



21 **Abstract**

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

39

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

## 42 **1. Introduction**

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

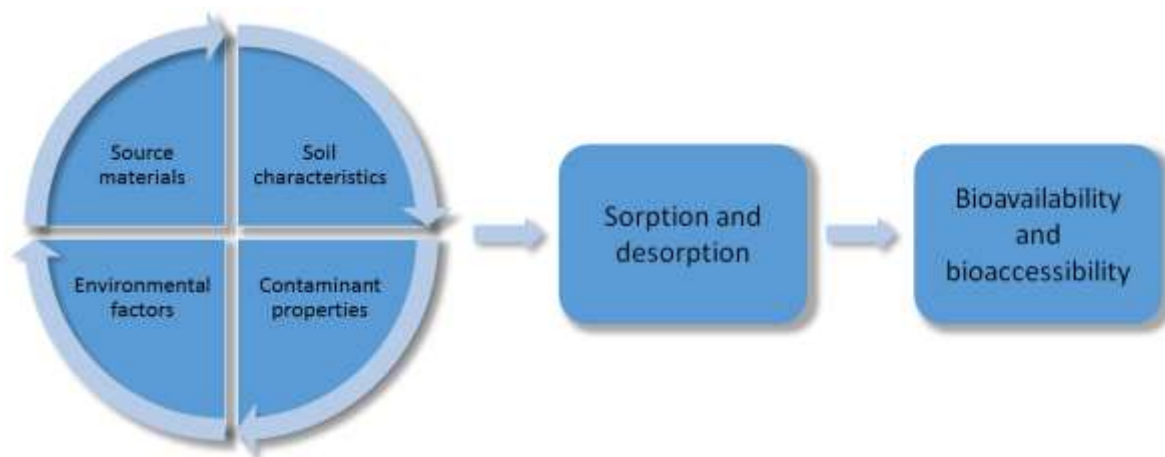
51 The remediation of PAH-contaminated land starts with robust and quantitative risk  
52 assessments. Risk assessment nowadays has moved towards a bioavailability-based practice  
53 to account for the sequestration of organic contaminants in soils over time (i.e. ageing)  
54 which reduces their bioavailability and associated risks (Alexander, 2000; Semple *et al.*, 2007;  
55 Duan *et al.*, 2014; Duan *et al.*, 2015b; Naidu *et al.*, 2015). It is widely accepted that  
56 bioavailability and bioaccessibility of organic contaminants are determined by their sorption  
57 and desorption in soils which are controlled by abiotic factors including soil characteristics,  
58 physio-chemical properties of the contaminants, as well as environmental factors (Fig. 1)  
59 (Nam *et al.*, 1998; Chung and Alexander, 2002; Ehlers and Loibner, 2006; Ruby *et al.*, 2016).  
60 With increasing number of aromatic rings, PAHs demonstrate increasing hydrophobicity and  
61 lipophilicity. Toxicity of different PAH congeners also varies. In a majority of studies,  
62 representative PAHs such as phenanthrene, pyrene, and benzo(a)pyrene are targeted (Table  
63 2, 3) due to their abundance in PAH-contaminated soils or carcinogenicity. Behaviour or  
64 levels of PAHs could also be reported as a total of 16 US EPA listed PAHs or carcinogenic  
65 PAHs (Table 2, 3) Unlike organic contaminants such as pesticides and polychlorinated

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

72         To achieve reliable risk assessment of contaminated land with PAHs, the effects of  
73 source materials on their bioavailability and bioaccessibility must be accounted for (Fig. 1).  
74 Therefore, this review has a particular focus on the effects of PAH source materials, along  
75 with the influences of other abiotic factors, on bioavailability and bioaccessibility of soil  
76 PAHs. It aims to: (1) provide a summary of the interactions between PAHs and different  
77 types of source materials and (2) the influences of PAH concentration as well as co-  
78 contaminants present in these materials on PAH behaviour; (3) evaluate current knowledge  
79 of the effects of soil composition/properties on PAH bioavailability and bioaccessibility; and  
80 (4) consider the implications of different types of risk assessment (ecological and human  
81 health) on current knowledge of factors controlling bioavailability and bioaccessibility.  
82 Based on this, the gaps in current knowledge are identified and the future direction of  
83 research is suggested. However, this article does not serve the purpose of a literature  
84 review that describes chemistry and processes of PAH-soil interactions in details, as such  
85 knowledge has been well documented in published papers. Instead, we emphasise on the  
86 discussion of aspects that are not well understood, such as effects of PAH source materials,  
87 and the evaluation of existing knowledge, such as the methodologies used to assess effects  
88 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).

91



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,

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

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

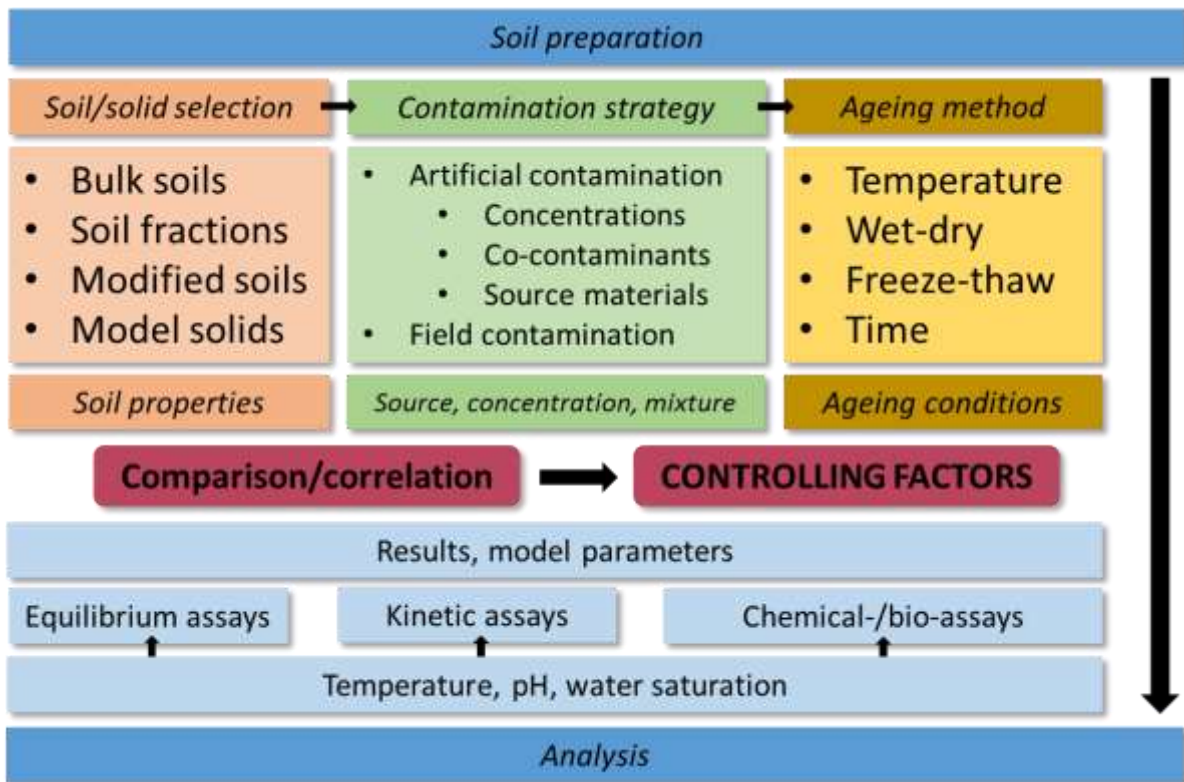
$$114 \quad C_S = K_F \times C_W^n \quad (1)$$

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

$$120 \quad S_t/S_0 = F_{rap} \times \exp(-k_{rap} \times t) + F_{slow} \times \exp(-k_{slow} \times t) \quad (2)$$

$$121 \quad S_t/S_0 = F_{rap} \times \exp(-k_{rap} \times t) + F_{slow} \times \exp(-k_{slow} \times t) + F_{very\ slow} \times \exp(-k_{very\ slow} \times t) \quad (3)$$

122  
123 where  $S_0$  and  $S_t$  are the amount of sorbed contaminant at the start of desorption and at  
124 time  $t$ , while  $F_{rap}$ ,  $F_{slow}$ ,  $F_{very\ slow}$  are the rapidly, slowly and very slowly desorbing fractions,  
125 respectively. Rate constants are designated as  $k_{rap}$ ,  $k_{slow}$ , and  $k_{very\ slow}$  in accordance to  $F_{rap}$ ,  
126  $F_{slow}$ , and  $F_{very\ slow}$ . By comparing or correlating model parameters from equilibrium or kinetic  
127 assays (e.g. in equations 1, 2, and 3), or results from chemical or biological assays, the  
128 factors controlling PAH bioavailability and bioaccessibility can be analysed (Fig. 2).



129

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

132 **3. Effects of PAH source materials**

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

143 these NAPLs, solids, and semi-solids all have high affinity to PAHs. For example, PAHs were  
144 found associated predominantly with source materials including coal tar pitch, coke, and  
145 coal in manufactured gas plant (MGP) impacted sediments (Khalil *et al.*, 2006) and with  
146 NAPL phases in petroleum and creosote contaminated soils (Zemanek *et al.*, 1997). Even at  
147 low levels these materials could dominate the sorption of PAHs (Jonker and Koelmans,  
148 2002b; Cornelissen *et al.*, 2005; Khalil *et al.*, 2006), while at 'hot spots' of PAH  
149 contamination (e.g. manufactured gas plants) high levels of source NAPLs present as  
150 xenobiotic organic matter (XOM) could make up the most of SOM (Bayard *et al.*, 2000).

### 151 ***Solid source materials***

152 Sorption of PAHs to solid source materials was suggested to be exceptionally strong  
153 (Cornelissen *et al.*, 2005; Rhodes *et al.*, 2008; Semple *et al.*, 2013). Solid-liquid partition  
154 coefficient ( $K_d$ ) values for soot and charcoal samples range from  $10^4$  to  $10^9$ , which is up to  
155 1000 times higher than natural organic matter (NOM) in soils (Jonker and Koelmans, 2002b).  
156 The Freundlich isotherms of PAH sorption to soot and charcoal also demonstrated high  
157 sorptive capacity ( $\log K_F = 5.5 - 5.6$ ) (Bucheli and Gustafsson, 2000; Karapanagioti *et al.*,  
158 2000; Kleineidam *et al.*, 2002) and non-linearity ( $n < 1$ ) (Cornelissen and Gustafsson, 2005).  
159 This indicates a site-specific adsorption mechanism involved in PAH association with these  
160 solids. After being produced in incomplete combustion, PAHs could strongly adsorb to  
161 surfaces or micropores of these source materials (Xing *et al.*, 1996; Luthy *et al.*, 1997; Xing  
162 and Pignatello, 1997; Ghosh *et al.*, 2000; Jonker and Koelmans, 2002a). The forces involved  
163 in such strong sorption include dipole-dipole interactions,  $\pi$ - $\pi$  interactions, hydrogen  
164 bonding, and steric hindrance (Zhu *et al.*, 2004). With the strong sorption, the release of  
165 PAHs from solid source materials is highly inhibited, leading to significantly reduced  
166 bioavailability (Rust *et al.*, 2004; Thorsen *et al.*, 2004; Jonker *et al.*, 2005). However, when



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

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

Material type	PAH source material	Process/activity <sup>a</sup>	Composition	Reference
NAPL	coal tar, oil tar	MGP <sup>b</sup> , coking, aluminium production, asphalt sealing	PAHs, BTEX <sup>c</sup> , TPHs <sup>d</sup> , substituted- and heterocyclic-PAHs, heavy metals, cyanides	(USEPA, 1988; Zimmerman, 1997; MacLeod <i>et al.</i> , 2001; ATSDR, 2002; Brown <i>et al.</i> , 2006; Roberts <i>et al.</i> , 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 <i>et al.</i> , 1987; Mastral and Callen, 2000; Hajaligol <i>et al.</i> , 2001; Jonker and Koelmans, 2002b, a; Koppolu <i>et al.</i> , 2003; Freddo <i>et al.</i> , 2012; Semple <i>et al.</i> , 2013)
	char	MGP, landfill, biomass combustion		
	soot	MGP, coking, foundry, oil refinery, landfill, biomass and fuel combustion		
	coke	Coking		

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

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

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

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

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

209 Other studies demonstrated non-ideal dissolution characteristics of PAHs from coal  
210 tar in terms of changing surface characteristics and internal diffusion of solutes. Accelerated  
211 naphthalene biodegradation was observed in coal tar dispersed in porous silica particles  
212 (~250  $\mu\text{m}$  diameter) compared to bulk coal tar due to increased surface area (Ghoshal *et al.*,  
213 1996). Film formation at coal tar-water interfaces after ageing was observed and suggested  
214 to be responsible for the significant deviation of PAH dissolution from ideal behaviour (Luthy  
215 *et al.*, 1993; Mahjoub *et al.*, 2000). In these cases the dissolution of PAHs at the water-NAPL  
216 interface is the rate-limiting step. Dissimilar release rates of different PAHs from NAPLs due  
217 to their water solubility and diffusivity within NAPLs was suggested to cause compositional  
218 changes in NAPLs and affect the subsequent release of remaining PAHs (Lee *et al.*, 1998). It  
219 was observed that the release of naphthalene, phenanthrene, and pyrene from NAPLs  
220 created depleted zones in viscous NAPLs and resulted in longer diffusion paths in the NAPLs  
221 that led to limited release of remaining PAHs (Ortiz *et al.*, 1999). Condensation of high  
222 molecular weight PAHs was also observed after abiotic oxidation of coal tar (Hanser *et al.*,  
223 2015). Depletion of PAHs in coal tar-based skeet was reported to lead to an exponential  
224 increase in the distribution coefficient of PAHs between water and the source material-  
225 amended soil (Xia *et al.*, 2016). The promotion of PAH diffusion in aged coal tar by  
226 surfactants was reported to enhance PAH release to soil (Yeom *et al.*, 1996; Adrion *et al.*,  
227 2016). These observations suggested that internal diffusion of PAHs in NAPLs can also be a  
228 rate-limiting step.

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

248           In many circumstances source materials in the forms of NAPLs, semi-solids, and  
249 solids are all present in PAH-contaminated soils (Khalil *et al.*, 2006) and have implications for  
250 bioavailability and bioaccessibility of PAHs (Ghosh *et al.*, 2003; Roberts *et al.*, 2016; Xia *et al.*,  
251 2016). The importance of non-specific partitioning and site-specific adsorption mechanisms

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

#### 254 **4. Effects of PAH concentrations and co-contaminants**

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

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

269 In contaminated sites PAHs co-exist with many other contaminants, both organic and  
270 inorganic (Sandrin and Maier, 2003; Lin *et al.*, 2008). Organic co-contaminants may displace  
271 PAHs from limited adsorption sites and lead to increased PAH desorption and  
272 bioavailability/bioaccessibility (White *et al.*, 1999a; White *et al.*, 1999b; White and  
273 Pignatello, 1999; van den Heuvel and van Noort, 2003; Stroud *et al.*, 2009; Wang *et al.*, 2014)  
274 (Table 2). Co-existing inorganic contaminants were found to enhance PAH sorption in soils  
275 as K<sub>oc</sub> 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- $\pi$  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).

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 <sup>a</sup>	PHE	5 µg/l 500 µg/l	K <sub>OC</sub> (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 K <sub>OC</sub> (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	accelerated apparent diffusion at higher concentrations
	(Braida <i>et al.</i> , 2001)	sorption equilibrium	7	PHE PYR	1.21 µg/l; 363 - 998 µg/l 1.52 - 4.3 µg/l; 91.4 - 92.7 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 Low concentration: 49.3% - 89.1% sorption, apparent equilibrium: > 57 - >84 d; high concentration: 29.8% - 73.6% sorption, apparent equilibrium: 35 - 84 d	accelerated apparent diffusion at higher concentrations; artefacts brought by 'shrinking gradient effects'
	(Braida <i>et al.</i> , 2002)	desorption kinetics by Tenax	6	PHE	160 - 980 µg/g-OC 2000 - 25000 µg/g-OC	resistant fraction 9 - 38%, diffusion rate: $3.8 \times 10^{-4}$ - $1.8 \times 10^{-3}$ resistant fraction 1 - 29%, diffusion rate: $4.2 \times 10^{-4}$ - $4.0 \times 10^{-3}$	influences from concentration dependent on linearity of sorption; conditioning effects on soil at higher concentrations
	(Wu and Sun, 2010)	sorption equilibrium successive desorption	2 <sup>b</sup>	PHE	100, 500 µg/l 1 - 3 mg/l	100 µg/l: K <sub>OC</sub> = $8.81 \times 10^3$ - $1.46 \times 10^4$ l/kg; 500 µg/l: K <sub>OC</sub> = $5.08 \times 10^3$ - $1.02 \times 10^4$ l/kg 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	conditioning effects on soil caused by higher concentrations led to increased irreversible sorption capacity
	(Li <i>et al.</i> , 2013)	desorption kinetics by XAD2	1	PHE PYR BaP	20, 100 mg/kg 20, 100 mg/kg 10, 50 mg/kg	low: F <sub>rap</sub> = 28.5%, k <sub>rap</sub> = 0.00697 h <sup>-1</sup> ; high: F <sub>rap</sub> = 13.2%, k <sub>rap</sub> = 1.65 h <sup>-1</sup> low: F <sub>rap</sub> = 3.2%, k <sub>rap</sub> = 0.00725 h <sup>-1</sup> ; high: F <sub>rap</sub> = 9.3%, k <sub>rap</sub> = 1.30 h <sup>-1</sup> low: F <sub>rap</sub> = 8.4%, k <sub>rap</sub> = 1.61 h <sup>-1</sup> ; high: F <sub>rap</sub> = 1.9%, k <sub>rap</sub> = 1.79 h <sup>-1</sup>	influences from concentration dependent on properties of PAHs
co-existing contaminants	(White <i>et al.</i> , 1999a)	microbial degradation ethanol/water extraction	3	PHE	20 µg/g ANT, 30 µg/g PYR 50 - 1000 µg ANT, 500 µg 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 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	dependence of the enhancement from co-existing PAHs on concentration and chemical structure
	(White and Pignatello, 1999)	sorption equilibrium	2	PHE	4840 µg/g-OC PYR	Log K <sub>F</sub> 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 <i>et al.</i> , 2014)	microbial degradation sequential extraction	1	BaP <sup>c</sup>	PYR 250 mg/kg	k <sub>deg</sub> 0.00412 - 0.00662 d <sup>-1</sup> without PYR, 0.00613 - 0.00762 d <sup>-1</sup> with PYR 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%	NA



(Stroud <i>et al.</i> , 2009)	microbial degradation HPCD extraction	1	PHE	NAPH, HD <sup>d</sup> , 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 <sup>e</sup>	FLA, BbF, BkF, BaP <sup>f</sup>	fresh PHE	F <sub>slow</sub> increased by 30 - 80% for FLA, 17 - 58% for BbF, 29 - 69% for BkF, 13 - 67% for BaP; F <sub>very slow</sub> decreased by 21 - 27% for fluoranthene, 12 -14% for BbF, 16 - 23% for BkF, 10 - 24% for BaP	NA
(Wang <i>et al.</i> , 2005)	sorption equilibrium	4	PYR	PHE	Log K <sub>F</sub> decreased by 0.01 - 0.05 with PHE, n increased by 0.19 - 0.55 towards 1	changed sorption domain of target PAHs
(Saison <i>et al.</i> , 2004)	sorption equilibrium	3	PHE	Cu, Cd, Pb, Zn	K <sub>F</sub> increased from 8.55 in single system to 21.48 in mixture with metals	increased PAH sorption in presence of metals
(Gao <i>et al.</i> , 2006)	sorption equilibrium	3	PHE	Pb, Zn, Cu 500 mg/kg amended respectively	K <sub>d</sub> 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 <i>et al.</i> , 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 <i>et al.</i> , 2016)	sorption equilibrium, quantum mechanical methods	2	NAPH, PHE, PYR	Cu, Pb, Cr	NAPH: K <sub>F</sub> increased by up to 27.5%, n decreased by up to 20.7%; PHE: K <sub>F</sub> increased by up to 24.8%, n decreased by up to 24.7%; PYR: K <sub>F</sub> 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

285 <sup>a</sup>: 7 USEPA reference soils and sediments, 3 shales, and 3 kerogen samples were used; <sup>b</sup>: 1 soil and 1 sediment were used; <sup>c</sup>: soil used was contaminated with Cd and BaP; <sup>d</sup>:

286 HD = hexadecane; <sup>e</sup>: 2 sediments were used; <sup>f</sup>: residual PAHs in field contaminated samples were targeted. Abbreviations of PAHs: NAPH = naphthalene, PHE =

287 phenanthrene, ANT = anthracene, FLA = fluoranthene, PYR = pyrene, BaP = benzo(a)pyrene, BbF = benzo(b)fluoranthene, BkF = benzo(k) fluoranthene.

## 288 **5. Effects of soil composition and properties**

289 PAHs released from source materials to soil undergo sequestration in the soil matrix  
290 over time and demonstrate reduced bioavailability and bioaccessibility. This process has  
291 been extensively studied and is accepted to be controlled by soil composition and  
292 properties (Naidu *et al.*, 2008a; Wilson and Naidu, 2008). It is now widely accepted that  
293 SOM is the most important soil component that determines PAH sequestration, provided it  
294 is above trace level (Xing *et al.*, 1996). Total organic carbon (TOC) has been shown to  
295 dominate the bioavailability and bioaccessibility of PAHs to different receptors (Nam *et al.*,  
296 1998; Alexander and Alexander, 2000; Chung and Alexander, 2002; Bogan and Sullivan, 2003;  
297 Pu *et al.*, 2004; Tao *et al.*, 2006; Rhodes *et al.*, 2010) (Table 3). Apart from the quantity of  
298 SOM, the dual-mode sorption mechanism, which is now widely acknowledged, indicates the  
299 quality of SOM is also important (Xing and Pignatello, 1996; Xing *et al.*, 1996; Huang *et al.*,  
300 1997; Xing and Pignatello, 1997). The focus of many researches then became the  
301 identification and quantification of the SOM fractions responsible for non-specific  
302 partitioning, designated as 'soft', 'labile', or 'amorphous' SOM, and for site-specific  
303 adsorption, designated as 'hard', 'recalcitrant', or 'condensed' SOM. Several strategies for  
304 differentiation of SOM, including alkaline extraction (humic substances), chemical or  
305 thermal oxidation (black carbon), soil particle size fractionation (fine particle associated  
306 carbon), and differentiating by its chemical structures, have been adopted in the literature.  
307 Direct quantification of the abundance of adsorption sites (pore volume) was also employed  
308 in many studies.

### 309 ***Distinguishing SOM by humic substances***

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

- 313 1. fulvic acid (FA), which is dissolved at pH 13 and remains dissolved at pH 2
- 314 2. humic acid (HA), which is soluble in alkaline solutions and precipitates at pH <  
315 2;
- 316 3. humin (HM), which is insoluble at any pH (Kohl and Rice, 1998).

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

### 323 ***Distinguishing SOM by black carbon***

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

### 332 ***Distinguishing SOM by soil particle size***

333 Soil particle size fractions, in particular the clay and silt fractions, have been found to  
334 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):

$$341 \quad \text{FPAC} = (\text{silt} + \text{clay})/\text{TOC} \quad (4)$$

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

360 between the volumes of pores with diameters  $< 6$  nm ( $PF_{6\text{ nm}}$ ) and rapid desorption of PAHs  
361 (Luo *et al.*, 2012). Recent studies also observed significant negative correlations between  
362 bioavailability and bioaccessibility of PAHs and  $PF_{6\text{ nm}}$  (Duan *et al.*, 2014; Duan *et al.*, 2015a)  
363 (Table 3). The strong association between pore volume and bioavailability of HOC is further  
364 confirmed in studies that manipulated soil pore volume by using specific amendments. For  
365 example, amendment with porous carbonaceous materials such as biochar and activated  
366 carbon was found to significantly reduce PAH bioavailability and bioaccessibility due to the  
367 increased pore volumes of the amended soils (Zimmerman *et al.*, 2004; Zimmerman *et al.*,  
368 2005; Yang *et al.*, 2009; Semple *et al.*, 2013; Ogbonnaya *et al.*, 2014).

### 369 ***Evaluation of the effects of soil composition and properties***

370 The alkaline extraction of SOM has been adopted in environmental science for a long  
371 time but humic substances have been increasingly criticised as method-defined, pseudo-  
372 materials (Lehmann and Kleber, 2015). Importantly, alkaline extraction induces significant  
373 change in soils (Doick *et al.*, 2005). It is therefore very questionable whether such soil  
374 fractions can account for variations in PAH bioavailability and bioaccessibility. Similar  
375 criticisms were also made concerning the use of thermal and chemical oxidation to quantify  
376 black carbon. The potential charring of labile SOM during heating and loss of small  
377 particulate black carbon during chemical oxidation could cause both over- and under-  
378 estimation (Cornelissen *et al.*, 2005), thus compromising the relevance of the correlation  
379 between obtained black carbon fractions and PAH bioavailability/bioaccessibility. Physical  
380 fractionation of soil based on particle size was suggested to be more appropriate due to less  
381 disturbance being imposed on the soil matrix (Northcott and Jones, 2000; Doick *et al.*,  
382 2005). A couple of studies have provided good correlations between PAH  
383 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 ( $PF_{6\text{ nm}}$ ) 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

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

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



(Chen <i>et al.</i> , 2007)	naphthalene, phenanthrene	spiked	1 soil and its humic acid, humin, and deashed humin	sorption equilibrium	humins	NA
(Pan <i>et al.</i> , 2006)	phenanthrene, pyrene	spiked	4 soil with their humic fractions	sorption equilibrium	humins	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 <i>et al.</i> , 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 <i>et al.</i> , 2013)	16 USEPA PAHs	coking plant contaminated soil	1 soil and its size fractions	Tenax extraction	fine silt	NA
(Amellal <i>et al.</i> , 2001)	8 PAHs	spiked	1 soil and its size fractions	chloroform Soxhlet extraction	silt	NA
(Siciliano <i>et al.</i> , 2010)	11 PAHs	roadside and residential soils	18	SHIME model	particles size < 45 $\mu$ m	PAHs are 3.7 times higher in fraction with particle size < 45 $\mu$ m and highly resistant to SHIME extraction

## 424 6. Effects of environmental factors

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

429 Soil pH may be changed by environmental events like precipitation (McFee *et al.*,  
430 1977) or during desorption facilitated by receptors (Dean and Ma, 2007). Under different pH  
431 conditions, SOM existed in different physical forms (coiled or stretched) and exhibited  
432 differing sorptive capacity for HOCs, which lead to different bioavailability and  
433 bioaccessibility (Murphy *et al.*, 1994; Feng *et al.*, 2005, 2006). This was supported by the  
434 observation of greater  $K_{OC}$  values of organo-clay complexes for phenanthrene with  
435 decreasing pH (Feng *et al.*, 2006), and greater BaP oral bioavailability at higher pH (Duan *et al.*,  
436 2014). Higher pH also promoted desorption of SOM, and thus that of PAHs, as a result of  
437 their increased solubility in aqueous phases (Yu *et al.*, 2016).

438 Variation in temperature during ageing and subsequent desorption of soil PAHs was  
439 demonstrated to lead to different bioavailability.  $K_{OC}$  values for HOCs in soils are inversely  
440 related to temperature (Schwarzenbach *et al.*, 2005). Desorption of PAHs from soil could be  
441 enhanced by up to 28 times when the temperature rose from 7 °C to 23 °C (Enell *et al.*,  
442 2005). Temperature variations brought about by freeze-thaw cycles was reported to  
443 decrease the stability of soil aggregates and promote the ageing of soil PAHs (Lehrsch *et al.*,  
444 1991; Zhao *et al.*, 2009; Shchegolikhina *et al.*, 2012; Zhao *et al.*, 2013).

445 The moisture contents of soils change under field conditions and play an important  
446 role in determining bioavailability/bioaccessibility of soil PAHs. Bioavailability and  
447 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).

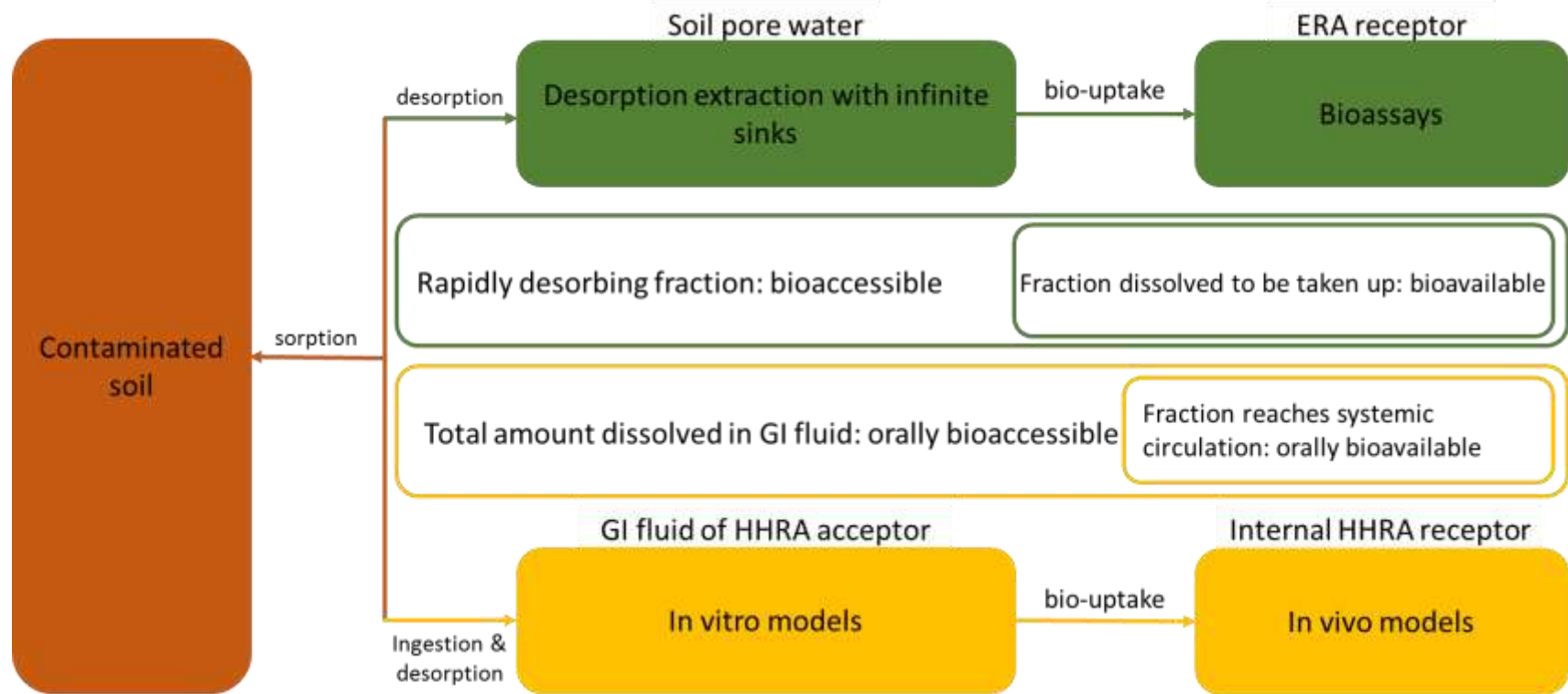
465 The receptors concerned in ERA are generally soil-dwelling organisms such as  
466 microorganisms, terrestrial invertebrates and plants. It was proposed that bioavailability is  
467 the quantity of a contaminant that is dissolved in the soil aqueous phase to cross the  
468 membranes of the receptors, 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.



**Total = un-extractable (non-desorbing) + extractable (rapidly, slowly, and very slowly desorbing)**  
**Extractable = non-bioaccessible (slowly and very slowly desorbing) + bioaccessible**  
**Bioaccessible = potentially bioavailable (rapidly desorbing) + bioavailable (dissolved)** } ERA

**Total = residual (un-dissolved in GI fluid) + orally bioaccessible (dissolved in GI fluid)**  
**Orally bioaccessible = orally bioavailable (absorbed) + non-bioavailable (un-absorbed)** } HHRA

505

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.

508 **8. Critique: what is ‘missing’ in our knowledge and how can we fill these gaps?**

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

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

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

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

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

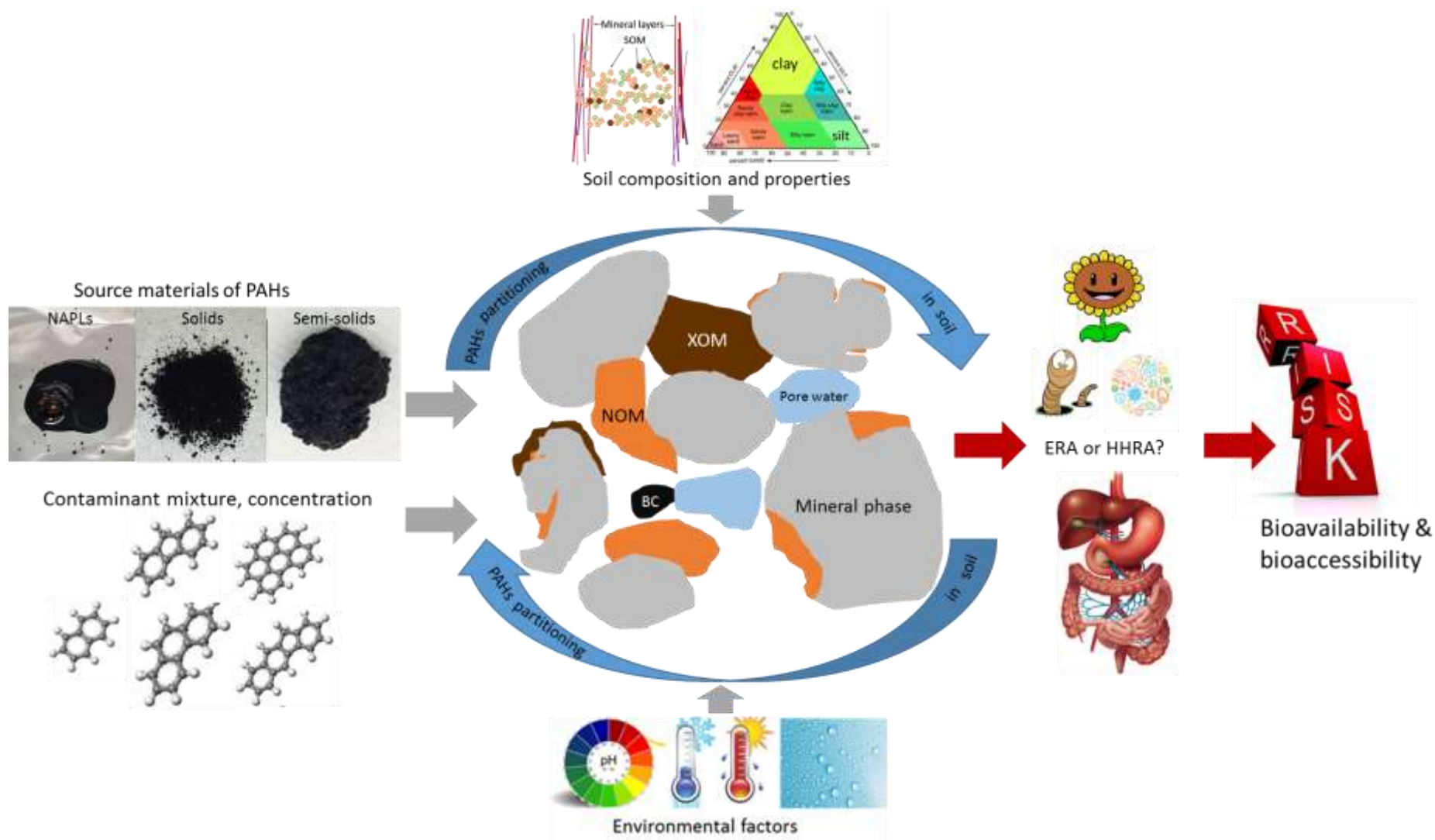
543 The effects of environmental factors, PAH concentration, and contaminant mixture  
544 on sorption and desorption of PAHs have been well-documented in the literature. The  
545 challenge now is to expand or extrapolate our knowledge obtained from controlled simple  
546 systems to more complex field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

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

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556

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

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