khalil *et al.*, 2006) and have implications for bioavailability and bioaccessibility of PAHs (Ghosh *et al.*, 2003; Roberts *et al.*, 2016; Xia *et al.*, 2016). The importance of non-specific partitioning and site-specific adsorption mechanisms

under such circumstances was proposed to be determined by their relative abundance (Hong *et al.*, 2003; Hong and Luthy, 2007).

4. Effects of PAH concentrations and co-contaminants

After PAHs are released from source materials to soil, their sorption and desorption, and thus bioavailability and bioaccessibility, can be influenced by their concentrations and the presence of other contaminants that may be released from source materials.

If large quantities of PAHs are released to soil, the sorption and desorption processes will take place at higher rates due to increased diffusivity in soil caused by steeper concentration gradients (Huang and Weber, 1998; Braida *et al.*, 2001; Braida *et al.*, 2002; Li *et al.*, 2013) (Table 2). Importantly, high concentrations of PAHs may induce 'conditioning effects' on soil matrices (Braida *et al.*, 2002). During sorption large quantities of incoming PAH molecules forced the sorbent matrix to soften and swell, leading to increased pore volumes or pore collapse that traps more organic molecules (Lu and Pignatello, 2002; Braida *et al.*, 2003). Such conditioning effects were demonstrated both in macroscale batch sorption assays and at molecular level using ^{1}H wide line and two-dimensional wide line separation (2D WISE) nuclear magnetic resonance (NMR) (Lu and Pignatello, 2002; Braida *et al.*, 2003; Sander and Pignatello, 2007; Cao *et al.*, 2016).

In contaminated sites PAHs co-exist with many other contaminants, both organic and inorganic (Sandrin and Maier, 2003; Lin *et al.*, 2008). Organic co-contaminants may displace PAHs from limited adsorption sites and lead to increased PAH desorption and bioavailability/bioaccessibility (White *et al.*, 1999a; White *et al.*, 1999b; White and Pignatello, 1999; van den Heuvel and van Noort, 2003; Stroud *et al.*, 2009; Wang *et al.*, 2014) (Table 2). Co-existing inorganic contaminants were found to enhance PAH sorption in soils as K_{OC} values for PAHs increased by 2% to more than 100% when different heavy metals

276 were present (Saison *et al.*, 2004; Gao *et al.*, 2006; Luo *et al.*, 2010; Zhang *et al.*, 2010;
277 Zhang *et al.*, 2011; Liang *et al.*, 2016) (Table 2). Such enhancement of sorption was proposed
278 to be caused by (a) reduced dissolved organic matter (DOM), (b) changed chemical
279 composition and conformation of SOM in the presence of heavy metals (Gao *et al.*, 2006;
280 Luo *et al.*, 2010), and (c) the cation-π binding sites provided by heavy metals adsorbed to
281 SOM surfaces (Zhang *et al.*, 2010; Liang *et al.*, 2016). However, the enhancement of PAH
282 sorption did not necessarily reduce the extractability of PAHs (Saison *et al.*, 2004) and it was
283 reported to be attenuated after ageing (Luo *et al.*, 2010).

284 Table 2. Selected research on the influences of PAH concentration and contaminant mixture on sorption, desorption, bioavailability and bioaccessibility of PAHs.

PAH profiles	Reference	Analysis methods	Soil types	Target PAH(s)	Treatment	Results	Comments/mechanisms
concentration	(Huang and Weber, 1998)	sorption equilibrium	13 [a]	PHE	5 μg/l	K_{OC}(t): 3.9 - 65.6 l/g-OC in soils and sediments, 177 - 5094 l/g-OC in shales and kerogens; apparent equilibrium in soils and sediments: up to 90 d	accelerated apparent diffusion at higher concentrations
					500 μg/l	K_{OC}(t): 2.8 - 21.0 l/g-OC in soils and sediments, 37 - 455 l/g-OC in shales and kerogens; apparent equilibrium in soils and sediments: a few hours	
	(Braida *et al.*, 2001)	sorption equilibrium	7	PHE	1.21 μg/l; 363 - 998 μg/l	low concentration: 29.9% - 86.0% sorption, apparent equilibrium: 30 - 180 d; high concentration: 11.9% - 74.5% sorption, apparent equilibrium: 17 - 180 d	accelerated apparent diffusion at higher concentrations; artefacts brought by 'shrinking gradient effects'
				PYR	1.52 – 4.3 μg/l; 91.4 – 92.7 μg/l	Low concentration: 49.3% - 89.1% sorption, apparent equilibrium: > 57 - >84 d; high concentration: 29.8% - 73.6% sorption, apparent equilibrium: 35 - 84 d	
	(Braida *et al.*, 2002)	desorption kinetics by Tenax	6	PHE	160 - 980 μg/g-OC	resistant fraction 9 - 38%, diffusion rate: 3.8×10^{-4} - 1.8×10^{-3}	influences from concentration dependent on linearity of sorption; conditioning effects on soil at higher concentrations
					2000 - 25000 μg/g-OC	resistant fraction 1 - 29%, diffusion rate: 4.2×10^{-4} - 4.0×10^{-3}	
	(Wu and Sun, 2010)	sorption equilibrium	2 [b]	PHE	100, 500 μg/l	100 μg/l: $K_{OC} = 8.81 \times 10^3$ - 1.46×10^4 l/kg; 500 μg/l: $K_{OC} = 5.08 \times 10^3$ - 1.02×10^4 l/kg	conditioning effects on soil caused by higher concentrations led to increased irreversible sorption capacity
		successive desorption			1 - 3 mg/l	irreversible sorption capacity: 1 mg/l: 10.07 - 20.48 mg/kg; 2 mg/l: 10.43 - 34.07 mg/kg; 3 mg/l: 11.20 - 36.95 mg/kg	
	(Li *et al.*, 2013)	desorption kinetics by XAD2	1	PHE	20, 100 mg/kg	low: F_{rap} = 28.5%, k_{rap} = 0.00697 h^{-1}; high: F_{rap} = 13.2%, k_{rap} = 1.65 h^{-1}	influences from concentration dependent on properties of PAHs
				PYR	20, 100 mg/kg	low: F_{rap} = 3.2%, k_{rap} = 0.00725 h^{-1}; high: F_{rap} = 9.3%, k_{rap} = 1.30 h^{-1}	
				BaP	10, 50 mg/kg	low: F_{rap} = 8.4%, k_{rap} = 1.61 h^{-1}; high: F_{rap} = 1.9%, k_{rap} = 1.79 h^{-1}	
co-existing contaminants	(White *et al.*, 1999a)	microbial degradation ethanol/ water extraction	3	PHE	20 μg/g ANT, 30 μg/g PYR	ANT: 2.9 and 4.8% increased mineralisation in 2 soils at 259 and 38 d; PYR: 5.2% increased mineralisation in 1 soil at 74 d	dependence of the enhancement from co-existing PAHs on concentration and chemical structure
					50 - 1000 μg ANT, 500 μg PYR	ANT: extractability increased by 2.3% at 50 μg, 12.6% at 1000 μg anthracene in 1 soil at 121 d, by 3.4% and 12.3% at 500 μg in 1 soil at 0 and 192 d; PYR: 13.2% increased extractability in 1 soil at 69 d	
	(White and Pignatello, 1999)	sorption equilibrium	2	PHE	4840 μg/g-OC PYR	Log K_F decreased 0.03 - 0.04 after 2 d of equilibration, increased 0.07 -0.08 after 33 d of equilibration; n increased 0.061 - 0.139 towards 1	existence of other PAHs changed the sorption domain of target PAHs
	(Wang *et al.*, 2014)	microbial degradation sequential extraction	1	BaP [c]	PYR 250 mg/kg	k_{deg} 0.00412 - 0.00662 d^{-1} without PYR, 0.00613 - 0.00762 d^{-1} with PYR	NA
						desorbing BaP increased from 55.4 - 57.7% to 58.1 - 60.0%; non-desorbing Bap decreased from 42.3 - 44.6% to 40.0 - 41.9%	

(Stroud *et al.*, 2009)	microbial degradation HPCD extraction	1	PHE	NAPH, HD [d], PYR 50 mg/kg	increased from 8.7% to 22.1, 41.4, 31.6% with NAPH, HD, and PYR after 75 d of ageing increased from 6.2% to 8.8, 28.3, 14.7% with naphthalene, hexadecane, and pyrene after 75 d of ageing	NA
(van den Heuvel and van Noort, 2003)	desorption kinetics by Tenax	2 [e]	FLA, BbF, BkF, BaP [f]	fresh PHE	F_{slow} increased by 30 - 80% for FLA, 17 - 58% for BbF, 29 - 69% for BkF, 13 - 67% for BaP; $F_{very\ slow}$ decreased by 21 - 27% for fluoranthene, 12 -14% for BbF, 16 - 23% for BkF, 10 - 24% for BaP	NA
(Wang *et al.*, 2005)	sorption equilibrium	4	PYR	PHE	Log K_F decreased by 0.01 - 0.05 with PHE, n increased by 0.19 - 0.55 towards 1	changed sorption domain of target PAHs
(Saison *et al.*, 2004)	sorption equilibrium	3	PHE	Cu, Cd, Pb, Zn	K_F increased from 8.55 in single system to 21.48 in mixture with metals	increased PAH sorption in presence of metals
(Gao *et al.*, 2006)	sorption equilibrium	3	PHE	Pb, Zn, Cu 500 mg/kg amended respectively	K_d and KOC increased by up to 24% in metal-amended soils	presence of metals contributed to adsorption of DOM to SOM and enhanced DOM sorptive capacity
(Luo *et al.*, 2010)	spectral and microscopic observation, sorption equilibrium	2	PHE	Cu, Ni, Pb 1mmol/l amended respectively	increased sorption capacity and non-linearity for phenanthrene when metals were present	changes in compositions and conformations of DOM, condensation of rubbery SOM in presence of metals, attenuation of these changes after ageing
(Liang *et al.*, 2016)	sorption equilibrium, quantum mechanical methods	2	NAPH, PHE, PYR	Cu, Pb, Cr	NAPH: K_F increased by up to 27.5%, n decreased by up to 20.7%; PHE: K_F increased by up to 24.8%, n decreased by up to 24.7%; PYR: K_F increased by up to 107.1%, n decreased by up to 18.2%	sorption increment correlated to electro-negativity and radius of metals, π-cation bonding as an important contributors to enhanced sorption

[a]: 7 USEPA reference soils and sediments, 3 shales, and 3 kerogen samples were used; [b]: 1 soil and 1 sediment were used; [c]: soil used was contaminated with Cd and BaP; [d]: HD = hexadecane; [e]: 2 sediments were used; [f]: residual PAHs in field contaminated samples were targeted. Abbreviations of PAHs: NAPH = naphthalene, PHE = phenanthrene, ANT = anthracene, FLA = fluoranthene, PYR = pyrene, BaP = benzo(a)pyrene, BbF = benzo(b)fluoranthene, BkF = benzo(k) fluoranthene.

5. Effects of soil composition and properties

PAHs released from source materials to soil undergo sequestration in the soil matrix over time and demonstrate reduced bioavailability and bioaccessibility. This process has been extensively studied and is accepted to be controlled by soil composition and properties (Naidu *et al.*, 2008a; Wilson and Naidu, 2008). It is now widely accepted that SOM is the most important soil component that determines PAH sequestration, provided it is above trace level (Xing *et al.*, 1996). Total organic carbon (TOC) has been shown to dominate the bioavailability and bioaccessibility of PAHs to different receptors (Nam *et al.*, 1998; Alexander and Alexander, 2000; Chung and Alexander, 2002; Bogan and Sullivan, 2003; Pu *et al.*, 2004; Tao *et al.*, 2006; Rhodes *et al.*, 2010) (Table 3). Apart from the quantity of SOM, the dual-mode sorption mechanism, which is now widely acknowledged, indicates the quality of SOM is also important (Xing and Pignatello, 1996; Xing *et al.*, 1996; Huang *et al.*, 1997; Xing and Pignatello, 1997). The focus of many researches then became the identification and quantification of the SOM fractions responsible for non-specific partitioning, designated as 'soft', 'labile', or 'amorphous' SOM, and for site-specific adsorption, designated as 'hard', 'recalcitrant', or 'condensed' SOM. Several strategies for differentiation of SOM, including alkaline extraction (humic substances), chemical or thermal oxidation (black carbon), soil particle size fractionation (fine particle associated carbon), and differentiating by its chemical structures, have been adopted in the literature. Direct quantification of the abundance of adsorption sites (pore volume) was also employed in many studies.

Distinguishing SOM by humic substances

Fractionation of SOM based on alkaline extraction is a classical method for both soil and environmental sciences (Lehmann and Kleber, 2015). Based on the solubility in alkaline and acidic solutions, SOM are fractionated into:

1. fulvic acid (FA), which is dissolved at pH 13 and remains dissolved at pH 2
2. humic acid (HA), which is soluble in alkaline solutions and precipitates at pH < 2;
3. humin (HM), which is insoluble at any pH (Kohl and Rice, 1998).

It was found that 20 – 90% of organic contaminants in soil were associated with the humic fraction (Xie *et al.*, 1997; Führ *et al.*, 1998; Burauel and Führ, 2000). PAHs could be primarily associated with FA (Yang *et al.*, 2010), HA (Nieman *et al.*, 1999), or HM (Doick *et al.*, 2005) as observed in different studies. Several studies demonstrated that HA and HM are the sources of non-linear, site-specific, and strong sorption of HOCs in soil (Chiou *et al.*, 2000; Kang and Xing, 2005; Pan *et al.*, 2006; Chen *et al.*, 2007) (Table 3).

Distinguishing SOM by black carbon

The SOM fraction responsible for site-specific adsorption is considered to be inert and in many papers deemed as a subset of black carbon which is a group of strong sorbents for organic compounds (Cornelissen *et al.*, 2005; Luo *et al.*, 2012; Semple *et al.*, 2013). Thus, an approach to distinguishing SOM fractions is through thermal or chemical oxidation that removes the labile SOM (Cornelissen *et al.*, 2005). For example, using multiple linear regression analysis, Luo et al. (2012) found that black carbon content in soils, determined by wet oxidation and thermal oxidation, was the major contributor to decreases in rate constants of slow desorption (k_{slow}) of PAHs (Luo *et al.*, 2012) (Table 3).

Distinguishing SOM by soil particle size

Soil particle size fractions, in particular the clay and silt fractions, have been found to play a significant role in the preservation of SOM and retention of organic contaminants.

335 Aged PAHs in a soil were found to be associated predominantly with fine silt and clay sized
336 particles with the silt fraction possessing the greatest affinity to PAHs (Amellal *et al.*, 2001;
337 Doick *et al.*, 2005; Siciliano *et al.*, 2010; Pernot *et al.*, 2013). The high affinity for PAHs led to
338 reduced bioavailability of these contaminants in these fine particles (Uyttebroek *et al.*, 2006;
339 Siciliano *et al.*, 2010) (Table 3). In a more recent study, Duan et al. (2014) defined fine
340 particle associated carbon (FPAC):

341 $$FPAC = (silt + clay)/TOC \qquad (4)$$

342 The authors demonstrated that FPAC was inversely correlated with oral bioavailability of
343 BaP in a swine model ($r^2 = 0.96$, $p < 0.001$) (Duan *et al.*, 2014) (Table 3).

344 ***Distinguishing SOM by chemical structure***

345 In essence, SOM fractions demonstrate different sorptive capacity for HOCs because of their
346 specific chemical structures. Domination of aliphatic and aromatic structures in humic substances
347 (Xu *et al.*, 2006; Chen *et al.*, 2007), black carbon (Cornelissen *et al.*, 2005; Semple *et al.*, 2013), and
348 SOM in soil fine particles (Kiem *et al.*, 2002; Krauss and Wilcke, 2002) has been observed. Direct
349 correlations were found between the quantities of aromatic/aliphatic structures and the K_{OC} of soils
350 (Xing, 1997; Wang *et al.*, 2007). Aliphaticity has been associated with an increase in the linearity of
351 PAH sorption while aromaticity increases the sorption non-linearity (Xu *et al.*, 2006; Chen *et al.*, 2007;
352 Wen *et al.*, 2007) (Table 3). For nonpolar contaminants like PAHs, the polarity of SOM also plays a
353 role in determining sorption and desorption, and therefore bioavailability and bioaccessibility (Liang
354 *et al.*, 2006; Wang *et al.*, 2007; Wen *et al.*, 2007).

355 ***Direct quantification of adsorption site by pore volume***

356 The declining bioavailability and bioaccessibility of HOCs in soil over time was
357 attributed to the diffusion of contaminants into micro-pores which are inaccessible to
358 receptors and extractants (Alexander, 2000; Jonker and Koelmans, 2002a; Semple *et al.*,
359 2013; Duan *et al.*, 2014; Duan *et al.*, 2015a). This was supported by the inverse relationship

between the volumes of pores with diameters < 6 nm ($PF_{6\,nm}$) and rapid desorption of PAHs (Luo *et al.*, 2012). Recent studies also observed significant negative correlations between bioavailability and bioaccessibility of PAHs and $PF_{6\,nm}$ (Duan *et al.*, 2014; Duan *et al.*, 2015a) (Table 3). The strong association between pore volume and bioavailability of HOC is further confirmed in studies that manipulated soil pore volume by using specific amendments. For example, amendment with porous carbonaceous materials such as biochar and activated carbon was found to significantly reduce PAH bioavailability and bioaccessibility due to the increased pore volumes of the amended soils (Zimmerman *et al.*, 2004; Zimmerman *et al.*, 2005; Yang *et al.*, 2009; Semple *et al.*, 2013; Ogbonnaya *et al.*, 2014).

Evaluation of the effects of soil composition and properties

The alkaline extraction of SOM has been adopted in environmental sicence for a long time but humic substances have been increasingly cirticised as method-defined, pseudo-materials (Lehmann and Kleber, 2015). Importantly, alkaline extraction induces significant change in soils (Doick *et al.*, 2005). It is therefore very questionable whether such soil fractions can account for variations in PAH bioavailability and bioaccessibility. Similar criticisms were also made concerning the use of thermal and chemical oxidation to quantify black carbon. The potential charring of labile SOM during heating and loss of small particulate black carbon during chemcial oxidation could cause both over- and under-estimation (Cornelissen *et al.*, 2005), thus compromising the relevance of the correlation between obtained black carbon fractions and PAH bioavailability/bioaccessibility. Physical fractionation of soil based on particle size was suggested to be more appropriate due to less disturbance being imposed on the soil matrix (Northcott and Jones, 2000; Doick *et al.*, 2005).A couple of studies have provided good correlations between PAH bioavailability/bioaccessibility and FPAC (Duan *et al.*, 2014; Duan *et al.*, 2015a), but the

384 effects of FPAC need to be further verified through empirical experiments and mechanistic
385 studies. Good correlations were also obtained between soil pore volumes ($PF_{6\,nm}$) and PAH
386 bioavailability and bioaccessibility (Luo *et al.*, 2012; Duan *et al.*, 2014). Although an
387 argument was made that pore volume is just a reflection of TOC (Nam *et al.*, 1998), recent
388 research has revealed that aliphatic and aromatic structures are responsible for formation
389 of pore structures in SOM (Han *et al.*, 2014). It is obvious that all the approaches to
390 differentiating SOM fractions are related to chemical structures of SOM. Yet quantification
391 of chemical structures present in soil can be methodologically challenging (Ehlers and
392 Loibner, 2006). Given the limitations of harsh treatments to quantify SOM responsible for
393 site-specific adsorption as outlined above, we suggest these treatments should be
394 abandoned and less-disruptive physical fractionation methods adopted.

395 Two components in contaminated soil should also be taken into account when
396 considering the factors controlling PAH bioavailability and bioaccessibility. Firstly, source
397 materials in PAH-contaminated soils should be identified to avoid confusion between NOM
398 that retains PAHs and XOM materials with high affinity to PAHs but which are actually
399 sources of these compounds. Such a distinction could be achieved through density
400 fractionation of contaminated soil (Khalil *et al.*, 2006). Additionally, the interactions
401 between xenobiotic source materials and natural soil components need to be considered. It
402 was suggested that soil texture and water content play key roles in the retention of NAPLs in
403 the soil matrix as they affect the dispersion of NAPLs on soil particles and their penetration
404 into soil pores (Wehrer *et al.*, 2011). Secondly, the role of soil minerals should not be
405 overlooked. The protection of SOM by mineral phases through occlusion and strong surface
406 association was demonstrated by numerous researchers (Torn *et al.*, 1997; Six *et al.*, 2000;
407 Lützow *et al.*, 2006; Lalonde *et al.*, 2012). In soil fine particles SOM is preferentially

associated with rough surfaces of organo-mineral clusters which exist as patches on mineral phases (Ransom *et al.*, 1997; Chenu and Plante, 2006; Vogel *et al.*, 2014; Xiao *et al.*, 2015). Highly reactive minerals such as allophane and ferrihydrite were suggested to determine the capacity of such SOM preservation (Xiao *et al.*, 2015). On the other hand, only 'mature' SOM is able to form a strong association with soil minerals (Lehmann and Kleber, 2015). This fraction of SOM is considered to be residues of soil biota at more advanced degradation stages and responsible for formation of bound residue of HOCs (Kaestner *et al.*, 2014). Such findings reflect a shift in viewing SOM: it is increasingly considered as a continuum of soil biota residues at different stages of organic carbon turnover, which is a kinetic process, rather than a static integration of labile and recalcitrant SOM (Lehmann and Kleber, 2015). Moreover, possible association between soil mineral surfaces with xenobiotic PAH source materials could also provide protection to these materials against degradation. This should be investigated in future research to integrate PAH source materials in the knowledge system of abiotic factors controlling PAH bioavailability and bioaccessibility.

422 Table 3. Selected literature that identified the effects of soil properties and environmental factors on bioavailability and bioaccessibility of PAHs in soils.

Reference	Target PAH(s)	Contaminant source	Soil type(s)/fractions	Analysis method(s)	Influencing soil property(s) identified	Correlation/comments
(Chung and Alexander, 2002)	phenanthrene	spiked	16	biodegradation & BuOH extraction	OC, particle size, CEC [a]	decrease in biodegradation = 1.123[OC] + 0.131[silt] + 10.35 (r^2 = 0.532, $p < 0.01$) decrease in extractability = -4.431log[OC] – 0.36[clay] + 0.798CEC + 19.94 (r^2 = 0.479, $p < 0.15$)
(Nam *et al.*, 1998)	phenanthrene	spiked	4 soils & 1 sand	biodegradation & BuOH extraction	OC, pore volume, SA [b]	NA [c]
(Alexander and Alexander, 2000)	BaP	spiked	6	microbial genotoxicity & BuOH extraction	SOM when > 0.7%	$r > 0.90$
(Bogan and Sullivan, 2003)	phenanthrene, pyrene	spiked	6	biodegradation	OC	r^2 = 0.41 - 0.90
	coal tar PAHs	spiked coal tar	6	BuOH extraction	OC	NA
(Carmichael *et al.*, 1997)	phenanthrene, chrysene	spiked	2	biodegradation, desorption kinetics	OC	k_{rap} lower in soil with higher OC
(Rhodes *et al.*, 2010)	phenanthrene	spiked	4	biodegradation, desorption kinetics	Total OC	F_{rap}, F_{slow} and $F_{very\ slow}$ affected by TOC
(Pu *et al.*, 2004)	phenanthrene	spiked	4	blood AUC in rats after oral dosing, PBET assay	OC	RBA and bioaccessibility dependent on OC
(Tao *et al.*, 2006)	naphthalene, acenaphthylene, fluorene, phenanthrene	spiked	7	plant root accumulation, sequential extraction	total organic matter (TOM)	accumulation and extractability inversely correlated to TOM
(Duan *et al.*, 2014)	BaP	spiked	8	blood AUC in swine after oral dosing	PF < 6 nm	r^2 = 0.99, $p < 0.01$
					FPAC (slit + clay)/TOC	r^2 = 0.96, $p < 0.01$
(Duan *et al.*, 2015a)	BaP	spiked	4	leaching	PF < 6 nm	r^2 = 0.996, p = 0.002
(Luo *et al.*, 2012)	phenanthrene, pyrene, BaP	spiked	7	desorption kinetics	PF < 6 nm	$k_{rap} = -0.456[PF_{6nm}] - 0.003[TOC] + 0.436$ (r^2 = 0.793, $p < 0.05$)
					hard OC	$k_{slow} = -3.3 \times 10^{-4}$[hard OC] - $4.7 \times 10^{-6}[PF_{6nm}] + 7.1 \times 10^{-5}$ (r^2 = 0.923, $p < 0.05$)
(Doick *et al.*, 2005)	fluoranthene, BaP	spiked	1 soil and 3 humic fractions	sample oxidation and 14C liquid scintillation	humin	NA
			1 soil and 3 size fractions	sample oxidation and 14C liquid scintillation	fine silt and clay	NA
			1 soil and its SOM and mineral phase	sample oxidation and 14C liquid scintillation	mineral phase	57 - 80% residual PAHs after removal of SOM

(Chen *et al.*, 2007)	naphthalene, phenanthrene	spiked	1 soil and its humic acid, humin, and deashed humin	sorption equilibrium	humin	NA
(Pan *et al.*, 2006)	phenanthrene, pyrene	spiked	4 soil with their humic fractions	sorption equilibrium	humin	NA
(Xing, 2001)	naphthalene, phenanthrene	spiked	1 soil at different depths and its humic fractions	sorption equilibrium	aromaticity	sorption nonlinearity increased proportional to aromaticity
(Xing, 1997)	naphthalene	spiked	5	sorption equilibrium	aromaticity	aromaticity correlated with K_d (r^2 = 0.994)
(Ghosh and Keinath, 1994)	naphthalene	spiked	not specified	sorption equilibrium and kinetics	expanding clay	NA
(Hwang and Cutright, 2002)	phenanthrene, pyrene	spiked	1 soil and its SOM and mineral phase	sorption and desorption equilibrium	expanding clay	sorption to minerals was more extensive than to SOM
(Hwang and Cutright, 2003)	pyrene	spiked	3	hexane desorption	expanding clay	total desorption inversely related to amount of expanding clay
(Jones and Tiller, 1999)	phenanthrene	spiked	kaolinite and illite	fluorescence quenching	organo-clay complex	NA
(Bonin and Simpson, 2007)	phenanthrene	spiked	4 soils and their humic fractions	sorption equilibrium	organo-clay complex	NA
(Ahangar *et al.*, 2008)	phenanthrene	spiked	agricultural soils and their SOM	sorption equilibrium	organo-clay complex	correlation with clay content and increasing of K_{OC} after mineral removal (r^2 = 0.43)
(Duan and Naidu, 2013)	phenanthrene	spiked	32	sorption equilibrium	ionic strength and index cation	NA
(Pernot *et al.*, 2013)	16 USEPA PAHs	coking plant contaminated soil	1 soil and its size fractions	Tenax extraction	fine silt	NA
(Amellal *et al.*, 2001)	8 PAHs	spiked	1 soil and its size fractions	chloroform Soxhlet extraction	silt	NA
(Siciliano *et al.*, 2010)	11 PAHs	roadside and residential soils	18	SHIME model	particles size < 45 um	PAHs are 3.7 times higher in fraction with particle size < 45 µm and highly resistant to SHIME extraction

423 [a] CEC = cation exchange capacity; [b] SA = surface area; [c] NA = not applicable

6. Effects of environmental factors

In addition to soil properties, environmental factors such as pH, temperature, as well as moisture content could all affect the bioavailability and bioaccessibility of soil PAHs (Ehlers and Loibner, 2006). These factors assert their influences through changing the properties of SOM and the release of PAHs from soil.

Soil pH may be changed by environmental events like precipitation (McFee *et al.*, 1977) or during desorption facilitated by receptors (Dean and Ma, 2007). Under different pH conditions, SOM existed in different physical forms (coiled or stretched) and exhibited differing sorptive capacity for HOCs, which lead to different bioavailability and bioaccessibility (Murphy *et al.*, 1994; Feng *et al.*, 2005, 2006). This was supported by the observation of greater K_{OC} values of organo-clay complexes for phenanthrene with decreasing pH (Feng *et al.*, 2006), and greater BaP oral bioavailability at higher pH (Duan *et al.*, 2014). Higher pH also promoted desorption of SOM, and thus that of PAHs, as a result of their increased solubility in aqueous phases (Yu *et al.*, 2016).

Variation in temperature during ageing and subsequent desorption of soil PAHs was demonstrated to lead to different bioavailability. K_{OC} values for HOCs in soils are inversely related to temperature (Schwarzenbach *et al.*, 2005). Desorption of PAHs from soil could be enhanced by up to 28 times when the temperature rose from 7 °C to 23 °C (Enell *et al.*, 2005). Temperature variations brought about by freeze-thaw cycles was reported to decrease the stability of soil aggregates and promote the ageing of soil PAHs (Lehrsch *et al.*, 1991; Zhao *et al.*, 2009; Shchegolikhina *et al.*, 2012; Zhao *et al.*, 2013).

The moisture contents of soils change under field conditions and play an important role in determining bioavailability/bioaccessibility of soil PAHs. Bioavailability and extractability of PAHs spiked to moist soil was found to be greater than that spiked to dry

448 soil (Kottler *et al.*, 2001). Phenanthrene bioavailability decreased when wet-dry cycles were
449 applied during short ageing periods (up to 58 d) (White *et al.*, 1997; White *et al.*, 1998) as
450 wet-dry cycles promote the ageing of soil PAHs. It was proposed that acceleration of ageing
451 could be due to structural changes in SOM brought about by swelling of soil pores during
452 wetting and exposure of hydrophobic SOM zones to external surfaces during drying
453 (Schaumann *et al.*, 2005; Wang *et al.*, 2016). Furthermore, the soil moisture content at the
454 moment of contamination also determines whether water or NAPLs would become the
455 predominant wetting fluid of the soil matrix, which affects the ability of NAPLs to penetrate
456 into and remain in soil pores (Wehrer *et al.*, 2011).

457 **7. Risk assessment type: an 'artificial' controlling factor?**

458 In addition to the abiotic factors discussed above, our perspectives on the concepts
459 of bioavailability and bioaccessibility could also influence the results we obtain. In the
460 context of soil contamination, bioavailability is a method-defined concept depending on the
461 receptor or toxicological endpoint being investigated (Kelsey *et al.*, 1997; White *et al.*, 1997;
462 Semple *et al.*, 2004; Semple *et al.*, 2007; Naidu *et al.*, 2008b). It could be included in two
463 types of risk assessment based on receptors: ecological risk assessment (ERA) and human
464 health risk assessment (HHRA).

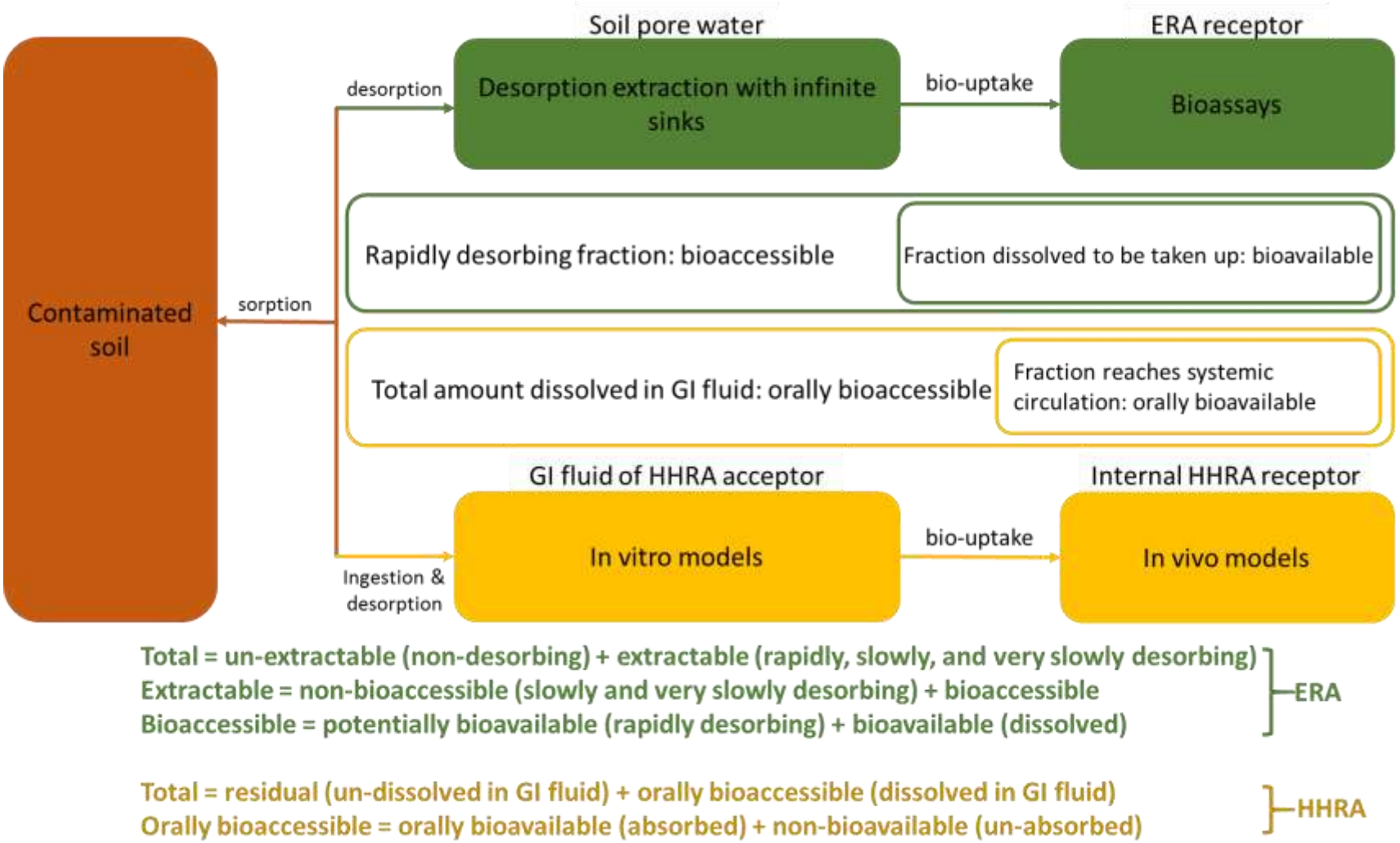
465 The receptors concerned in ERA are generally soil-dwelling organisms such as
466 microorganisms, terrestrial invertebrates and plants. It was proposed that bioavailability is
467 the quantity of a contaminant that is dissolved in the soil aqueous phase to cross the
468 membranes of the receptors, while the bioaccessibility is the total amount of a contaminant
469 that is rapidly desorbing from the soil solid phase to the aqueous phase (Semple *et al.*, 2004;
470 Ortega-Calvo *et al.*, 2015). The bioavailable fraction may be seen as a subset of the
471 bioaccessible fraction (Fig. 3). Bioavailability of soil PAHs to ERA receptors could be

472 measured by toxicity assays on soil organisms, biodegradation assays using PAH-degrading
473 microbes, and accumulation assays using earthworms and plants (MacLeod *et al.*, 2001;
474 Semple *et al.*, 2003; Lanno *et al.*, 2004; Peijnenburg *et al.*, 2012; Duan *et al.*, 2015b).
475 Bioaccessibility can be assessed by chemical methods based on (1) mild organic solvents, (2)
476 desorption reagents with infinite sinks, and (3) chemical reactivity (Semple *et al.*, 2003;
477 Semple *et al.*, 2007; Cui *et al.*, 2013; Cachada *et al.*, 2014), among which infinite sinks are
478 considered better methods (Brand *et al.*, 2009) (Fig. 3).

479 For HHRA incidental ingestion of contaminated soil is considered the most important
480 exposure route (Cave *et al.*, 2010; Ruby and Lowney, 2012). In this case the amount of a soil
481 contaminant dissolved in simulated gastrointestinal (GI) fluid in a given time is defined as
482 the orally bioaccessible fraction, while the amount of a contaminant that enters the
483 systemic circulation from GI lumen is defined as the orally bioavailable fraction (Ruby *et al.*,
484 1999) (Fig.3). Animal surrogates are used to assess oral bioavailability for HHRA. Metabolism
485 related biomarkers such as urinary metabolites, DNA-adducts, and enzyme induction, as
486 well as absorption indicators such as blood and faecal concentrations have been used to
487 estimate PAH oral bioavailability (Duan *et al.*, 2015b; Duan *et al.*, 2016; Ruby *et al.*, 2016)
488 (Fig. 3). *In vitro* models mimicking human digestive systems have also been developed to
489 assess oral bioaccessibility (Lal *et al.*, 2015; Cui *et al.*, 2016; Ruby *et al.*, 2016) (Fig.3).

490 From a risk-based standpoint the role of desorption in determination of
491 bioavailability and bioaccessibility should be emphasised (Ortega-Calvo *et al.*, 2015) as
492 contaminants have to be absorbed by receptors to exert toxic effects, while biological
493 uptake of organic substances mainly takes place in the dissolved phase (Cerniglia, 1992;
494 Vasiluk *et al.*, 2007; EFSA, 2009) (Fig. 3). However, the environments in which PAHs are
495 released from soils can be very different for ERA and HHRA. In ERA scenarios, PAHs desorb

496 from the soil solid phase to soil pore water, while in oral HHRA PAHs are released from soil
497 to GI fluid, which has very different chemical composition, pH, and temperature to soil pore
498 water (Fig. 3). Therefore, the selection of risk assessment scenario (i.e. ERA or HHRA) will
499 have an 'artificial' impact on the bioavailability and bioaccessibility of PAHs finally
500 determined. Among the literatures discussed in this review, there are ample studies
501 depicting the mechanisms involved in sorption and desorption of soil HOCs and factors that
502 influence these processes based on ERA scenarios, while only a few studies were based on
503 HHRA scenarios. It is necessary to question how relevant our knowledge acquired from ERA-
504 based studies is in the context of HHRA.



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506 Fig. 3. A schematic of widely used definition and measurement of bioavailability and bioaccessibility of organic contaminants in soil in both ERA and HHRA.

507 Desorption here is emphasised as a key risk driver.

8. Critique: what is 'missing' in our knowledge and how can we fill these gaps?

A massive body of knowledge about the factors controlling bioavailability and bioaccessibility of PAHs has been acquired. However, a set of descriptive soil parameters explaining bioavailability and bioaccessibility variations is still lacking. This is because all the abiotic factors controlling bioavailability and bioaccessibility of PAHs in soil are still yet to be understood and integrated in a comprehensive knowledge system – just like the missing pieces in a bigger picture (Fig. 4).

Firstly, the effects of source materials on the release of PAHs from soil are overlooked in the majority of the research. It is a routine practice to spike soils with PAHs in volatile solvents (see Table 2, 3), but such an approach fails to reflect the reality as unlike many other organic contaminants, PAHs enter the environment in complex contaminant mixtures carried by source materials. In published studies PAH source materials are often considered as sorption phases for PAHs due to their high partitioning coefficients. This could result in the categorisation of source material-associated PAHs under residual fraction and brings extra uncertainties to risk assessment (Umeh *et al.*, 2017). Future research should focus on their roles in the release of PAHs as high affinity for PAHs does not necessarily mean irreversible sorption. Importantly, time-dependent changes of PAH source materials in soils and their interactions with natural soil components could affect the behaviour and bioavailability/bioaccessibility of PAHs. This calls for an update of our current knowledge, much of which was acquired using soils spiked with PAHs in volatile solvents.

Secondly, the diverse methods adopted to identify and analyse the factors controlling bioavailability and bioaccessibility of PAHs in soil have made the comparison of results from different studies impractical, if not impossible (see Table 2, 3). Sorption equilibrium assays have been criticised for likely observation of 'pseudo-equilibrium'

(Pignatello and Xing, 1996). Parameters obtained from these assays could be irrelevant to bioavailability as reversibility of sorption is not indicated. Future studies should focus more on desorption kinetics, validated non-exhaustive chemical extraction, and biological assays which are directly linked to bioavailability and bioaccessibility.

Thirdly, chemical or thermal treatments to fractionate SOM to analyse key soil components controlling PAH bioavailability and bioaccessibility should be replaced by non-disruptive physical treatments and measurement of pore volume. It is also important that in future studies a distinction between natural NOM and PAH source materials (XOM) is made, to avoid confusion of sorbents and sources of soil PAHs. Our perception of SOM should also evolve so that the kinetic nature of organic carbon turnover as well as the importance of organo-mineral complexes are accounted for.

The effects of environmental factors, PAH concentration, and contaminant mixture on sorption and desorption of PAHs have been well-documented in the literature. The challenge now is to expand or extrapolate our knowledge obtained from controlled simple systems to more complex field systems in which all these factors interplay.

Last but not least, artificial effects arising from the different types of risk assessment (HHRA and ERA) on PAH bioavailability and bioaccessibility should not be ignored. Desorption of PAHs in HHRA scenarios is very different from that in ERA scenarios in terms of liquid phase content, pH, and temperature, while most of our knowledge about the controlling factors of PAH bioavailability and bioaccessibility has been obtained in ERA-based systems. Again, this raises the need to update our knowledge.

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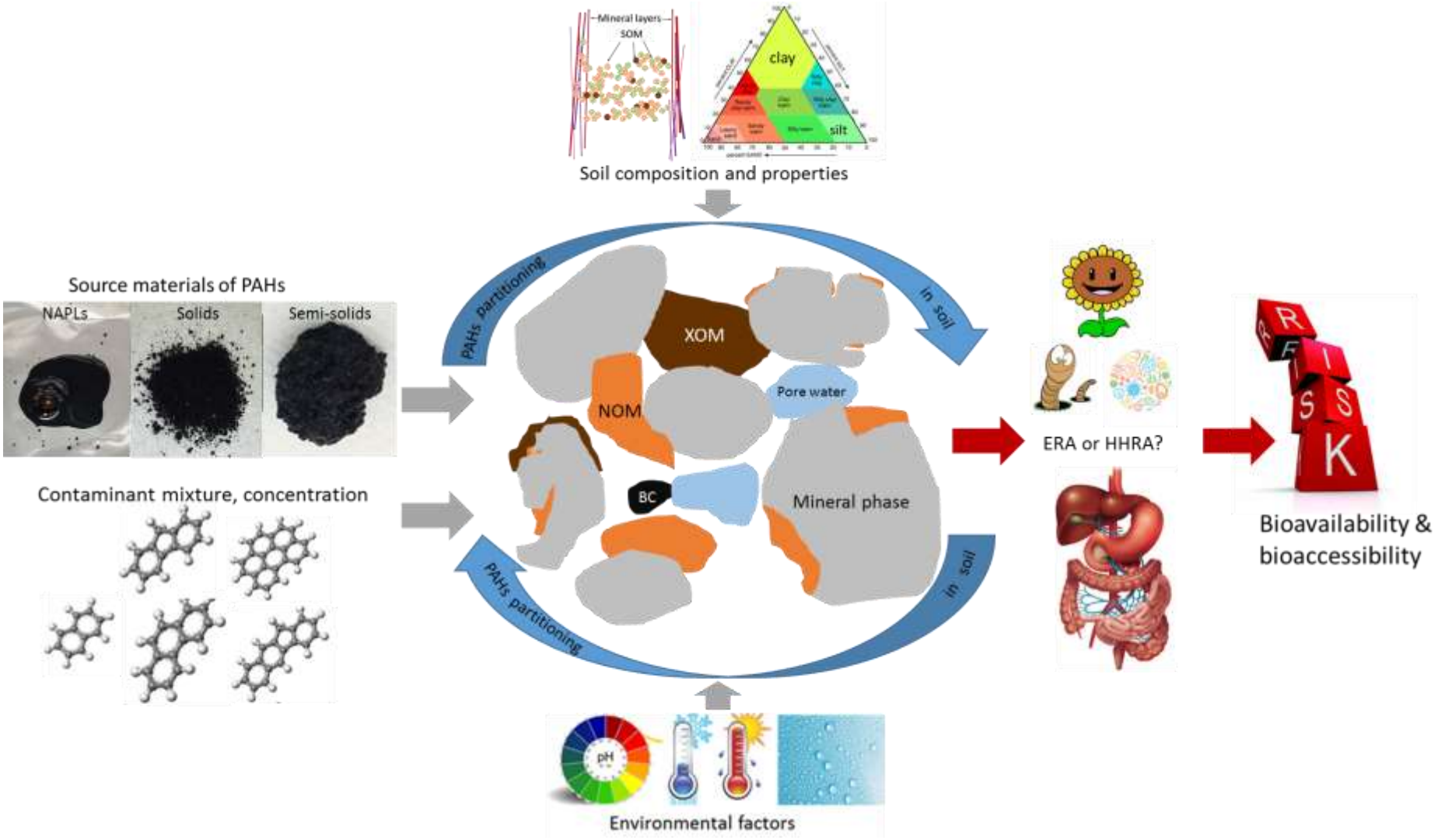

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557 Fig. 4. A diagram of abiotic factors controlling bioavailability and bioaccessibility of PAHs in soil.

References:

Adrion, A. C., Nakamura, J., Shea, D. & Aitken, M. D. 2016. Screening Nonionic Surfactants for Enhanced Biodegradation of Polycyclic Aromatic Hydrocarbons Remaining in Soil After Conventional Biological Treatment. *Environmental science & technology,* 50**,** 3838-3845.

Ahangar, A. G., Smernik, R. J., Kookana, R. S. & Chittleborough, D. J. 2008. Separating the effects of organic matter–mineral interactions and organic matter chemistry on the sorption of diuron and phenanthrene. *Chemosphere,* 72**,** 886-890.

Alexander, M. 2000. Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environmental science & technology,* 34**,** 4259-4265.

Alexander, R. R. & Alexander, M. 2000. Bioavailability of genotoxic compounds in soils. *Environmental science & technology,* 34**,** 1589-1593.

Amellal, N., Portal, J.-M. & Berthelin, J. 2001. Effect of soil structure on the bioavailability of polycyclic aromatic hydrocarbons within aggregates of a contaminated soil. *Applied Geochemistry,* 16**,** 1611-1619.

ATSDR 2002. Toxicological profile for wood creosote, coal tar creosote, coal tar, coal tar pitch, and coal tar pitch volatiles. Agency for Toxic Substances and Disease Registry.

Bayard, R., Barna, L., Mahjoub, B. & Gourdon, R. 2000. Influence of the presence of PAHs and coal tar on naphthalene sorption in soils. *Journal of contaminant hydrology,* 46**,** 61-80.

Benhabib, K., Simonnot, M.-O. & Sardin, M. 2006. PAHs and organic matter partitioning and mass transfer from coal tar particles to water. *Environmental science & technology,* 40**,** 6038-6043.

Bogan, B. W. & Sullivan, W. R. 2003. Physicochemical soil parameters affecting sequestration and mycobacterial biodegradation of polycyclic aromatic hydrocarbons in soil. *Chemosphere,* 52**,** 1717-1726.

Bonin, J. L. & Simpson, M. J. 2007. Variation in phenanthrene sorption coefficients with soil organic matter fractionation: the result of structure or conformation? *Environmental science & technology,* 41**,** 153-159.

Boyd, S. A. & Sun, S. 1990. Residual petroleum and polychlorobiphenyl oils as sorptive phases for organic contaminants in soils. *Environmental science & technology,* 24**,** 142-144.

Braida, W. J., Pignatello, J. J., Lu, Y., Ravikovitch, P. I., Neimark, A. V. & Xing, B. 2003. Sorption hysteresis of benzene in charcoal particles. *Environmental science & technology,* 37**,** 409-417.

Braida, W. J., White, J. C., Ferrandino, F. J. & Pignatello, J. J. 2001. Effect of solute concentration on sorption of polyaromatic hydrocarbons in soil: uptake rates. *Environmental science & technology,* 35**,** 2765-2772.

Braida, W. J., White, J. C., Zhao, D., Ferrandino, F. J. & Pignatello, J. J. 2002. Concentration‐dependent kinetics of pollutant desorption from soils. *Environmental Toxicology and Chemistry,* 21**,** 2573-2580.

Brand, E., Peijnenburg, W., Goenenberg, B., Vink, J., Lijzen, J., Ten Hulscher, D., Jonker, C., Romkens, P. & Roex, E. 2009. Towards implementation of bioavailability measurements in the Dutch regulatory framework. RIVM.

Brown, D. G., Gupta, L., Kim, T.-H., Moo-Young, H. K. & Coleman, A. J. 2006. Comparative assessment of coal tars obtained from 10 former manufactured gas plant sites in the Eastern United States. *Chemosphere,* 65**,** 1562-1569.

Bucheli, T. D. & Gustafsson, Ö. 2000. Quantification of the soot-water distribution coefficient of PAHs provides mechanistic basis for enhanced sorption observations. *Environmental science & technology,* 34**,** 5144-5151.

Burauel, P. & Führ, F. 2000. Formation and long-term fate of non-extractable residues in outdoor lysimeter studies. *Environmental Pollution,* 108**,** 45-52.

Cachada, A., Pereira, R., da Silva, E. F. & Duarte, A. 2014. The prediction of PAHs bioavailability in soils using chemical methods: State of the art and future challenges. *Science of the Total Environment,* 472**,** 463-480.

608 Cao, X., Lattao, C., Schmidt-Rohr, K., Mao, J. & Pignatello, J. J. 2016. Investigation of sorbate-induced
609 plasticization of Pahokee peat by solid-state NMR spectroscopy. *Journal of Soils and*
610 *Sediments,* 16**,** 1841-1848.
611 Carmichael, L. M., Christman, R. F. & Pfaender, F. K. 1997. Desorption and mineralization kinetics of
612 phenanthrene and chrysene in contaminated soils. *Environmental science & technology,* 31**,**
613 126-132.
614 Cave, M. R., Wragg, J., Harrison, I., Vane, C. H., Wiele, T. V. d., Groeve, E. D., Nathanail, C. P.,
615 Ashmore, M., Thomas, R. & Robinson, J. 2010. Comparison of batch mode and dynamic
616 physiologically based bioaccessibility tests for PAHs in soil samples. *Environmental science &*
617 *technology,* 44**,** 2654-2660.
618 Cerniglia, C. E. 1992. Biodegradation of polycyclic aromatic hydrocarbons. *Microorganisms to*
619 *combat pollution.* Springer.
620 Chen, D., Xing, B. & Xie, W. 2007. Sorption of phenanthrene, naphthalene and o-xylene by soil
621 organic matter fractions. *Geoderma,* 139**,** 329-335.
622 Chenu, C. & Plante, A. 2006. Clay‐sized organo‐mineral complexes in a cultivation
623 chronosequence: revisiting the concept of the ‘primary organo‐mineral complex’.
624 *European journal of soil science,* 57**,** 596-607.
625 Chiou, C. T., Kile, D. E., Rutherford, D. W., Sheng, G. & Boyd, S. A. 2000. Sorption of selected organic
626 compounds from water to a peat soil and its humic-acid and humin fractions: Potential
627 sources of the sorption nonlinearity. *Environmental science & technology,* 34**,** 1254-1258.
628 Chung, N. & Alexander, M. 2002. Effect of soil properties on bioavailability and extractability of
629 phenanthrene and atrazine sequestered in soil. *Chemosphere,* 48**,** 109-115.
630 Cornelissen, G. & Gustafsson, Ö. 2004. Sorption of phenanthrene to environmental black carbon in
631 sediment with and without organic matter and native sorbates. *Environmental science &*
632 *technology,* 38**,** 148-155.
633 Cornelissen, G. & Gustafsson, Ö. 2005. Importance of unburned coal carbon, black carbon, and
634 amorphous organic carbon to phenanthrene sorption in sediments. *Environmental science &*
635 *technology,* 39**,** 764-769.
636 Cornelissen, G., Gustafsson, Ö., Bucheli, T. D., Jonker, M. T., Koelmans, A. A. & van Noort, P. C. 2005.
637 Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments
638 and soils: mechanisms and consequences for distribution, bioaccumulation, and
639 biodegradation. *Environmental science & technology,* 39**,** 6881-6895.
640 Cui, X.-Y., Xiang, P., He, R.-W., Juhasz, A. & Ma, L. Q. 2016. Advances in in vitro methods to evaluate
641 oral bioaccessibility of PAHs and PBDEs in environmental matrices. *Chemosphere,* 150**,** 378-
642 389.
643 Cui, X., Mayer, P. & Gan, J. 2013. Methods to assess bioavailability of hydrophobic organic
644 contaminants: Principles, operations, and limitations. *Environmental Pollution,* 172**,** 223-234.
645 Dean, J. R. & Ma, R. 2007. Approaches to assess the oral bioaccessibility of persistent organic
646 pollutants: a critical review. *Chemosphere,* 68**,** 1399-1407.
647 Doick, K. J., Burauel, P., Jones, K. C. & Semple, K. T. 2005. Distribution of aged 14C-PCB and 14C-PAH
648 residues in particle-size and humic fractions of an agricultural soil. *Environmental science &*
649 *technology,* 39**,** 6575-6583.
650 Duan, L. & Naidu, R. 2013. Effect of ionic strength and index cation on the sorption of phenanthrene.
651 *Water, Air, & Soil Pollution,* 224**,** 1-17.
652 Duan, L., Naidu, R., Liu, Y., Dong, Z., Mallavarapu, M., Herde, P., Kuchel, T. & Semple, K. T. 2016.
653 Comparison of oral bioavailability of benzo [a] pyrene in soils using rat and swine and the
654 implications for human health risk assessment. *Environment international,* 94**,** 95-102.
655 Duan, L., Naidu, R., Liu, Y., Palanisami, T., Dong, Z., Mallavarapu, M. & Semple, K. T. 2015a. Effect of
656 ageing on benzo [a] pyrene extractability in contrasting soils. *Journal of hazardous materials,*
657 296**,** 175-184.

Duan, L., Naidu, R., Thavamani, P., Meaklim, J. & Megharaj, M. 2015b. Managing long-term polycyclic aromatic hydrocarbon contaminated soils: a risk-based approach. *Environmental Science and Pollution Research,* 22**,** 8927-8941.
Duan, L., Palanisami, T., Liu, Y., Dong, Z., Mallavarapu, M., Kuchel, T., Semple, K. T. & Naidu, R. 2014. Effects of ageing and soil properties on the oral bioavailability of benzo [a] pyrene using a swine model. *Environment international,* 70**,** 192-202.
Eberhardt, C. & Grathwohl, P. 2002. Time scales of organic contaminant dissolution from complex source zones: coal tar pools vs. blobs. *Journal of contaminant hydrology,* 59**,** 45-66.
EFSA 2009. Scientific Opinion of the Panel on Plant Protection Products and their Residues on a request from EFSA on the usefulness of total concentrations and pore water concentrations of pesticides in soil as metrics for the assessment of ecotoxicological effects. *The EFSA Journal,* 922**,** 1-90.
Ehlers, G. A. & Loibner, A. P. 2006. Linking organic pollutant (bio) availability with geosorbent properties and biomimetic methodology: A review of geosorbent characterisation and (bio) availability prediction. *Environmental Pollution,* 141**,** 494-512.
Enell, A., Reichenberg, F., Ewald, G. & Warfvinge, P. 2005. Desorption kinetics studies on PAH-contaminated soil under varying temperatures. *Chemosphere,* 61**,** 1529-1538.
Feng, X., Simpson, A. J. & Simpson, M. J. 2005. Chemical and mineralogical controls on humic acid sorption to clay mineral surfaces. *Organic Geochemistry,* 36**,** 1553-1566.
Feng, X., Simpson, A. J. & Simpson, M. J. 2006. Investigating the role of mineral-bound humic acid in phenanthrene sorption. *Environmental science & technology,* 40**,** 3260-3266.
Freddo, A., Cai, C. & Reid, B. J. 2012. Environmental contextualisation of potential toxic elements and polycyclic aromatic hydrocarbons in biochar. *Environmental Pollution,* 171**,** 18-24.
Führ, F., Hance, R., Plimmer, J. & Nelson, J. The lysimeter concept: environmental behavior of pesticides. The Division of Agrochemicals, 213th National Meeting of the American Chemcial Society. 13-17 April, 1997., 1998 San Fransisco, California, USA. American Chemical Society.
Gao, Y., Xiong, W., Ling, W. & Xu, J. 2006. Sorption of phenanthrene by soils contaminated with heavy metals. *Chemosphere,* 65**,** 1355-1361.
Ghosh, D. R. & Keinath, T. M. 1994. Effect of clay minerals present in aquifer soils on the adsorption and desorption of hydrophobic organic compounds. *Environmental progress,* 13**,** 51-59.
Ghosh, U., Gillette, J. S., Luthy, R. G. & Zare, R. N. 2000. Microscale location, characterization, and association of polycyclic aromatic hydrocarbons on harbor sediment particles. *Environmental science & technology,* 34**,** 1729-1736.
Ghosh, U. & Hawthorne, S. B. 2010. Particle-scale measurement of PAH aqueous equilibrium partitioning in impacted sediments. *Environmental science & technology,* 44**,** 1204-1210.
Ghosh, U., Zimmerman, J. R. & Luthy, R. G. 2003. PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH bioavailability. *Environmental science & technology,* 37**,** 2209-2217.
Ghoshal, S., Ramaswami, A. & Luthy, R. G. 1996. Biodegradation of naphthalene from coal tar and heptamethylnonane in mixed batch systems. *Environmental science & technology,* 30**,** 1282-1291.
Hajaligol, M., Waymack, B. & Kellogg, D. 2001. Low temperature formation of aromatic hydrocarbon from pyrolysis of cellulosic materials. *Fuel,* 80**,** 1799-1807.
Hale, S., Hanley, K., Lehmann, J., Zimmerman, A. & Cornelissen, G. 2011. Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar. *Environmental science & technology,* 45**,** 10445-10453.
Han, L., Sun, K., Jin, J., Wei, X., Xia, X., Wu, F., Gao, B. & Xing, B. 2014. Role of structure and microporosity in phenanthrene sorption by natural and engineered organic matter. *Environmental science & technology,* 48**,** 11227-11234.
Hanser, O., Biache, C., Boulangé, M., Parant, S., Lorgeoux, C., Billet, D., Michels, R. & Faure, P. 2015. Evolution of dissolved organic matter during abiotic oxidation of coal tar—comparison with

contaminated soils under natural attenuation. *Environmental Science and Pollution Research,* 22**,** 1431-1443.
Hong, L., Ghosh, U., Mahajan, T., Zare, R. N. & Luthy, R. G. 2003. PAH sorption mechanism and partitioning behavior in lampblack-impacted soils from former oil-gas plant sites. *Environmental science & technology,* 37**,** 3625-3634.
Hong, L. & Luthy, R. G. 2007. Availability of polycyclic aromatic hydrocarbons from lampblack‐impacted soils at former oil‐gas plant sites in California, USA. *Environmental Toxicology and Chemistry,* 26**,** 394-405.
Huang, W. & Weber, W. J. 1998. A distributed reactivity model for sorption by soils and sediments. 11. Slow concentration-dependent sorption rates. *Environmental science & technology,* 32**,** 3549-3555.
Huang, W., Young, T. M., Schlautman, M. A., Yu, H. & Weber, W. J. 1997. A distributed reactivity model for sorption by soils and sediments. 9. General isotherm nonlinearity and applicability of the dual reactive domain model. *Environmental science & technology,* 31**,** 1703-1710.
Hwang, S. & Cutright, T. J. 2002. Impact of clay minerals and DOM on the competitive sorption/desorption of PAHs. *Soil and Sediment Contamination,* 11**,** 269-291.
Hwang, S. & Cutright, T. J. 2003. Preliminary exploration of the relationships between soil characteristics and PAH desorption and biodegradation. *Environment international,* 29**,** 887-894.
Jones, K. D. & Tiller, C. L. 1999. Effect of solution chemistry on the extent of binding of phenanthrene by a soil humic acid: a comparison of dissolved and clay bound humic. *Environmental science & technology,* 33**,** 580-587.
Jonker, M. T. & Barendregt, A. 2006. Oil is a sedimentary supersorbent for polychlorinated biphenyls. *Environmental science & technology,* 40**,** 3829-3835.
Jonker, M. T., Hawthorne, S. B. & Koelmans, A. A. 2005. Extremely slowly desorbing polycyclic aromatic hydrocarbons from soot and soot-like materials: evidence by supercritical fluid extraction. *Environmental science & technology,* 39**,** 7889-7895.
Jonker, M. T. & Koelmans, A. A. 2002a. Extraction of polycyclic aromatic hydrocarbons from soot and sediment: solvent evaluation and implications for sorption mechanism. *Environmental science & technology,* 36**,** 4107-4113.
Jonker, M. T. & Koelmans, A. A. 2002b. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: mechanistic considerations. *Environmental science & technology,* 36**,** 3725-3734.
Jonker, M. T., Sinke, A. J., Brils, J. M. & Koelmans, A. A. 2003. Sorption of polycyclic aromatic hydrocarbons to oil contaminated sediment: unresolved complex? *Environmental science & technology,* 37**,** 5197-5203.
Juhasz, A. L. & Naidu, R. 2000. Bioremediation of high molecular weight polycyclic aromatic hydrocarbons: a review of the microbial degradation of benzo [a] pyrene. *International biodeterioration & biodegradation,* 45**,** 57-88.
Kaestner, M., Nowak, K. M., Miltner, A., Trapp, S. & Schaeffer, A. 2014. Classification and modelling of nonextractable residue (NER) formation of xenobiotics in soil–a synthesis. *Critical reviews in environmental science and technology,* 44**,** 2107-2171.
Kang, S. & Xing, B. 2005. Phenanthrene sorption to sequentially extracted soil humic acids and humins. *Environmental science & technology,* 39**,** 134-140.
Karapanagioti, H. K., Kleineidam, S., Sabatini, D. A., Grathwohl, P. & Ligouis, B. 2000. Impacts of heterogeneous organic matter on phenanthrene sorption: equilibrium and kinetic studies with aquifer material. *Environmental science & technology,* 34**,** 406-414.
Kelsey, J. W., Kottler, B. D. & Alexander, M. 1997. Selective chemical extractants to predict bioavailability of soil-aged organic chemicals. *Environmental science & technology,* 31**,** 214-217.

759 Khalil, M. F., Ghosh, U. & Kreitinger, J. P. 2006. Role of weathered coal tar pitch in the partitioning of
760 polycyclic aromatic hydrocarbons in manufactured gas plant site sediments. *Environmental*
761 *science & technology,* 40**,** 5681-5687.
762 Kiem, R., Knicker, H. & Kögel-Knabner, I. 2002. Refractory organic carbon in particle-size fractions of
763 arable soils I: distribution of refractory carbon between the size fractions. *Organic*
764 *Geochemistry,* 33**,** 1683-1697.
765 Kleineidam, S., Schüth, C. & Grathwohl, P. 2002. Solubility-normalized combined adsorption-
766 partitioning sorption isotherms for organic pollutants. *Environmental science & technology,*
767 36**,** 4689-4697.
768 Kohl, S. & Rice, J. 1998. The binding of contaminants to humin: a mass balance. *Chemosphere,* 36**,**
769 251-261.
770 Koppolu, L., Agblevor, F. A. & Clements, L. D. 2003. Pyrolysis as a technique for separating heavy
771 metals from hyperaccumulators. Part II: Lab-scale pyrolysis of synthetic hyperaccumulator
772 biomass. *Biomass and Bioenergy,* 25**,** 651-663.
773 Kottler, B. D., White, J. C. & Kelsey, J. W. 2001. Influence of soil moisture on the sequestration of
774 organic compounds in soil. *Chemosphere,* 42**,** 893-898.
775 Krauss, M. & Wilcke, W. 2002. Sorption strength of persistent organic pollutants in particle-size
776 fractions of urban soils. *Soil Science Society of America Journal,* 66**,** 430-437.
777 Lal, V., Peng, C. & Ng, J. 2015. A review of non-exhaustive chemical and bioavailability methods for
778 the assessment of polycyclic aromatic hydrocarbons in soil. *Environmental Technology &*
779 *Innovation,* 4**,** 159-167.
780 Lalonde, K., Mucci, A., Ouellet, A. & Gélinas, Y. 2012. Preservation of organic matter in sediments
781 promoted by iron. *Nature,* 483**,** 198-200.
782 Lanno, R., Wells, J., Conder, J., Bradham, K. & Basta, N. 2004. The bioavailability of chemicals in soil
783 for earthworms. *Ecotoxicology and environmental safety,* 57**,** 39-47.
784 Lee, L., Priddy, N., Augustijn, D., Rubin, H., Narkins, N. & Carberry, J. 1998. Estimating mass transfer
785 of polycyclic aromatic hydrocarbons from coal tar-contaminated soil. *Soil and Aquifer*
786 *Pollution: Non-aqueous Phase Liquids e Contamination and Reclamation. Springer, Berlin*.
787 Lee, L. S., Rao, P. S. C. & Okuda, I. 1992. Equilibrium partitioning of polycyclic aromatic hydrocarbons
788 from coal tar into water. *Environmental science & technology,* 26**,** 2110-2115.
789 Lehmann, J. & Kleber, M. 2015. The contentious nature of soil organic matter. *Nature,* 528**,** 60-68.
790 Lehrsch, G., Sojka, R., Carter, D. & Jolley, P. 1991. Freezing effects on aggregate stability affected by
791 texture, mineralogy, and organic matter. *Soil Science Society of America Journal,* 55**,** 1401-
792 1406.
793 Li, X., Shuang, S., Li, X., Kong, L., Xu, L., Tai, P., Lin, X., Jia, C. & Gong, Z. 2013. The effect of
794 concentrations and properties of phenanthrene, pyrene, and benzo (a) pyrene on desorption
795 in contaminated soil aged for 1 year. *Journal of Soils and Sediments,* 13**,** 375-382.
796 Liang, C., Dang, Z., Xiao, B., Huang, W. & Liu, C. 2006. Equilibrium sorption of phenanthrene by soil
797 humic acids. *Chemosphere,* 63**,** 1961-1968.
798 Liang, X., Zhu, L. & Zhuang, S. 2016. Sorption of polycyclic aromatic hydrocarbons to soils enhanced
799 by heavy metals: perspective of molecular interactions. *Journal of Soils and Sediments,* 16**,**
800 1509-1518.
801 Lin, Q., Shen, K.-L., Zhao, H.-M. & Li, W.-H. 2008. Growth response of Zea mays L. in pyrene–copper
802 co-contaminated soil and the fate of pollutants. *Journal of hazardous materials,* 150**,** 515-
803 521.
804 Lu, Y. & Pignatello, J. J. 2002. Demonstration of the “conditioning effect” in soil organic matter in
805 support of a pore deformation mechanism for sorption hysteresis. *Environmental science &*
806 *technology,* 36**,** 4553-4561.
807 Luo, L., Lin, S., Huang, H. & Zhang, S. 2012. Relationships between aging of PAHs and soil properties.
808 *Environmental Pollution,* 170**,** 177-182.

809 Luo, L., Zhang, S. & Christie, P. 2010. New insights into the influence of heavy metals on
810 phenanthrene sorption in soils. *Environmental science & technology,* 44**,** 7846-7851.
811 Luthy, R. G., Aiken, G. R., Brusseau, M. L., Cunningham, S. D., Gschwend, P. M., Pignatello, J. J.,
812 Reinhard, M., Traina, S. J., Weber, W. J. & Westall, J. C. 1997. Sequestration of hydrophobic
813 organic contaminants by geosorbents. *Environmental science & technology,* 31**,** 3341-3347.
814 Luthy, R. G., Ramaswami, A., Ghoshal, S. & Merkel, W. 1993. Interfacial films in coal tar nonaqueous-
815 phase liquid-water systems. *Environmental science & technology,* 27**,** 2914-2918.
816 Lützow, M. v., Kögel‐Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B. &
817 Flessa, H. 2006. Stabilization of organic matter in temperate soils: mechanisms and their
818 relevance under different soil conditions–a review. *European journal of soil science,* 57**,** 426-
819 445.
820 MacLeod, C. J., Morriss, A. & Semple, K. T. 2001. The role of microorganisms in ecological risk
821 assessment of hydrophobic organic contaminants in soils. *Advances in applied microbiology,*
822 48**,** 171-212.
823 Mahjoub, B., Jayr, E., Bayard, R. & Gourdon, R. 2000. Phase partition of organic pollutants between
824 coal tar and water under variable experimental conditions. *Water Research,* 34**,** 3551-3560.
825 Mastral, A. M. & Callen, M. S. 2000. A review on polycyclic aromatic hydrocarbon (PAH) emissions
826 from energy generation. *Environmental science & technology,* 34**,** 3051-3057.
827 McFee, W., Kelly, J. & Beck, R. 1977. Acid precipitation effects on soil pH and base saturation of
828 exchange sites. *Water, air, and soil pollution,* 7**,** 401-408.
829 Mersch-Sundermann, V., Mochayedi, S. & Kevekordes, S. 1992. Genotoxicity of polycyclic aromatic
830 hydrocarbons in Escherichia coli PQ37. *Mutation Research/Genetic Toxicology,* 278**,** 1-9.
831 Murphy, E. M., Zachara, J. M., Smith, S. C., Phillips, J. L. & Wietsma, T. W. 1994. Interaction of
832 hydrophobic organic compounds with mineral-bound humic substances. *Environmental*
833 *science & technology,* 28**,** 1291-1299.
834 Naidu, R., Pollard, S., Bolan, N., Owens, G. & Pruszinski, A. 2008a. Bioavailability: the underlying basis
835 for risk-based land management. *Developments in soil science,* 32**,** 53-72.
836 Naidu, R., Semple, K. T., Megharaj, M., Juhasz, A. L., Bolan, N. S., Gupta, S., Clothier, B. & Schulin, R.
837 2008b. Bioavailability: Definition, assessment and implications for risk assessment.
838 *Developments in soil science,* 32**,** 39-51.
839 Naidu, R., Wong, M. & Nathanail, P. 2015. Bioavailability—the underlying basis for risk-based land
840 management. *Environmental Science and Pollution Research,* 22**,** 8775-8778.
841 Nam, J. J., Sweetman, A. J. & Jones, K. C. 2009. Polynuclear aromatic hydrocarbons (PAHs) in global
842 background soils. *Journal of Environmental Monitoring,* 11**,** 45-48.
843 Nam, J. J., Thomas, G. O., Jaward, F. M., Steinnes, E., Gustafsson, O. & Jones, K. C. 2008. PAHs in
844 background soils from Western Europe: influence of atmospheric deposition and soil organic
845 matter. *Chemosphere,* 70**,** 1596-1602.
846 Nam, K., Chung, N. & Alexander, M. 1998. Relationship between organic matter content of soil and
847 the sequestration of phenanthrene. *Environmental science & technology,* 32**,** 3785-3788.
848 Nieman, J. K. C., Sims, R. C., Sims, J. L., Sorensen, D. L., McLean, J. E. & Rice, J. A. 1999. [14C] Pyrene
849 bound residue evaluation using MIBK fractionation method for creosote-contaminated soil.
850 *Environmental science & technology,* 33**,** 776-781.
851 Northcott, G. L. & Jones, K. C. 2000. Experimental approaches and analytical techniques for
852 determining organic compound bound residues in soil and sediment. *Environmental*
853 *Pollution,* 108**,** 19-43.
854 Ogbonnaya, O., Adebisi, O. & Semple, K. T. 2014. The impact of biochar on the bioaccessibility of 14
855 C-phenanthrene in aged soil. *Environmental Science: Processes & Impacts,* 16**,** 2635-2643.
856 Ortega-Calvo, J.-J., Harmsen, J., Parsons, J. R., Semple, K. T., Aitken, M. D., Ajao, C., Eadsforth, C.,
857 Galay-Burgos, M., Naidu, R. & Oliver, R. 2015. From bioavailability science to regulation of
858 organic chemicals. *Environmental science & technology,* 49**,** 10255-10264.

859 Ortiz, E., Kraatz, M. & Luthy, R. G. 1999. Organic phase resistance to dissolution of polycyclic
860 aromatic hydrocarbon compounds. *Environmental science & technology,* 33**,** 235-242.
861 Pan, B., Xing, B., Liu, W., Tao, S., Lin, X., Zhang, X., Zhang, Y., Xiao, Y., Dai, H. & Yuan, H. 2006.
862 Distribution of sorbed phenanthrene and pyrene in different humic fractions of soils and
863 importance of humin. *Environmental Pollution,* 143**,** 24-33.
864 Peijnenburg, W., Capri, E., Kula, C., Liess, M., Luttik, R., Montforts, M., Nienstedt, K., Römbke, J.,
865 Sousa, J. P. & Jensen, J. 2012. Evaluation of exposure metrics for effect assessment of soil
866 invertebrates. *Critical reviews in environmental science and technology,* 42**,** 1862-1893.
867 Pernot, A., Ouvrard, S., Leglize, P. & Faure, P. 2013. Protective role of fine silts for PAH in a former
868 industrial soil. *Environmental Pollution,* 179**,** 81-87.
869 Pignatello, J. J. & Xing, B. S. 1996. Mechanisms of slow sorption of organic chemicals to natural
870 particles. *Environmental science & technology,* 30**,** 1-11.
871 Pu, X., Lee, L. S., Galinsky, R. E. & Carlson, G. P. 2004. Evaluation of a rat model versus a
872 physiologically based extraction test for assessing phenanthrene bioavailability from soils.
873 *Toxicological Sciences,* 79**,** 10-17.
874 Ramaswami, A. & Luthy, R. G. 1997. Mass transfer and bioavailability of PAH compounds in coal tar
875 NAPL-slurry systems. 1. Model development. *Environmental science & technology,* 31**,** 2260-
876 2267.
877 Ransom, B., Bennett, R., Baerwald, R. & Shea, K. 1997. TEM study of in situ organic matter on
878 continental margins: occurrence and the "monolayer" hypothesis. *Marine Geology,* 138**,** 1-9.
879 Reid, B. J., Jones, K. C. & Semple, K. T. 2000. Bioavailability of persistent organic pollutants in soils
880 and sediments—a perspective on mechanisms, consequences and assessment.
881 *Environmental Pollution,* 108**,** 103-112.
882 Rhodes, A. H., Carlin, A. & Semple, K. T. 2008. Impact of black carbon in the extraction and
883 mineralization of phenanthrene in soil. *Environmental science & technology,* 42**,** 740-745.
884 Rhodes, A. H., McAllister, L. E. & Semple, K. T. 2010. Linking desorption kinetics to phenanthrene
885 biodegradation in soil. *Environmental Pollution,* 158**,** 1348-1353.
886 Roberts, S. M., Munson, J. W., Ruby, M. V. & Lowney, Y. W. 2016. Effects of Source and
887 Concentration on Relative Oral Bioavailability of Benzo (a) pyrene from Soil. *Environmental*
888 *science & technology*.
889 Ruby, M., Schoof, R., Brattin, W., Goldade, M., Post, G., Harnois, M., Mosby, D., Casteel, S., Berti, W.
890 & Carpenter, M. 1999. Advances in evaluating the oral bioavailability of inorganics in soil for
891 use in human health risk assessment. *Environmental science & technology,* 33**,** 3697-3705.
892 Ruby, M. V. & Lowney, Y. W. 2012. Selective soil particle adherence to hands: implications for
893 understanding oral exposure to soil contaminants. *Environmental science & technology,* 46**,**
894 12759-12771.
895 Ruby, M. V., Lowney, Y. W., Bunge, A. L., Roberts, S. M., Gomez-Eyles, J. L., Ghosh, U., Kissel, J.,
896 Tomlinson, P. & Menzie, C. A. 2016. Oral Bioavailability, Bioaccessibility, and Dermal
897 Absorption of PAHs from Soil—State of the Science. *Environmental science & technology,* 50**,**
898 2151-2164.
899 Rust, A. J., Burgess, R. M., McElroy, A. E., Cantwell, M. G. & Brownawell, B. J. 2004. Influence of soot
900 carbon on the bioaccumulation of sediment‐bound polycyclic aromatic hydrocarbons by
901 marine benthic invertebrates: An interspecies comparison. *Environmental Toxicology and*
902 *Chemistry,* 23**,** 2594-2603.
903 Saison, C., Perrin-Ganier, C., Amellal, S., Morel, J.-L. & Schiavon, M. 2004. Effect of metals on the
904 adsorption and extractability of 14 C-phenanthrene in soils. *Chemosphere,* 55**,** 477-485.
905 Sander, M. & Pignatello, J. J. 2007. On the reversibility of sorption to black carbon: distinguishing
906 true hysteresis from artificial hysteresis caused by dilution of a competing adsorbate.
907 *Environmental science & technology,* 41**,** 843-849.
908 Sandrin, T. R. & Maier, R. M. 2003. Impact of metals on the biodegradation of organic pollutants.
909 *Environmental health perspectives,* 111**,** 1093.

910 Schaumann, G. E., Hobley, E., Hurraß, J. & Rotard, W. 2005. H-NMR relaxometry to monitor wetting
911 and swelling kinetics in high-organic matter soils. *Plant and Soil,* 275**,** 1-20.
912 Schwarzenbach, R. P., Gschwend, P. M. & Imboden, D. M. 2005. *Environmental organic chemistry*,
913 John Wiley & Sons.
914 Semple, K. T., Doick, K. J., Jones, K. C., Burauel, P., Craven, A. & Harms, H. 2004. Peer reviewed:
915 defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated.
916 *Environmental science & technology,* 38**,** 228A-231A.
917 Semple, K. T., Doick, K. J., Wick, L. Y. & Harms, H. 2007. Microbial interactions with organic
918 contaminants in soil: definitions, processes and measurement. *Environmental Pollution,* 150**,**
919 166-176.
920 Semple, K. T., Morriss, A. & Paton, G. 2003. Bioavailability of hydrophobic organic contaminants in
921 soils: fundamental concepts and techniques for analysis. *European journal of soil science,* 54**,**
922 809-818.
923 Semple, K. T., Riding, M. J., McAllister, L. E., Sopena-Vazquez, F. & Bending, G. D. 2013. Impact of
924 black carbon on the bioaccessibility of organic contaminants in soil. *Journal of hazardous*
925 *materials,* 261**,** 808-816.
926 Shchegolikhina, A., Schulz, S. & Marschner, B. 2012. Interacting effects of cation saturation and
927 drying, freezing, or aging on the extractability of nonylphenol and phenanthrene from a
928 sandy soil. *Journal of Soils and Sediments,* 12**,** 1280-1291.
929 Siciliano, S. D., Laird, B. & Lemieux, C. 2010. Polycyclic aromatic hydrocarbons are enriched but
930 bioaccessibility reduced in brownfield soils adhered to human hands. *Chemosphere,* 80**,**
931 1101-1108.
932 Sims, R. C. & Overcash, M. R. 1983. Fate of Polynuclear Aromatic-Compounds (Pnas) in Soil-Plant
933 Systems. *Residue Reviews,* 88**,** 1-68.
934 Singh, N. & Kookana, R. S. 2009. Organo-mineral interactions mask the true sorption potential of
935 biochars in soils. *Journal of Environmental Science and Health Part B,* 44**,** 214-219.
936 Six, J., Elliott, E. & Paustian, K. 2000. Soil macroaggregate turnover and microaggregate formation: a
937 mechanism for C sequestration under no-tillage agriculture. *Soil Biology and Biochemistry,*
938 32**,** 2099-2103.
939 Stroo, H. F., Jensen, R., Loehr, R. C., Nakles, D. V., Fairbrother, A. & Liban, C. B. 2000. Environmentally
940 acceptable endpoints for PAHs at a manufactured gas plant site. *Environmental science &*
941 *technology,* 34**,** 3831-3836.
942 Stroud, J. L., Paton, G. I. & Semple, K. T. 2009. Predicting the biodegradation of target hydrocarbons
943 in the presence of mixed contaminants in soil. *Chemosphere,* 74**,** 563-567.
944 Tao, S., Xu, F., Liu, W., Cui, Y. & Coveney, R. M. 2006. A chemical extraction method for mimicking
945 bioavailability of polycyclic aromatic hydrocarbons to wheat grown in soils containing
946 various amounts of organic matter. *Environmental science & technology,* 40**,** 2219-2224.
947 Thorsen, W. A., Cope, W. G. & Shea, D. 2004. Bioavailability of PAHs: Effects of soot carbon and PAH
948 source. *Environmental science & technology,* 38**,** 2029-2037.
949 Torn, M. S., Trumbore, S. E., Chadwick, O. A., Vitousek, P. M. & Hendricks, D. M. 1997. Mineral
950 control of soil organic carbon storage and turnover. *Nature,* 389**,** 170-173.
951 Umeh, A. C., Duan, L., Naidu, R. & Semple, K. T. 2017. Residual hydrophobic organic contaminants in
952 soil: Are they a barrier to risk-based approaches for managing contaminated land?
953 *Environment international,* 98**,** 18-34.
954 USEPA 1988. US production of manufactured gases: assessment of past disposal practices. Research
955 Triangle Inst., Research Triangle Park, NC (USA).
956 Uyttebroek, M., Breugelmans, P., Janssen, M., Wattiau, P., Joffe, B., Karlson, U., Ortega‐Calvo, J. J.,
957 Bastiaens, L., Ryngaert, A. & Hausner, M. 2006. Distribution of the Mycobacterium
958 community and polycyclic aromatic hydrocarbons (PAHs) among different size fractions of a
959 long‐term PAH‐contaminated soil. *Environmental microbiology,* 8**,** 836-847.

van den Heuvel, H. & van Noort, P. C. 2003. Competition for adsorption between added phenanthrene and in situ PAHs in two sediments. *Chemosphere,* 53**,** 1097-1103.
Vasiluk, L., Pinto, L. J., Walji, Z. A., Tsang, W. S., Gobas, F. A., Eickhoff, C. & Moore, M. M. 2007. Benzo [a] pyrene bioavailability from pristine soil and contaminated sediment assessed using two in vitro models. *Environmental Toxicology and Chemistry,* 26**,** 387-393.
Vogel, C., Mueller, C. W., Höschen, C., Buegger, F., Heister, K., Schulz, S., Schloter, M. & Kögel-Knabner, I. 2014. Submicron structures provide preferential spots for carbon and nitrogen sequestration in soils. *Nature communications,* 5.
Wang, K., Chen, X.-x., Zhu, Z.-q., Huang, H.-g., Li, T.-q. & Yang, X.-e. 2014. Dissipation of available benzo [a] pyrene in aging soil co-contaminated with cadmium and pyrene. *Environmental Science and Pollution Research,* 21**,** 962-971.
Wang, X., Cook, R., Tao, S. & Xing, B. 2007. Sorption of organic contaminants by biopolymers: Role of polarity, structure and domain spatial arrangement. *Chemosphere,* 66**,** 1476-1484.
Wang, X., Sato, T. & Xing, B. 2005. Sorption and displacement of pyrene in soils and sediments. *Environmental science & technology,* 39**,** 8712-8718.
Wang, X., Sato, T. & Xing, B. 2006. Competitive sorption of pyrene on wood chars. *Environmental science & technology,* 40**,** 3267-3272.
Wang, Z., Liu, Z., Liu, M., Xu, K. & Mayer, L. M. 2016. The impact of drying on structure of sedimentary organic matter in wetlands: Probing with native and amended polycyclic aromatic hydrocarbons. *Science of the Total Environment,* 568**,** 42-51.
Wehrer, M., Rennert, T., Mansfeldt, T. & Totsche, K. U. 2011. Contaminants at former manufactured gas plants: sources, properties, and processes. *Critical reviews in environmental science and technology,* 41**,** 1883-1969.
Wehrer, M., Rennert, T. & Totsche, K. U. 2013. Kinetic control of contaminant release from NAPLs–Experimental evidence. *Environmental Pollution,* 179**,** 315-325.
Wen, B., Zhang, J.-j., Zhang, S.-z., Shan, X.-q., Khan, S. U. & Xing, B. 2007. Phenanthrene sorption to soil humic acid and different humin fractions. *Environmental science & technology,* 41**,** 3165-3171.
White, J. C., Alexander, M. & Pignatello, J. J. 1999a. Enhancing the bioavailability of organic compounds sequestered in soil and aquifer solids. *Environmental Toxicology and Chemistry,* 18**,** 182-187.
White, J. C., Hunter, M., Pignatello, J. J. & Alexander, M. 1999b. Increase in bioavailability of aged phenanthrene in soils by competitive displacement with pyrene. *Environmental Toxicology and Chemistry,* 18**,** 1728-1732.
White, J. C., Kelsey, J. W., Hatzinger, P. B. & Alexander, M. 1997. Factors affecting sequestration and bioavailability of phenanthrene in soils. *Environmental Toxicology and Chemistry,* 16**,** 2040-2045.
White, J. C. & Pignatello, J. J. 1999. Influence of bisolute competition on the desorption kinetics of polycyclic aromatic hydrocarbons in soil. *Environmental science & technology,* 33**,** 4292-4298.
White, J. C., Quiñones‐Rivera, A. & Alexander, M. 1998. Effect of wetting and drying on the bioavailability of organic compounds sequestered in soil. *Environmental Toxicology and Chemistry,* 17**,** 2378-2382.
Williamson, D. G., Loehr, R. C. & Kimura, Y. 1998. Release of chemicals from contaminated soils. *Journal of Soil Contamination,* 7**,** 543-558.
Wilson, S. & Naidu, R. 2008. Organic contaminant speciation and bioavailability in the terrestrial environment. *Developments in soil science,* 32**,** 187-229.
Wornat, M. J., Sarofim, A. F. & Longwell, J. P. 1987. Changes in the degree of substitution of polycyclic aromatic compounds from pyrolysis of a high-volatile bituminous coal. *Energy & fuels,* 1**,** 431-437.
Wu, W. & Sun, H. 2010. Sorption–desorption hysteresis of phenanthrene–effect of nanopores, solute concentration, and salinity. *Chemosphere,* 81**,** 961-967.

Xia, H., Gomez-Eyles, J. L. & Ghosh, U. 2016. Effect of Polycyclic Aromatic Hydrocarbon Source Materials and Soil Components on Partitioning and Dermal Uptake. *Environmental science & technology,* 50**,** 3444-3452.

Xiao, J., Wen, Y., Li, H., Hao, J., Shen, Q., Ran, W., Mei, X., He, X. & Yu, G. 2015. In situ visualisation and characterisation of the capacity of highly reactive minerals to preserve soil organic matter (SOM) in colloids at submicron scale. *Chemosphere,* 138**,** 225-232.

Xie, H., Guetzloff, T. F. & Rice, J. A. 1997. Fractionation of pesticide residues bound to humin. *Soil Science,* 162**,** 421-429.

Xing, B. 1997. The effect of the quality of soil organic matter on sorption of naphthalene. *Chemosphere,* 35**,** 633-642.

Xing, B. 2001. Sorption of naphthalene and phenanthrene by soil humic acids. *Environmental Pollution,* 111**,** 303-309.

Xing, B. & Pignatello, J. J. 1996. Time‐dependent isotherm shape of organic compounds in soil organic matter: Implications for sorption mechanism. *Environmental Toxicology and Chemistry,* 15**,** 1282-1288.

Xing, B. & Pignatello, J. J. 1997. Dual-mode sorption of low-polarity compounds in glassy poly (vinyl chloride) and soil organic matter. *Environmental science & technology,* 31**,** 792-799.

Xing, B., Pignatello, J. J. & Gigliotti, B. 1996. Competitive sorption between atrazine and other organic compounds in soils and model sorbents. *Environmental science & technology,* 30**,** 2432-2440.

Xu, D., Zhu, S., Chen, H. & Li, F. 2006. Structural characterization of humic acids isolated from typical soils in China and their adsorption characteristics to phenanthrene. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 276**,** 1-7.

Yang, Y., Hunter, W., Tao, S., Crowley, D. & Gan, J. 2009. Effect of activated carbon on microbial bioavailability of phenanthrene in soils. *Environmental Toxicology and Chemistry,* 28**,** 2283-2288.

Yang, Y., Zhang, N., Xue, M. & Tao, S. 2010. Impact of soil organic matter on the distribution of polycyclic aromatic hydrocarbons (PAHs) in soils. *Environmental Pollution,* 158**,** 2170-2174.

Yeom, I. T., Ghosh, M. M. & Cox, C. D. 1996. Kinetic aspects of surfactant solubilization of soil-bound polycyclic aromatic hydrocarbons. *Environmental science & technology,* 30**,** 1589-1595.

Yu, L., Vázquez-Cuevas, G., Duan, L. & Semple, K. T. 2016. Buffered cyclodextrin extraction of ^{14}C-phenanthrene from black carbon amended soil. *Environmental Technology & Innovation,* 6**,** 177 - 184.

Zemanek, M. G., Pollard, S. J., Kenefick, S. L. & Hrudey, S. E. 1997. Multi-phase partitioning and co-solvent effects for polynuclear aromatic hydrocarbons (PAH) in authentic petroleum-and creosote-contaminated soils. *Environmental Pollution,* 98**,** 239-252.

Zhang, W., Cao, J., Huang, H. & Zhang, R. 2010. Effect of coexisting lead and phenanthrene on their individual sorption on a clayish soil. *Soil and Sediment Contamination,* 19**,** 322-337.

Zhang, W., Zhuang, L., Yuan, Y., Tong, L. & Tsang, D. C. 2011. Enhancement of phenanthrene adsorption on a clayey soil and clay minerals by coexisting lead or cadmium. *Chemosphere,* 83**,** 302-310.

Zhao, Q., Li, P., Stagnitti, F., Ye, J., Dong, D., Zhang, Y. & Li, P. 2009. Effects of aging and freeze-thawing on extractability of pyrene in soil. *Chemosphere,* 76**,** 447-452.

Zhao, Q., Xing, B., Tai, P., Li, H., Song, L., Zhang, L. & Li, P. 2013. Effect of freeze–thawing cycles on soil aging behavior of individually spiked phenanthrene and pyrene at different concentrations. *Science of the Total Environment,* 444**,** 311-319.

Zhu, D., Hyun, S., Pignatello, J. J. & Lee, L. S. 2004. Evidence for π-π electron donor-acceptor interactions between π-donor aromatic compounds and π-acceptor sites in soil organic matter through pH effects on sorption. *Environmental science & technology,* 38**,** 4361-4368.

Zimmerman, A. 1997. *Mobility, Toxicity and Volume of Coal Tar at a Former Manufactured Gas Plant Site,* Georgia Institute of Technology.

1062 Zimmerman, J. R., Ghosh, U., Millward, R. N., Bridges, T. S. & Luthy, R. G. 2004. Addition of carbon
1063 sorbents to reduce PCB and PAH bioavailability in marine sediments: Physicochemical tests.
1064 *Environmental science & technology,* 38**,** 5458-5464.
1065 Zimmerman, J. R., Werner, D., Ghosh, U., Millward, R. N., Bridges, T. S. & Luthy, R. G. 2005. Effects of
1066 dose and particle size on activated carbon treatment to sequester polychlorinated biphenyls
1067 and polycyclic aromatic hydrocarbons in marine sediments. *Environmental Toxicology and*
1068 *Chemistry,* 24**,** 1594-1601.

1069