

## **Effect of Co-existing Heavy Metals and Natural Organic Matter on Sorption/Desorption of Polycyclic Aromatic Hydrocarbons in Soil: A Review**

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**ABSTRACT:** Polycyclic aromatic hydrocarbons (PAHs), abundant in mixed contaminant sites, often coexist with heavy metals. The fate and remediation of PAHs depend heavily on the sorption and desorption behavior of these contaminants. The sorption behavior can in turn be highly affected by certain soil components and properties, such as soil organic matter (SOM) and the presence of heavy metals. Through review of the literature focused on research from 2006 to 2018, this paper discusses interactions, challenges, influencing factors and potential synergies in sorption/desorption of mixed PAHs and heavy metal contamination of soil. The presence of either natural organic matter or heavy metals can enhance the sorption capability of fine soil, retarding the PAHs in the solid matrix. The co-existence of SOM and heavy metals has been reported to have synergistic effect on PAHs sorption. Enhanced and surfactant desorption of PAHs are also affected by the presence of both SOM and metals. Remediation techniques for PAHs removal from soil, such as soil washing, soil flushing and electrokinetics, can be affected by the presence of SOM and heavy metals. More detailed studies on the simultaneous effects of soil components and properties on the sorption/desorption of PAHs are needed to enhance the effectiveness of PAHs remediation technologies.

**Keywords:** PAHs sorption/desorption; soil organic matter; heavy metal effect.

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### **INTRODUCTION**

Polycyclic aromatic hydrocarbons (PAHs) constitute a group of chemical compounds containing benzene rings in their molecular structure. PAHs are naturally present in oil and bitumen and can form during incomplete combustion (Omores et al., 2017). Certain PAHs, such as benzo[a]pyrene, can interact with DNA and are genotoxic (Ewa and Danuta, 2017; Jiao et al., 2017). Other adverse health effects of PAHs include

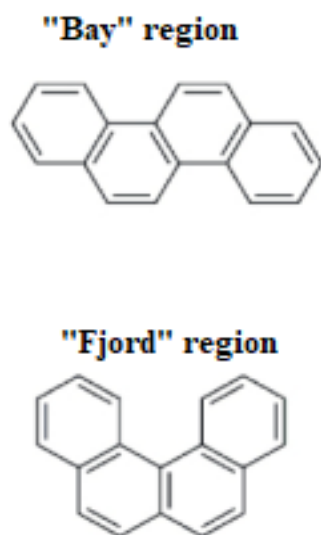
carcinogenicity, birth defects, and skin and liver damage. There is human health risk in both short and long-term exposure to PAHs (ATSDR, 2009; ATSDR, 1995).

The U.S. Environmental Protection Agency has selected sixteen PAHs as priority pollutants (USEPA, 2008; USEPA, 1993). PAHs molecular structures, can affect human health (Ewa and Danuta, 2017). For example, structural features formed between aromatic rings named as “fjord” or “bay” regions (Fig. 1) are important in determining

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the health effects of PAHs. Molecules contain “fjord” regions (such as dibenzo[a,l]pyrene) prefer to bind to adenine nucleotides, whereas PAHs having a “bay” region (such as benzo[a]pyrene) bind to guanine nucleotides. PAHs containing both four or more rings and a “bay” region in their structure can induce gene mutations that initiate cancer whereas others with 2 to 4 aromatic rings are known as co-carcinogens, affecting cancer promotion or progression (Bostrom et al., 2002; Baird et al., 2005).



**Fig. 1. Bay and fjord regions in PAHs molecular structures**

Table 1 and Fig. 2 provide the names, molecular structures, properties and chemical structures of the 16 USEPA priority PAHs. Because of toxicity, ecosystem life cycling, and non-degradability of heavy metals (HMs), they are of environmental concern. Accumulation of HMs in the environment, particularly in soil and sediment, is a common problem in many countries (Su et al., 2014); with negative impact on people on a global scale (UNEP, 2012). Although

HMs is naturally present in soil as background content, they are present at much higher concentrations in heavy-metal-contaminated soils.

The major sources of PAHs in the environment are oil and gas and related products production, storage and transportation, and spills (Choi et al., 2009; CCME, 2010a). There are some natural sources, such as volcanoes and forest fires as well. Many of these sources release both PAHs and toxic heavy metals into the environment. Therefore, due to their common sources, PAHs coexist with heavy metals in many contaminated soils (Fazeli et al., 2019; Marija et al., 2017; Wang et al., 2004; Morillo et al., 2008; Thavamani et al., 2011; Thavamani et al., 2012).

There are thousands of contaminated sites around the world. There were estimated to be 294,000 in the US (USEPA, 2004). 1337 superfund sites are listed in a national priorities list of the United States (USEPA, 2019). In Canada, there are 22, 000 federal contaminated sites (FCSI, 2018). These numbers are likely to increase as contaminated sites continue to be identified. About 29% of contaminated sites in the US contain a single contaminant (metals, PAHs, PCBs or VOCs), whereas 71% are contaminated by two or more types of contaminant (USEPA, 2018). Among the contaminated sites, 12.3 and 3.7% are contaminated by mixed heavy metals and PAHs in the US and Canada, respectively (USEPA, 2018; FCSI, 2018). Many other sites contain other types of contaminants in addition to HMs and PAHs (Afkhami et al., 2013). Table 2 summarizes the proportions of sites contaminated solely by metals, PAHs or both in the US, Canada and Europe.

Remediating these mixed-contaminated sites poses great challenges, because of the different physicochemical properties and the broad ranges of contaminants, each requiring different technologies (Eghbal et al., 2019).

Table 1. USEPA's 16 priority pollutant PAHs and selected properties (Wick et al., 2011; CCME, 2010b)

PAH name	Number of rings	Molecular Weight G mol <sup>-1</sup>	Water solubility mg l <sup>-1</sup>	Log K <sub>ow</sub> **	Log K <sub>oc</sub> ***	Vapor pressure mmHg	Henry's law constant atm-m <sup>3</sup> mol <sup>-1</sup>
Acenaphthene	3	154.2	1.93	3.98	3.66	4.47×10 <sup>-3</sup>	7.91×10 <sup>-5</sup>
Acenaphthylene	3	152.2	3.93	4.07	1.40	0.029	1.45×10 <sup>-3</sup>
Anthracene	3	178.2	0.076	4.45	4.15	1.7×10 <sup>-5</sup>	1.77×10 <sup>-5</sup>
Benzo[a]anthracene*	4	228.2	0.01	5.61	5.30	2.2×10 <sup>-8</sup>	1×10 <sup>-6</sup>
Benzo[a]pyrene*	5	252.3	2.3×10 <sup>-3</sup>	6.06	6.74	5.6×10 <sup>-9</sup>	4.9×10 <sup>-7</sup>
Benzo[b]fluoranthene*	5	252.3	0.0012	6.04	5.74	5×10 <sup>-7</sup>	1.22×10 <sup>-5</sup>
Benzo[k]fluoranthene*	5	252.3	7.6×10 <sup>-4</sup>	6.06	5.74	9.59×10 <sup>-11</sup>	3.87×10 <sup>-5</sup>
Benzo[g,h,i]perylene*	6	276.3	2.6×10 <sup>-4</sup>	6.50	6.20	1.03×10 <sup>-10</sup>	1.44×10 <sup>-7</sup>
Chrysene*	4	228.3	2.8×10 <sup>-3</sup>	5.16	5.30	6.3×10 <sup>-7</sup>	1.05×10 <sup>-6</sup>
Dibenz[a,h]anthracene*	6	278.3	5×10 <sup>-4</sup>	6.84	6.52	1×10 <sup>-11</sup>	7.3×10 <sup>-8</sup>
Fluoranthene	4	202.3	0.2-0.26	4.90	4.58	5×10 <sup>-6</sup>	6.5×10 <sup>-6</sup>
Fluorene	3	166.2	1.68-1.98	4.18	3.86	3.2×10 <sup>-4</sup>	1×10 <sup>-4</sup>
Indeno[1,2,3-c,d]pyrene*	6	276.3	0.062	6.58	6.20	1×10 <sup>-10</sup>	6×10 <sup>-8</sup>
Naphthalene	2	128.2	39.06	-	-	-	-
Phenanthrene	3	178.2	1.20	4.45	4.15	6.8×10 <sup>-4</sup>	2.56×10 <sup>-5</sup>
Pyrene	4	202.3	0.077	4.88	4.58	2.5×10 <sup>-6</sup>	1.14×10 <sup>-5</sup>

\* The USEPA has classified these PAH as possible human carcinogens

\*\* Octanol-Water partition coefficient

\*\*\* Organic carbon-water partition coefficient

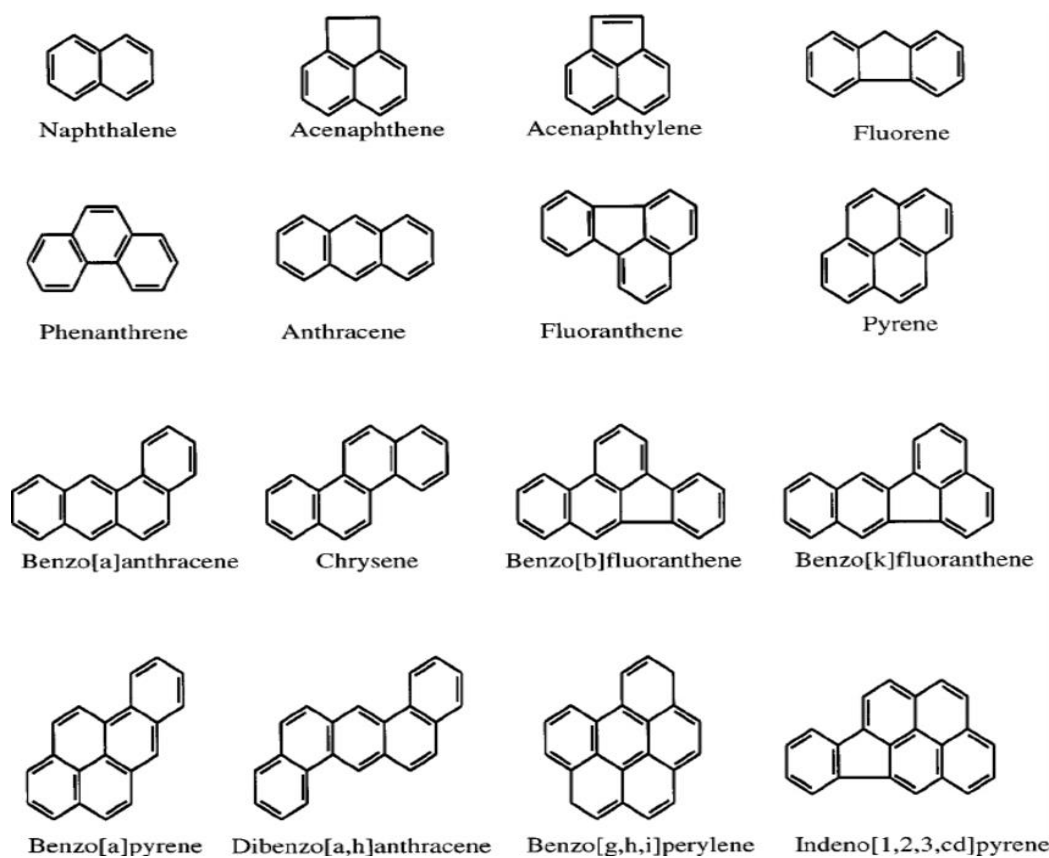


Fig. 2. Molecular structures of 16 PAHs in priority list of the USEPA

**Table 2. Sites contaminated solely by metals, PAHs or both in the US, Canada and Europe (% of total contaminated sites in each)**

Region	Solely HM contamination	Solely PAH contamination	Mixed contamination by PAH+ HMs	Reference
USA	16.8%	4.3%	12.4%	USEPA (2018)
Canada	34.1%	2.6%	3.7%	FCSI (2018)
Europe	34.8%	10.9%	–	Panagos et al. (2013)

Since HMs are neither biodegraded nor transported by air in soil matrices, a technology for simultaneous remediation of PAHs co-existing with HMs in soil should be either based on desorbing and solubilizing them into a liquid to carry the mixed contaminants, or solidifying/stabilizing them into the soil matrix. However, sorption/desorption behavior and reaction kinetics influence the mobility and subsequent removal of the contaminants in soil.

Except for naphthalene, because of low solubility and high sorption affinity to soil and organic matter of PAHs, the chemical fate of PAHs is predominantly controlled by sorption and desorption processes in soil environments. From an enhanced soil washing/flushing remediation point of view, sorption/desorption and mobility of contaminants influence the remediation reaction/retention times, clean-up efficiency and cost of remediation.

Given that in the soils of many PAH contaminated sites, there are co-existing heavy metals, there is a need to study sorption/desorption of PAHs co-existing with heavy metals in soil. Among soil characteristics, organic matter content is vital to sorption/desorption, ultimate fate and mobility of both PAHs and HMs in soil (Kaschl et al., 2002). PAHs and HMs both interact with organic matter in soil-water systems (Gao et al., 2006; Zhang and Ke, 2004). Therefore, sorption/desorption of PAHs can be influenced by the presence of heavy metals in the system (Walter and Weber, 2002). Understanding these mechanisms for PAHs in soil is vital to better assess soil pollution risks, as well as to design remediation systems based on enhanced soil washing/flushing.

Among the soil properties influencing

sorption of PAHs onto soil, organic matter content seems to be the most important one. From the remediation of PAH-contaminated, co-existing heavy metals point of view, the effect of heavy metals on the sorption/desorption of PAHs in soil is an essential, but less studied, subject. Therefore, the main objective of this chapter is to review and evaluate the probable effect of soil organic matter and co-existing HMs on sorption/desorption of PAHs, based on previously published literature. The contents of this chapter should help researchers find gaps in the field of sorption/desorption of PAHs in soil, taking into account the effects of co-existing HMs and SOM.

## METHODOLOGY

In this study literature on the sorption and desorption of PAHs in soil is reviewed with emphasis on the effect of soil organic matter and co-existing heavy metals on the process. References are used to explain principles of PAHs sorption and affecting factors. More recent published research (from 2006 to 2018) relevant to the aim of this chapter were collected and reviewed to be summarize and presented in the following sections; i) sorption of PAHs in soil, ii) effect of soil organic matter on PAHs sorption, iii) effect of co-existing heavy metals, iv) other factors related to PAH sorption, v) desorption of PAHs. Based on the review, conclusions and future research needs are identified.

### Sorption of PAHs in soil

The term "sorption" is used to cover the adhesion of contaminants to solid particles by absorption, adsorption, ion exchange and partitioning mechanisms. Sorption can occur by several mechanisms, including absorption

into soil natural organic matter (partitioning); adsorption to mineral surfaces via van der Waals/London dispersion forces; adsorption through electrostatic attractive forces to sites with opposite charge on solid surfaces; and chemical sorption (covalent bonding to surface functional groups) on the soil solid particles (Hemond and Fechner-Levy, 2015).

If the adsorbed molecules interact with solid surface physically, the process is called physisorption. On the other hand, if there is chemical bonding between adsorbed molecules and the solid surface, the adsorption process is called chemisorption. Chemisorption is mostly irreversible and occurs only as a monolayer. Depending on the sorbent, sorbate and the environmental conditions, physisorption and chemisorption may occur simultaneously or alternatively. For hydrophobic organic contaminants, partitioning into soil organic matter in soil-water system often takes place.

Solids capable of sorbing PAHs in soil include minerals, particularly clay minerals, and natural organic matter. Many sorption reactions are completely or partly reversible. Depending on the conditions, nature and composition of the sorbent and sorbate chemical, the relationship between the amounts of dissolved contaminant in the aqueous phase and the amount of sorbed (partitioning), may be linear or non-linear. The distribution coefficient ( $K_d$ ) represents a ratio, indicating the amount of sorbed contaminant to its aqueous phase equilibrium concentration:

$$K_d = (C_s / C_e) \quad (1)$$

where  $K_d$  is distribution coefficient ( $L^3 M^{-1}$ ),  $C_s$  is the concentration of sorbed contaminant in soil ( $M M^{-1}$ ) and  $C_e$  is the equilibrium concentration of sorbate in aqueous phase ( $M L^{-3}$ ). There are many non-linear equations, called isotherm equations, expressing the relationship between the sorbed contaminants and sorbate concentration. Among these, the Freundlich and Langmuir isotherms are

most often used to describe the sorption of contaminants in soil environments. The Freundlich isotherm equation is

$$C_s = K_f (C_e)^n \quad (2)$$

whereas the Langmuir isotherm equation is

$$C_s = (bkC_e) / (1 + kC_e) \quad (3)$$

$K_f$  is the Freundlich constant,  $n$  a constant reflecting the degree of non-linearity,  $C_s$  is the concentration of sorbed contaminant in soil ( $M M^{-1}$ ) and  $C_e$  is the aqueous equilibrium concentration of sorbate ( $M L^{-3}$ );  $b$  and  $k$  are Langmuir constants, with  $k$  reflecting the maximum sorption capacity of a sorbent.

Table 3 summarizes research on the sorption of PAHs onto soil/minerals since 2006. Because sorption is a key process in the fate, transport and remediation of PAHs in contaminated soil, this information can also be useful for such studies in contaminated sites. It can be concluded that parameters, test conditions, contaminants and results of published studies on sorption of PAHs onto soil/minerals are too scattered for there to be simple plain rules. Most previous studies on PAH sorption are conducted through batch tests, with phenanthrene, pyrene and naphthalene receiving the greatest attention. The best-fitted isotherm models have been reported to be those of Freundlich and Langmuir, in that order. Linear behavior is reported for sorption of benzo(a)pyrene onto minerals, phenanthrene onto quartz (Muller et al., 2007), phenanthrene onto poor-organic content soils and phenanthrene sorption from dilute solutions ( $< 100 \mu g L^{-1}$ ) (Sun et al., 2010). Most tests are performed at room temperature or 20-25 °C, but some studies have examined the sorption of PAHs at 10 and 15°C (Ping et al., 2006; Kaya et al., 2013) and 40 and 50°C (Rivas et al., 2008), in addition to 20°C. Overall, findings indicate that sorption is higher at lower temperatures.

Other test conditions and results are very scattered. Contact times tested have varied

from 20 min to more than 48 h. Times needed to reach sorption equilibrium have been reported to be from 4 h to more than 34 h. However, it seems that in most cases there is rapid sorption in the first 10 to 90 min during which about 90% of the overall sorption takes place (Muller et al., 2007; Rivas et al., 2008; Sun et al., 2010; Osagie and Owabor, 2015 a,b). Initial concentrations of PAHs in solution were in the wide range of 0.0006 to 400 mg L<sup>-1</sup>. Even sorbent-to-solution ratio and amounts used in tests have

varied widely. Therefore, it is not surprising that the results on PAHs sorption amounts and coefficients have varied greatly from study to study. For example, K<sub>f</sub> values in different studies for phenanthrene have ranged from 0.21 to 220 L kg<sup>-1</sup> for different soils and minerals under different test conditions. In addition, sorption amounts of phenanthrene have been reported to range from three to 400 mg kg<sup>-1</sup> for soils and minerals with different compositions.

**Table 3. Summary of research studies and results for sorption of PAHs onto soils/minerals**

PAHs	Sorbent material	Sorption test conditions	Sorption model (isotherm)	Sorption capacity/property <sup>c</sup>	Highlighted findings	Comments/Limitations	Reference
PHE <sup>a</sup>	HA <sup>b</sup> and FA	Batch 1 mg L <sup>-1</sup> PHE mixed with HA and FA 0-10 g kg <sup>-1</sup> soil for pH range 3-6 for 24 h Temperature effect examined at pH 3 for temperatures of 15 and 25°C	Freundlich	Highest adsorption was at pH 3 for HA K <sub>f</sub> values for HA: 221 L kg <sup>-1</sup> for FA: 176 L kg <sup>-1</sup>	Sorption was higher at 15°C than at 25°C		Ping et al. (2006)
PHE, PYR <sup>d</sup> , BAP <sup>e</sup>	quartz, goethite-coated quartz, and quartz-montmorillonite mixture	Batch tests From 4 to 20 h at 8 time steps Initial concentration: 10% of each PAH aqueous solubility Sorbent to solution ratio: 1:5 (15 g 75 mL)	Freundlich: PHE and PYR Linear: PHE to quartz Linear: BAP	K <sub>f</sub> values; PHE: 0.21-2.46 L kg <sup>-1</sup> PYR: 0.36-3.43 L kg <sup>-1</sup> K <sub>d</sub> values; BAP: 48-154 L kg <sup>-1</sup> PHE to quartz: 0.2 L kg <sup>-1</sup>	Equilibrium time: 4 h Instantaneous kinetics Cation-π interactions seemed an important sorption and retention mechanism for low organic matter soil environments	PHE and PYR showed the weakest sorption onto quartz-montmorillonite mixture in spite of the greatest surface area	Muller et al. (2007)
ANA <sup>f</sup> , PHE, AN <sup>g</sup> , FLAN <sup>h</sup>	Natural soil	Batch Temperature 298, 313, and 333 K	Oswin, Freundlich and Caurie		Three PAHs except for acenaphthene showed anomalous isotherms when tested individually As mixture non showed abnormal sorption trend Sorption kinetics was quite fast (10-20 min) Sorption amounts order is the same order as the solubility of PAHs (ANA > PHE > FLAN > AN)	trapping of PAHs by SOM released to water is the main cause No information given on soil properties other than SOM and particle size	Rivas et al. (2008)
PHE, PYR	8 European soils	24 h Batch Initial concentrations: PYR: 0.0009 to 0.1 mg L <sup>-1</sup> PHE: 0.0006 to 1.1 mg L <sup>-1</sup>	Freundlich	PYR: 3-4.5 mg kg <sup>-1</sup> PHE: 30-50 mg kg <sup>-1</sup>	Freundlich sorption coefficients, correlated well with the soil organic carbon contents Sorption predictions based on organic matter and one additional simple soil parameter (e.g., clay content, cation exchange capacity, or pH) yielded accurate sorption predictions of Freundlich coefficient	Sorption could not be predicted from soil organic carbon contents alone	De Jonge et al. (2008)
PHE	Different natural soil samples: top, aeration zone, and aquifer zone soil samples	Sorbent to solution: 3.5 g: 210 mL From 20 to 480 min in 7 time steps	Linear in OM-poor soil Linear at < 100 µg L <sup>-1</sup> of PHE in solution Nonlinear at > 100 µg L <sup>-1</sup> of PHE in solution	< 50 µg g <sup>-1</sup> in soils at < 1.5% OM 90-100 µg g <sup>-1</sup> in soils at > 1.5% OM	Equilibrium time: 8 h (90% of sorption in first 1.5 h) The more organic content the more time to reach sorption equilibrium linear relation between organic fraction of the soil and Freundlich sorption coefficient	Soil samples texture and compositions not determined Single contaminant	Sun et al. (2010)
PHE	Cation modified clay minerals (smectite, kaolinite, vermiculite)	Batch Initial concentration: 0.025-1.0 mg L <sup>-1</sup> Minerals modified by Na, K and Ca cations Contact time: 48 h at 25°C	Freundlich	K <sub>f</sub> values for Ca, K and Na modified Smectite: 20.72, 14.65, 13.72 L kg <sup>-1</sup> for kaolinite: 7.39, 6.83, 6.61 L kg <sup>-1</sup> for vermiculite: 7.22, 7.8 9.694 L kg <sup>-1</sup>			Zhang et al. (2011)
NAP <sup>i</sup>	NB <sup>j</sup> and HB <sup>k</sup>	Batch Sorbent to solution: 0.05: 50 g mL <sup>-1</sup> Initial concentration: 7.5-20 mg L <sup>-1</sup> At 10, 15 and 20°C	Freundlich, Langmuir	22.45 mg g <sup>-1</sup>	K <sub>f</sub> values; for NB: 0.397-0.706 L g <sup>-1</sup> for HB: 1.58-3.66 L g <sup>-1</sup>		Kaya et al. (2013)
FL, PHE, FLAN, PYR	Silty-clay soil	Column test Test duration: 34 d Constant flow rate: 200 mL d <sup>-1</sup> Initial concentrations: 100 µg L <sup>-1</sup>	Langmuir		1 <sup>st</sup> -order Lagergren and Bangham equation describes sorption rate. Clay minerals responsible for sorption because of low soil SOM Sorption is not completely reversible. Sorption kinetics follows a 2 <sup>nd</sup> -order kinetics model.	Types and content of soil clay minerals not determined	Yang et al. (2013)

**Table 3. Summary of research studies and results for sorption of PAHs onto soils/minerals (continued)**

PAHs	Sorbent material	Sorption test conditions	Sorption model (isotherm)	Sorption capacity/property <sup>c</sup>	Highlighted findings	Comments/ Limitations	Reference
PHE and PYR	Two types of natural soil; sandy loam and clay loam	Batch PAH solution concentrations: 50-400 mg L <sup>-1</sup> contact time: 24 h	Freundlich	350-400 mg kg <sup>-1</sup>	SOM is predominant in PAHs sorption More SOM led to more sorption and less desorption		Yu et al. (2014)
NAP	Sandy soil (sieved to < 2.5 mm) Clay soil (sieved to < 220 μm)	Batch solution/sorbent: 500 mL:100 g PAH solution concentration range: 50-250	Freundlich for clay soil Langmuir for sandy soil	5.73	Equilibrium time: 20 and 24 h for sandy and clay soil Sorption kinetics fits pseudo-2 <sup>nd</sup> order model	Correlation between model and observed data was lower for sandy soil than for clay soil Correlations for kinetics model and observed data were much lower in clay soil than sandy soil Single contaminant study	Osagie and Owabor (2015a)
PYR	Sandy soil (sieved to < 2.5 mm) Clay soil (sieved to < 220 μm)	Batch solution/sorbent: 500 mL:100 g PAH solution concentration range: 50-250	Langmuir	0.286 mg g <sup>-1</sup> for clay 0.225 mg g <sup>-1</sup> for sandy soil	Sorption kinetics fits pseudo-2 <sup>nd</sup> order model Equilibrium time: 28 and 34 h for sandy and clayey soil Pseudo-2 <sup>nd</sup> order rate constant: 0.00088 for clay and 0.00085 for sandy soil	Single contaminant Correlations between kinetics model and observed data were lower for clay soil than sandy soil Correlation between sorption isotherm model and observed data were not very high	Osagie and Owabor (2015b)
PHE, PYR, FLAN	River sediment	Batch Initial concentration of each PAH: 10-100 mg L <sup>-1</sup> Mixing at 25°C for 8 h sediment size with highest sorption: < 38 μm.	Freundlich	K <sub>f</sub> values: phenanthrene: 88.54 L g <sup>-1</sup> fluorene: 188.71 L g <sup>-1</sup> pyrene: 91.46 L g <sup>-1</sup>			Wang et al. (2015)

<sup>a</sup> PHE: Phenanthrene, <sup>b</sup> HA: Humic acid, FA: Fulvic acid, <sup>c</sup> K<sub>f</sub>: Freundlich sorption coefficient, <sup>d</sup> PYR: Pyrene, <sup>e</sup> BAP: Benzo(a)pyrene, <sup>f</sup> ANA: Acenaphthene, <sup>g</sup> AN: Anthracene, <sup>h</sup> FLAN: Fluoranthene, <sup>i</sup> NAP: Naphthalene, <sup>j</sup> NB: Natural bentonite, <sup>k</sup> HB: Modified bentonite

### Effect of soil organic matter

Natural organic compounds entering natural systems undergo complex microbial and abiotic transformations that produce what is called natural organic matter (NOM). NOM contains fulvic, humic and humin materials. In general, NOM refers to thousands to tens of thousands of different complex chemical structures, such that no two molecules can be found to be identical (Hayes et al., 1990; Suffet and MacCarthy, 1989).

While recent research (Saeedi et al., 2018a; Zhang et al., 2010; Zhang et al., 2011) has shown that PAHs can adsorb onto clay minerals in soil matrix, it is widely believed that the partitioning (absorption) into the natural organic matters of soil (SOM) is the primary sorption mechanism of PAHs (Ping et al., 2006). Polarity, aromatic carbon and aliphatic groups of organic matter are believed to control the PAHs sorption onto soil. Aromatic domains of organic matter have also been reported to play an important role in sorption PAHs to soil and sediment (Ahangar, 2010). Based on the

assumption that soil organic matter is mainly responsible for PAH sorption, methods have been developed for approximating K<sub>d</sub>, taking both sorbate and sorbent properties into consideration. Since PAHs are mostly non-polar hydrocarbons, they have large octanol-water partitioning coefficient (K<sub>ow</sub>) values, showing less tendency to dissolve in water and more tendency to sorb onto organic matter of the soil. Larger PAH molecules with higher K<sub>ow</sub> are more likely to sorb onto soil particles. To predict K<sub>d</sub> values for a given PAH in soil, the fraction of organic carbon of the soil (f<sub>oc</sub>) and the K<sub>ow</sub> of the PAH are used. In this method, it is assumed that the sorption occurs as soil organic matter partitioning. K<sub>d</sub> is then calculated as;

$$K_d = f_{oc} \cdot K_{oc} \quad (4)$$

where f<sub>oc</sub> is the organic carbon fraction in the soil, and K<sub>oc</sub> (chemical concentration sorbed to organic carbon/chemical concentration in water) is the organic carbon-water partition coefficient.

Based on laboratory data, several regression equations have been reported in

the literature for different organic chemicals to predict  $K_{oc}$  as a function of  $K_{ow}$  (Lyman et al., 1990). Based on this approach, one can calculate the  $K_d$  (sorption or distribution coefficient) values for a given PAH using  $K_{ow}$  of that PAH and the measured organic carbon of the soil.

De Jonge et al. (2008) reported that  $K_d$  values of a given PAH with different sorbents were proportional to the organic carbon contents of the soil. Important characteristics of organic matter in the sorption of PAHs are chemical properties, molecular sizes, and functional groups. Fig. 3 depicts the two representative structures of NOM, with (a) showing the structure of fulvic acid and (b) a conceptualized NOM structure (Dunnivant and Anders, 2005). As shown in Fig. 3, there are numerous hydrophobic centers and ionic sorption sites in such large organic matter molecules. These are key

features that can enhance the sorption of polar organic compounds, HOCs such as PAHs, and ionic contaminants such as heavy metals, in soils containing NOM compared to the same soil without any NOM.

The chemical functionality of NOM is also important in its effect on the sorption of different contaminants in soil environments. The main functional groups observed and identified in NOM are summarized in Table 4. Water molecules in soil can form hydrogen bonds with charged and polar functional groups. The density of these groups results in hydrophobic character to organic matter on a macroscopic scale (Laird and Koskinen, 2008). On the other hand, aliphatic groups may form localized hydrophobic regions on a molecular scale. Therefore, NOM in soil can enhance sorption of both heavy metals and PAHs.

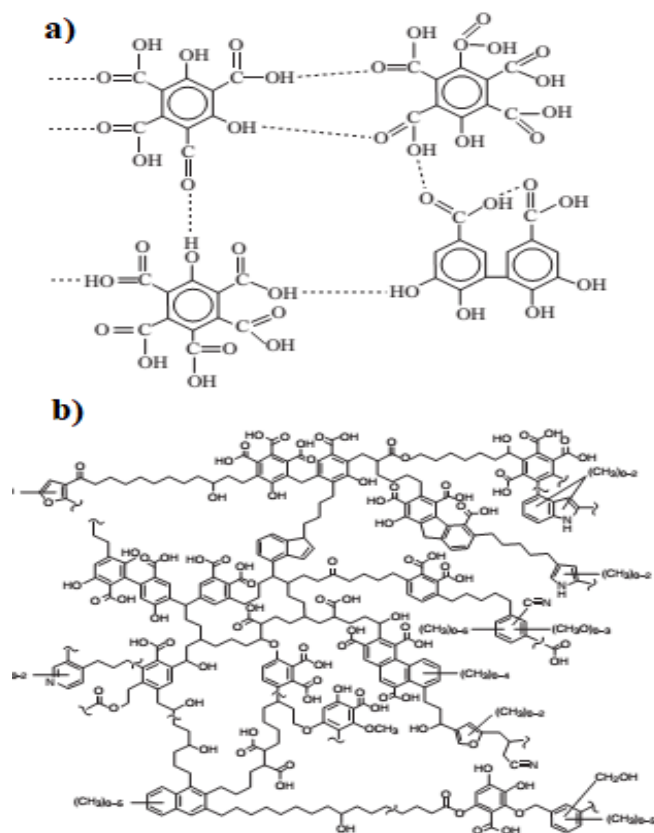









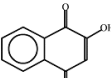

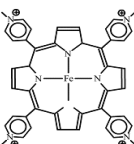


Fig. 3. Structures of natural organic matter (Dunnivant and Anders, 2005), a) representative of fulvic acid, b) a conceptualized NOM structure



**Table 4. Functional groups identified and observed in different NOM (Dunnivant and Anders, 2005; Killops and Killops, 1993)**

Symbol/molecular structure	Name	Resulting compound
ROH	Hydroxyl	Alcohol Phenol
	Carbonyl	Aldehyde Ketone Quinone
	Carboxyl	Carboxylic acid
	Oxo	Ether
	Amino	Amine
	Amido	Amide
	Thio	Thiol
	R=CH <sub>2</sub> Indenyl R= O Furanyl R= NH Pyrrol R= S Thiophenyl	Indene Furan Pyrrole Thiophene
	R= CH Phenyl R= N Pyridinyl	Benzene Pyridine
	Pyranyl	Pyran
	LAW	H <sub>2</sub> LAW
	Quinone	Hydroquinone
	Iron (II) Porphyrin	Iron (II) Porphyrin

Several researchers (Hassett et al., 1980; Means et al., 1980; Delle Site, 2001; Ping et al., 2006) have shown that there are good correlations between the sorption of PAHs and other hydrophobic organic compounds (HOCs), and SOM. Hassett et al. (1980) showed that factors such as total clay content and mineralogy, cation exchange capacity, surface area and pH were not significant compared to organic matter of the soil in sorption of dibenzothiophene by soil and sediment.

Other researchers have demonstrated the role of SOM in sorption of HOCs by

removing NOM from the soil by extractants or by oxidation, then investigating the sorption process (Yaron et al., 1967; Wolcott et al., 1970; Wahid and Sethunathan, 1979). They concluded that, in addition to NOM, other soil properties appear to be responsible for sorption, but their role could be masked by the SOM effect. For "organic poor" soils, at no or low organic matter content, sorption coefficients ( $K_d$ ) are expected to be much lower than in the same soil at high OM contents (Schwarzenbach and Westall, 1981).

On the importance of the OM in

controlling sorption of HOCs with water solubility less than  $10^{-3}$  M (all USEPA-listed PAHs except naphthalene, acenaphthene and acenaphthylene), the following constants have been defined (Delle Site, 2001):

$$K_{om}=K_d / f_{om} \quad \text{or} \quad K_{oc}=K_d / f_{oc} \quad (5)$$

where  $f_{om}$  and  $f_{oc}$  denote the fractions of organic matter and organic carbon (OC) in the soil, respectively.  $K_{om}$  and  $K_{oc}$  are expressed in  $\text{cm}^3 \text{g}^{-1}$  or  $\text{dm}^3 \text{kg}^{-1}$  of organic matter and organic carbon, respectively. The association of HOCs with SOM is attributable to hydrophobic bonding because of combined van der Waals forces thermodynamic gradient that drives non-polar organics out of aqueous solution. The interactions of non-polar organic compounds with SOM are thermodynamically preferred to those of compound-water or compound-compound (Gauthier et al., 1987; Weber et al., 1991). Some previous researchers have provided a “rule of thumb” to determine if SOM or clay minerals are responsible for sorption of HOCs in a given soil. HOCs sorption on clay surfaces dominates the organic matter partitioning if the clay/OC ratio is high (Karickhoff, 1984; Weber et al., 1992). A ratio of (clay mineral)/(organic carbon) = 30 (corresponding to a clay/OM ratio of 15) was proposed by Karickhoff (1984) as a threshold. Therefore, regardless of the mineral content, if the mass ratio of clay mineral to OM in soil  $< 30$ , mineral contributions in sorption is masked by organic matter. The ratio, however, might depend on the hydrophobicity of the sorbate, type of minerals, and functional groups and chemical composition of OM.

The critical organic carbon fraction ( $f_{oc}$ ), below which mineral adsorption dominates over OM partitioning of HOCs, was suggested by McCarty et al. (1981) to be:

$$f_{oc} = SA / [200 (K_{ow})^{0.84}] \quad (6)$$

where SA is the specific surface area of the mineral.

Table 5 summarizes recent studies on the effect of soil organic matter on sorption of PAHs onto soil. These studies confirm the enhancing effect of SOM on sorption of PAHs. However, reports show that the composition of SOM is important in the sorption of PAHs. Ping et al. (2006) reported that fulvic acids do not enhance the sorption of phenanthrene at low pH. Wu et al. (2011) also found that pH had no significant effect on the sorption of phenanthrene onto organic matter-added montmorillonite. While PAHs tend to sorb onto fulvic and humic acids rather than humins in soil, the fraction of larger PAH molecules sorbed onto humins is greater than the fraction sorbed onto lower molecular weight PAHs (Yang et al., 2010). On the other hand, Ukalska-Jaruga et al. (2018) reported that low-molecular-weight (two and three rings) PAHs had stronger bonds with humins in contaminated natural soil. They found no significant relationship between humic and fulvic acids for PAHs accumulation in contaminated soil. Yang et al. (2010) also noted that with increasing SOM, most PAHs tend to accumulate in fulvic acids rather than humins.

Overall, although it is well known that SOM enhances PAHs sorption, there seems to be a minimum level of SOM in soil for them to predominate. Although threshold ratios and relationships like equation 2.6 have been suggested for the minimum level, it appears to be interrelated with the properties and composition of both SOM and other components of soil, as well as mineralogy. Most previous studies indicate that the Freundlich isotherm is commonly a good model for sorption of PAHs in soil containing organic matter. It has also been found that increasing SOM content slows the rapid phase of PAH sorption towards reaching equilibrium.

**Table 5. Summary of recent research results on the effect of soil organic matter on PAHs sorption and retention**

Soil	Types of PAHs	Description of the study	Highlighted findings	Reference
Agricultural top soil treated with humic acid (HA) and fulvic acid (FA)	Phenanthrene	<p>Isotherm tests conducted at initial concentrations of 0.025, 0.050, 0.100, 0.25, 0.50, and 1.0 mg L<sup>-1</sup>; 15 and 25°C temperatures tested, test duration: 24 h</p> <p>Exogenous humic acids (HAs) were added to soil to enhance the amount of soil organic carbon (SOC) by 2.5, 5.0, and 10.0 g kg<sup>-1</sup></p> <p>Sorption and desorption for pH of 3 and 6 and at 15 and 25°C were evaluated,</p>	<p>Humic acid and fulvic acid showed different effects on adsorption.</p> <p>Adsorption increased at first, then decreased with increasing fulvic acid</p> <p>At pH=3, Adsorption in FA treated soil was lower than untreated and HA treated soil</p> <p>Sorption fitted the Freundlich isotherm HA increased Freundlich sorption coefficients</p>	Ping et al. (2006)
8 European soils with different properties	phenanthrene, pyrene	24 h Batch tests	<p>Freundlich sorption coefficients correlated well with soil organic carbon content.</p> <p>Soil organic carbon content alone is not adequate for sorption behavior quantitative predictions.</p>	De Jonge et al. (2008)
Five surface soil samples from Shisanlin, Beijing, with different SOM and humic acids, fulvic acids and humins	acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene	Studied impact of SOM on distribution of PAHs in soils.	<p>Humins sorbed fraction of PAHs increased with increasing PAH molecular weight</p> <p>Sorption of PAHs increased with increasing SOM content in soil.</p> <p>With increasing SOM, fraction of each individual PAH in fulvic acids increased, whereas the fraction in humins decreased.</p>	Yang et al. (2010)
Montmorillonite (MMT) and dissolved organic matter (DOM) modified montmorillonite (DOM-MMT)	Phenanthrene	<p>Batch sorption tests were carried out as a function of contact time, temperature, and adsorbent dose.</p> <p>Sorption at 25, 35 and 45°C was tested</p>	<p>Sorption isotherm fitted by Freundlich isotherm</p> <p>Sorption capacity of organic matter added montmorillonite was greatly enhanced compared to MMT.</p> <p>Effects on sorption could be related to changes in surface structure, specific surface area, hydrophobicity and the average pore size of MMT.</p> <p>Sorption is exothermic and decreased with temperature in both MMT and DOC-MMT.</p> <p>pH had no significant effect on sorption.</p> <p>Adsorption capacity of DOM-MMT decreased with increasing adsorbent dose.</p> <p>Sorption of PHE on complex was rapid; and the kinetics could be described well by both pseudo-first-order and pseudo-second-order models, with an equilibrium time of 120 min.</p>	Wu et al. (2011)
Commercial HAs, as well as those obtained from Umbric Andosol, Dystric Cambisol, and cow manure compost and fractionated Aldrich humic acid (AHA).	Pyrene	Relationship between the chemical properties of various types of humic acids sorption ability was investigated in batch experiments.	<p>Positive relationship between K<sub>des</sub> and aromaticity</p> <p>Factors other than aromaticity may also influence the sorption of pyrene.</p>	Kobayashi and Sumida (2015)
Potentially contaminated natural soils from southwestern Poland	16 PAHs	to evaluate the mutual relations between the soil organic matter fractions: fulvic acids, humic acids, humins, black carbon and the PAHs accumulation level in agricultural soils	<p>Positive relations between PAH concentrations and TOC content</p> <p>Links between humins and PAHs were stronger for low-molecular weight (two and three rings) PAHs.</p> <p>Relations among PAHs, humins and black carbon were statistically significant only in soils with TOC content ≥ 12 g kg<sup>-1</sup>.</p> <p>Black carbon fraction showed higher correlations with high-molecular-weight PAHs.</p> <p>Fulvic acids and humic acids showed no significant relationship with PAHs.</p>	Ukalska-Jaruga et al. (2018)

### **Effect of co-existing heavy metals on PAH sorption**

Recent studies demonstrate that the coexistence of heavy metals and other metals can also contribute to sorption of PAHs to soil. It is believed that this effect is greater in low organic content soils or for high metal concentrations in soil (Obuekwe and Semple 2013; Zhang et al., 2011; Hwang and Cutright, 2004; Walter and Weber, 2002). Some of the reports speculate on probable causes and mechanisms for this effect.

Accumulation of sorbed heavy metals on soil (particularly clay) particle surfaces can make cation- $\pi$ -bonds with PAHs (Zhu et al., 2004). These authors introduced a new perspective on the sorption of PAHs onto mineral surfaces. They reported that exchangeable cations on clay mineral interlayers could condition mineral surfaces, opening more adsorption sites for strong cation- $\pi$ -bonds with PAHs.

Nguyen et al. (2013) reported that larger size pores, clay fraction aggregation and more hydrophobicity are some of the effects of metal cations in clay minerals and soils, causing more PAH sorption (Zhang et al., 2011). Heavy metals on clay surfaces could play a bridging role between PAHs and clay minerals.

Gao et al. (2006) showed that sorption of phenanthrene was significantly increased by the presence of heavy metals (Cu, Pb and Zn). They also found that phenanthrene sorption was intensified when concentrations of metals in soil increased. They suggested that the bridging effects of heavy metals could transform some dissolved organic matter (DOM) in the system to particulates and to the adsorbed phase in soil (soil organic matter), resulting in more phenanthrene sorption (mainly partitioning) by the solid phase. Reducing the dissolved organic matter could also decrease the dissolved organic complexes containing phenanthrene. They also mentioned that the presence of heavy metals creates more

capacity to sorb PAHs in adsorbed organic matter, than the original soil organic matter. Tao et al. (2013) reported that the sorption of phenanthrene onto biomass depended on the type and concentration of heavy metals present in the system.

Table 6 summarizes some previously published work on the effect of co-existing metals on PAH sorption. Overall, the few studies published on the effect of co-existing soil heavy metals show that for all PAHs/soil types/minerals tested, co-existence of heavy metals in soil enhances the sorption of PAHs. However, the extent of enhancement differs for different physical/chemical conditions. Zhang et al. (2011) studied the effects of pH, SOM and Pb on sorption of phenanthrene onto the clay content of soil and reported that the presence of Pb and SOM increases phenanthrene sorption in soil. They also reported that changes in pH affect soil properties, influencing the capacity for phenanthrene sorption. Fonseca et al. (2011) reported that co-existence of phenanthrene could prolong the Pb retention in soil.

As discussed before, in soil-water systems PAHs interact with soil organic matter and heavy metals cations to form complexes with organic molecules in soil solids (Gao et al., 2003; Zhang and Ke, 2004; Gao et al., 2006), enhancing the sorption of PAHs onto soils. Moreover, Saeedi et al. (2018a) showed that the presence of both heavy metals and organic matter in soil can enhance PAHs sorption to an even greater extent than the total of the separate effects of metals and SOM. In other words, co-existence of SOM and heavy metals causes synergistic effects on the sorption of PAHs onto soil and clay mineral mixtures (Saeedi et al. 2018a). They reported 10 to 48% increments in PAH sorption enhancement by both SOM and heavy metals compared to summation of their individual effects for different PAHs and soils. Their results showed that this effect increased with increasing PAH molecular size and aromaticity.

Metal cations can form bonds with organic matter functional groups in soil-water systems. This connects the organic molecules creating hydrophobic sites for PAH molecules sorption. Heavy metals also bridge the dissolved organic matter in the system, changing them into the solid phase of the soil. This could increase soil organic matter, reduce the association of

PAHs to DOM, and consequently increase the accumulation of PAHs in the particulate phase (Obuekwe and Semple, 2013).

Table 7 summarizes the reported mechanisms that enhance PAH sorption when heavy metals and soil organic matter co-exist, with categorization of the type of metal cation function.

**Table 6. Summary of previous work on the effect of heavy metals on sorption of PAHs**

Soil/Mineral	PAHs and metal co-contaminants	Sorption Isotherm	Sorption coefficients studied	Sorption coefficient result	Reference
Montmorillonite	PHE + Pb	Linear	$K_d$ (L kg <sup>-1</sup> )	Only PHE: 1130 PHE+Pb: 1352	Zhang et al. (2011)
olinite	PHE + Pb	Linear	$K_d$ (L kg <sup>-1</sup> )	Only PHE: 531 PHE+Pb : 572	
Montmorillonite	PHE + Cd	Linear	$K_d$ (L kg <sup>-1</sup> )	Only PHE: 1130 PHE +Cd : 1247	Saison et al. (2004)
Silty Clay	PHE/PHE + Metals	Freundlich	$K_f$ (L kg <sup>-1</sup> )	Only PHE:8.55 PHE+Metals: 21.48	
Natural soil spiked with heavy metals	PHE + Pb, Zn or Cu	Linear	$K_d/K_{oc}$	$K_{oc}$ values for metal spiked soils were 24% larger than for unspiked ones. Increased SOM as a result of co-existing metals enhanced phenanthrene sorption.	Gao et al. (2006)
Paddy and Black Soil	NAP NAP+Cu NAP+Pb NAP+Cr PHE PHE+Cu PHE+Pb PHE+Cr PYN PYN+Cu PYN+Pb PYN+Cr	Freundlich	$K_f$ (modified Freundlich parameter) mg kg <sup>-1</sup>	(Paddy Soil: 96.5)(Black Soil: 799) (Paddy Soil: 101)(Black Soil: 846) (Paddy Soil: 116)(Black Soil: 877) (Paddy Soil: 123)(Black Soil: 896) (Paddy Soil: 33.7)(Black Soil: 246) (Paddy Soil: 35.1)(Black Soil: 251) (Paddy Soil: 40.7)(Black Soil: 270) (Paddy Soil: 41.5)(Black Soil: 307) (Paddy Soil: 12.6)(Black Soil: 178) (Paddy Soil: 15.6)(Black Soil: 186) (Paddy Soil: 19.5)(Black Soil: 215) (Paddy Soil: 26.1)(Black Soil: 236)	Liang et al. (2016)
Kaolinite	ANA, FL, FLAN (ANA, FL, FLAN)+(Pb, Ni, Zn)	Linear	$K_d$ (L kg <sup>-1</sup> )	ANA: 193, FL:213, FLAN: 2175 ANA:203, FL: 239, FLAN:2566	Saeedi et al. (2018a)
Sand+kaolinite	ANA, FL, FLAN (ANA, FL, FLAN)+(Pb, Ni, Zn)	Linear		ANA: 122, FL: 128, FLAN: 1714 ANA: 130, FL: 140, FLAN: 1872	
Sand+kaolinite+bentonite	ANA, FL, FLAN (ANA, FL, FLAN)+(Pb, Ni, Zn)	Linear		ANA: 140, FL: 152, FLAN: 1607 ANA: 150, FL: 159, FLAN: 1880	

**Table 7. Effect of metals on sorption of PAHs in minerals and organic matter contained soil**

Cation functioning mechanism	Effect on PAH sorption	Result of cation interaction	Reference
Bridging among SOM molecules	Enhancement	Creating and concentrating hydrophobic sites desirable for PAH sorption	Obuekwe and Semple, (2013)
Bridging between DOM and soil	Enhancement	Transforms DOM into SOM resulting in reduction of mobile PAHs Increases SOM with greater sorption capacity	Jones and Tiller (1999) Traina et al. (1989) Saison et al. (2004) Gao et al. (2006)
Bonds between soil adsorbed metals and aromatic rings	Enhancement	Cation- $\pi$ bond between metal cation and PAH	Zhu et al. (2004) Zhang et al. (2011)

### **Other factors affecting PAH sorption**

Based on our review of previous research, the distribution and partition coefficients of PAHs can depend on multiple factors of soil and environmental conditions. Because of the multiple factors affecting sorption of PAHs in soil, there is considerable uncertainty in predicting  $K_d$  for a given PAH. That is why for PAHs and some other organic and inorganic chemicals, sorption properties are usually determined in laboratory experiments.

Other factors affecting the sorption process include temperature, pH, ionic strength, soil particle size and surface area, soil composition and mineralogy, initial concentration of PAHs, contact time and kinetics of sorption, and PAH properties such as solubility. Some of these factors and their effects on PAHs sorption in soil environments are briefly described in this section.

#### **Surface area**

The soil surface area is believed to be inversely proportional to sorption capacity of any sorbate (Wang et al., 2015). Since adsorption is a surface phenomenon, the extent of adsorption per mass of soil is proportional to the surface area. Previous work on sorption behaviour of different particle sizes of adsorptive media has confirmed this general rule (Cornelissen and Gustafsson, 2004; Lemic et al., 2007; Wang et al., 2015). However, since the sorption is not exactly the same as adsorption and includes other mechanisms like ion exchange, the sorption amount and the behavior of PAHs may differ from expectations based solely on the specific surface area of the sorbent.

#### **Ionic strength and salinity**

Increasing the ionic strength and salinity of the solution has been found to increase the sorption of PAHs onto soil and sediment.

Inorganic ions can bind water molecules into hydration shells (Weston et al., 2010) reducing the water solubility of PAHs onto

the soil and organic particles surface. Karickhoff et al. (1979) reported 15% increase in phenanthrene sorption when it was transferred from pure water to KCl solution at 0.34 M concentration.

Inorganic ions can decrease the solubility of PAHs, leading them onto sorbent material surfaces (Weston et al., 2010). Increasing the sorption coefficient and amount of phenanthrene in water containing higher ionic concentrations has been reported (Karickhoff et al., 1979; El-Nahhal and Safi, 2004).

#### **Solubility**

The solubility of PAHs is inversely proportional to their molecular weight and  $K_{ow}$ . Lower solubility and higher  $K_{ow}$  indicate greater hydrophobicity of a PAH. Higher hydrophobicity in turn leads to greater sorption and a higher partition coefficient. Increased sorption capacity for decreased solubility of PAHs has been reported in most previous studies (Hu et al., 2008; Balati et al., 2015). Solubility and  $K_{ow}$  are among the main PAHs properties affecting sorption and desorption behavior.

#### **Temperature**

Most previous studies have reported increased sorption at lower temperatures and decreased sorption at higher temperatures (Table 2) (He et al., 1995; Podoll et al., 1989). For example, Hiller et al. (2008) reported decreased sorption of pyrene, phenanthrene and naphthalene with the temperature increased from 4 to 27°C. Generally, sorption is exothermic; therefore, higher temperatures result in lower sorption. However, some studies have reported the opposite effect, confirming an endothermic reaction for sorption (Balati et al., 2015). According to Kipling (1965), it is expected that compounds whose solubility increase with increasing temperature will show lower sorption capacities. For compounds whose solubility is inversely proportional to temperature, the lower the temperature, the more sorption takes place.

## **pH**

It seems that pH affects the sorption of PAHs due to a sorbent's change in surface charge distribution and functional groups (Gao and Pedersen, 2005; Ping et al., 2006; Putra et al., 2009). However, some researchers (Mader et al., 1997; Raber et al., 1998; Zeledon-Toruno et al., 2007; Hu et al., 2014) have reported that they did not observe pH as a significant factor in the sorption of PAHs onto solid media.

## **Contact time and kinetics**

Sorption of PAHs onto soil usually occurs in two stages. The first stage, physical adsorption onto minerals and other components of soil, is rapid. This is followed by a slower stage of chemical sorption onto organic matter (Semple et al., 2007). Most previous work (Zeledon-Toruno et al., 2007; Awoyemi, 2011; Hu et al., 2014; Gupta, 2015) confirms this two-stage kinetics. Based on this, although a considerable portion of PAH sorption onto soil may occur in the early hours, completion of the process may require much more time as it approaches the maximum sorption capacity. The equilibrium time for PAH sorption has even been reported to be 34 h, but mostly less than 24 h (Table 3).

## **Clay and minerals**

For fine soils that contain clay minerals, recent research (Saeedi et al., 2018a; Zhang et al., 2010; Zhang et al., 2011; Hwang et al., 2003; Zhu et al., 2004) has shown that PAHs can sorb onto the soil, even in the absence of soil organic matter.

In clay minerals, surface area may be the main factor influencing the sorption of PAHs. Hydrogen bonding between a PAH and the oxygen of the clay mineral surfaces may take place. Nevertheless, this might not be the only factor determining the sorption capacity of clay minerals for non-polar organic compounds such as PAHs. Brindley et al. (1963) surprisingly reported that the order of sorption of acetoacetic ethylester and  $\beta$ ,  $\beta$ -oxydipropionitrile on clay minerals per

unit of surface area was gibbsite > kaolinite > montmorillonite. They explained that the hydroxyl surfaces in gibbsite and kaolinite could sorb more effectively than the oxygen surfaces in montmorillonite. However, for aromatic hydrocarbons such as benzene, toluene and xylene, lower  $K_f$  values were reported for kaolinite than for montmorillonite and illite. This was explained based on the clay mineral surfaces of these clays: montmorillonite ( $8 \times 10^6 \text{ m}^2 \text{ kg}^{-1}$ ), illite ( $10^5 \text{ m}^2 \text{ kg}^{-1}$ ) and kaolinite ( $3 \times 10^4 \text{ m}^2 \text{ kg}^{-1}$ ) (Li and Gupta 1994). For minerals other than clays, it seems that sorption of PAHs does not occur significantly on mineral surfaces. Mader et al. (1997) showed that PAHs interact weakly and non-specifically with some non-clay mineral surfaces ( $\alpha\text{-Fe}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ ). In summary, it is clear that clay minerals can be relatively good sorbents of PAHs in soil environments. The sorption capacity of different clay minerals for PAHs seems to be proportional to the surface area of the clay and to be dependent on the clay mineralogical and crystallographic structure in terms of the number of layers and their expandability.

## **Desorption of PAHs**

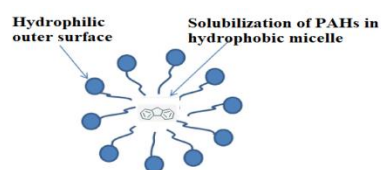
The fate of PAHs in soil is mainly controlled by sorption-desorption processes. Since some of the mechanisms that take place in sorption process are equilibrium reactions, most factors affecting sorption also affect desorption. Mobility of PAHs in soil can be influenced by soil properties, PAH physical/chemical properties and coexistence of other contaminants. As discussed above, soil organic matter and heavy metals are among the factors which play key roles in sorption-desorption processes. However, regarding hydrophobicity of PAHs, most studies on the natural desorption and mobility of PAHs have shown that their mobility is very low compared to the sorption amounts (Saeedi et al., 2018b; Olu-Owolabi et al., 2014; Yang et al., 2013; Barnier et al., 2014). On the other hand,

higher amounts of desorption are needed for soil washing/flushing and electrokinetic remediation of PAH-contaminated soil.

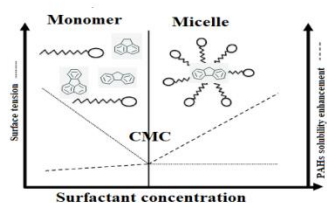
Application of surfactants/biosurfactants and some organic and weak acids to desorb and extract PAHs or heavy metals from soil has been widely investigated (Maceiras et al., 2018; Maturi and Reddy, 2006; Alcántara et al., 2008; Song et al., 2008; Cao et al., 2013; Saichek and Reddy, 2005; Saichek and Reddy, 2004; Jin et al., 2013; Sánchez-Trujillo et al., 2013; Ling et al., 2015; Sales and Fernandez, 2016; Greish et al., 2018).

Lamichhane et al. (2017) reviewed previous studies on surfactant-enhanced remediation of PAHs. They reported that factors such as surfactant type and concentration, hydrophobicity of PAH molecules, temperature, pH, salinity, dissolved organic matter and microbial community could affect remediation of PAHs by surfactants. Cheng et al. (2017) reviewed the advantages and challenges of Tween 80-surfactant enhanced remediation for hydrophobic organic compounds. They summarized research on Tween 80 compared with other surfactants in remediation of hydrophobic organic compounds, such as PAHs. Research showed desorption and removal efficiencies in the range of 36-84%

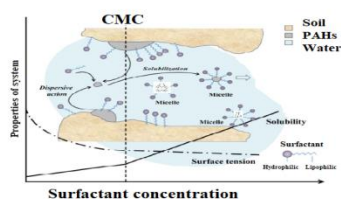
for phenanthrene, fluoranthene and benzo[a]pyrene using Tween 80, Triton X-100 and Brij 35 in soil washing (Cheng and Wong, 2006; Ahn et al., 2008; Alcántara et al. 2008, 2009). Non-ionic surfactants showed better efficiency in removing PAHs than ionic ones (Lamichhane et al., 2017; Cheng et al., 2017). These surfactants have hydrophobic and hydrophilic groups in their structure. Hydrophilic groups of surfactants enter the aqueous phase and the lipophilic groups (tails) attach to soil particles and PAHs and soil organic matter (Mao et al., 2015; Wan et al., 2011). Surfactants accumulate at solid-liquid and solid-contaminant interfaces as monomers at low concentrations. As the concentrations of surfactants increase, they replace water molecules, reducing the polarity of the aqueous phase and the surface tension. Surfactant molecules adsorbed on the solid phase creating repulsion between soil particles and hydrophobic groups then desorb PAHs from soil (Cheng et al., 2017). If the concentrations of surfactants increase further, micelles start to form that can greatly improve the solubility and desorption of PAHs (Yeom et al., 1996; Liang et al., 2017). A schematic of surfactant enhanced desorption of PAHs is presented in Fig. 4.



a) Modified from Lamichhane et al. (2018)



b) Modified from Trelu et al. (2016)



c) Modified from Mao et al. (2015)

Fig. 4. Schematic of surfactant enhanced desorption of PAHs.



**Table 8. Summary of recent studies on the effect of organic matter and heavy metals on PAHs desorption**

Soil/material	Type of PAHs	Test details	Co-existing organic matter/heavy metal	Highlighted findings	Reference
Spiked three types of natural soil from Hangzhou City, China	Phenanthrene, fluorene, acenaphthene, naphthalene	Batch sorption of PAHs followed by surfactants (TX-100, TX-114 and TX-305) enhanced desorption tests. In batch desorption tests 2 g of soils mixed with 20 ml of surfactant solution at different concentrations for 48 h	Organic matter; measured as organic carbon. Organic matter contents were different in samples	Surfactants were more effective to desorb PAHs in soils with higher organic carbon content and lower clay content. Desorption by water was too low except for naphthalene, whereas the surfactants were more effective for PAHs with higher $K_{ow}$ than water insoluble ones	Zhou and Zhu (2007)
Sediment (Yangtze River)	Phenanthrene, acenaphthene, fluorine, fluoranthene, pyrene (Multiple sorbates)	Sorption-desorption (no surfactant); Sorption with solid to liquid ratio of 1:100 ( $g mL^{-1}$ ), initial concentration: $10-100 \mu g L^{-1}$ , 12 h test time then desorption carried out by replacing 96% supernatant with water for 12 h test.	Natural organic matter contents in samples; measured as TOC	Sorption was affected by both carbonate and organic matter. Organic matter plays a more important role for larger PAHs with greater $K_{ow}$ s. Lower-ring PAHs desorb faster than PAHs having more rings; more tightly sorbed PAHs desorb with more difficulty. Organic matter may inhibit the diffusion of PAHs from sediment to water. Desorption of PAHs into water ranged from 0.25 to 8% of total sorption, which was rather low. However lighter PAHs showed higher desorption amounts.	Wang et al. (2008)
Natural contaminated soil sample spiked with phenanthrene	Phenanthrene	Batch tests to evaluate desorption and desorption kinetics. Soil-to-solution ratios of 1:2.5, 1:5 and 1:10 were tested for 24 h. Combined and single solutions of Tween 80, Brij 35 and EDTA were used as extractants.	Lead	Addition of phenanthrene to soil reduced Pb desorption from 100% to 48%. Combined solutions enhanced solubilisation of mixed Pb and phenanthrene. Desorption kinetics fitted empirical power function and pseudo-second-order equation.	Fonseca et al. (2011)
Bentonite and humic/fulvic acid-coated bentonite	Phenanthrene	Batch sorption and desorption/extraction experiments (no surfactant); 0.1 g: 25 mL of solution for 72 h. Desorption/leachability then was assessed by deionized water, 0.1 M $NaNO_3$ for 60 min, Modified Krauss sequential extraction of phenanthrene with methanol, and Tessier (1979) extraction of Pb and Cd.	Lead, Cadmium, humic/fulvic acid	Co-existing phenanthrene enhanced Pb sorption. Enhancement was greater for humic acid-coated bentonite due to greater phenanthrene sorption. Phenanthrene sorption was also increased by the co-existing Pb. Co-existing phenanthrene and Pb redistributed each other from weak bonds to strongly bonded fractions. Humic acid coating reduced this effect. Presence of Pb decreased desorption of phenanthrene from bentonite. Presence of both humic acids and Pb reduced the desorption of phenanthrene to a greater extent. Desorption of phenanthrene to water was very low compared to sorption	Zhang et al. (2015)
Kaolinite, Sand+kaolinite, sand+kaolinite+bentonite	Acenaphthene, fluorene, fluoranthene	Batch desorption tests on spiked samples with added and non-added heavy metals and humic acids. Extracting solutions were $CaCl_2$ (0.01M), combined EDTA (0.01M) and Tween 80, combined EDTA (0.01M) and Triton X100	Humic acid, heavy metals (Pb, Ni and Zn)	Heavy metals and humic acid decreased the desorption of PAHs. Humic acid had greater decreasing effect than heavy metals. Desorption reducing effects were greater for larger PAH than lighter ones. Greater clay content in the soil mixture led to more desorption decrease by heavy metals and humic acid.	Saeedi et al. (2018b)

Compared to extensive research on the effect of surfactants in desorption and solubilization of PAHs, published work on the effect of soil organic matter and particularly heavy metals on desorption and removal efficiency of PAHs is limited.

Obuekwe and Semple (2013) found that the presence of Cu and Al enhanced the extraction of  $^{14}\text{C}$ -phenanthrene by  $\text{CaCl}_2$  and hydroxypropyl- $\beta$ -cyclodextrin (HPCD). They concluded that high concentrations of metals could affect phenanthrene mobility/accessibility in soil.

Saison et al. (2004) clearly demonstrated that the fate of PAHs in soil cannot be easily predicted because it greatly depends on co-pollution with metals. Yang et al. (2001) showed that, under the effect of complexing agents (EDTA, citric acid), other metal ions like Fe and Al are mobilized, loosening humic-cation-mineral bonds and resulting in dissolution of some soil organic matter, in turn mobilizing the PAHs in soil. Table 8 summarizes recent studies on the effect of soil organic matter and/or heavy metals on the desorption of PAHs from soil.

Most previous work on co-existing contaminant has investigated either the effect of organic matter or heavy metals on desorption of PAHs. There are very few published papers on the mobility and desorption of both PAHs and heavy metals in the presence of soil organic matter. There are some discrepancies regarding the effect of heavy metals and SOM on the desorption of PAHs, but this appears to be due to the number of affecting factors and variations in the composition of the soils tested in previous research. However, some consistent findings are important with respect to fate and/or remediation of mixed-contaminated soils.

Based on the chemical properties of the PAHs and findings of previous researchers, it is clear that sorbed PAHs in soil are not desorbed in great amounts by water. Previous findings also show that SOM increases the retention of PAHs in soil. Co-existence of heavy metals reduces the

extractability and desorption of PAHs. It seems also that co-existence of PAHs and heavy metals affects the chemical bonds within the soil matrix. This can affect the environmental and ecological risk of both groups of contaminants. PAHs with higher  $K_{ow}$  (i.e. larger ones with more rings) are retained by SOM in soil more than smaller PAH molecules.

Desorption kinetics of PAH removal from a mixed-contaminated soil by surfactants and enhancing solutions fit a pseudo-second-order kinetic equation and empirical function (Fonseca et al., 2011; Wang et al, 2010), whereas the sorption of PAHs to soils, particularly at higher SOM contents, has been mostly reported to follow linear kinetics.

Findings also show that application of combined surfactants and chelating agents/organic acids is effective in simultaneously desorbing PAHs and heavy metals for soil washing/flushing (Fonseca et al., 2011; Maturi and Reddy, 2008) and electrokinetic remediation methods.

## CONCLUSION AND RESEARCH NEEDS

Heavy metals and PAHs have totally different chemical properties in terms of sorption, desorption and remediation. Sorption and desorption of PAHs in soil are the main processes affecting remediation technologies, particularly in fine soils and soils containing natural organic matter, heavy metals or both. Given that most mixed-contaminated sites contain different types of coexisting PAHs and heavy metals, it is essential to study their combined behavior in fine and clayey soil environments in terms of sorption/desorption, as the main processes determining their environmental fate and transport, as well as remediation techniques.

The presence of either natural organic matter or heavy metals can enhance the sorption capability of fine soil, retarding the spread of PAHs in the solid matrix. Although, enhancing agents and surfactants have been reported to be able to increase

the desorption and removal of PAHs from soil, at least one report (Saeedi et al., 2018a) shows that co-existing heavy metals and organic matter in soil have synergistic effects on the sorption of PAHs, leading to much lower desorption efficiencies. This can challenge remediation technologies based on removing contaminants by a liquid by electrokinetics and chemically-enhanced soil washing/soil flushing.

Overall, it is important to study the mechanisms of PAH sorption in relation to SOM composition and the interrelation with other main soil components and properties, such as types and contents of minerals, co-existing contaminants such as heavy metals and soil physical/chemical properties. More detailed investigations are needed to determine affecting factors and conditions for heavy metals and SOM on PAH sorption and desorption, and their effects on remediation.

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#### **CONFLICT OF INTEREST**

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

#### **LIFE SCIENCE REPORTING**

No life science threat was practiced in this research.

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