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Review

Sorption, transport and biodegradation – An insight into bioavailability of persistent organic pollutants in soil

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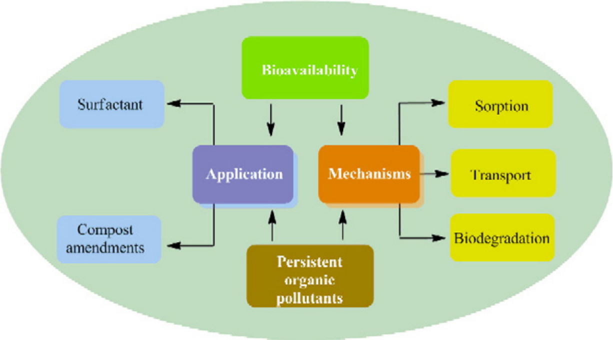
HIGHLIGHTS

- Microbial degradation of persistent organic pollutants (POPs) is limited by their low bioavailability.
- Sorption, transport and physiological aspects of POPs bioavailability are reviewed.
- Surfactants and compost amendments affect the bioavailability of POPs.
- Further researches should focus on the influence of various bioremediation strategies on the bioavailability of POPs.

GRAPHICAL ABSTRACT



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ABSTRACT

Contamination of soils with persistent organic pollutants (POPs), such as organochlorine pesticide, polybrominated diphenyl ethers, halohydrocarbon, polycyclic aromatic hydrocarbons (PAHs) is of increasing concern. Microbial degradation is potential mechanism for the removal of POPs, but it is often restricted by low bioavailability of POPs. Thus, it is important to enhance bioavailability of POPs in soil bioremediation. A series of reviews on bioavailability of POPs has been published in the past few years. However, bioavailability of POPs in relation to soil organic matter, minerals and soil microbes has been little studied. To fully understand POPs bioavailability in soil, research on interactions of POPs with soil components and microbial responses in bioavailability limitation conditions are needed. This review focuses on bioavailability mechanisms of POPs in terms of sorption, transport and microbial adaptation, which is particularly novel. In consideration of the significance of bioavailability, further studies should investigate the influence of various bioremediation strategies on POPs bioavailability.

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1. Introduction

Contamination of soils with persistent organic pollutants (POPs) has achieved high concerns in recent years. The POPs of particular concern include organochlorine pesticide, polybrominated diphenyl ethers (PBDEs), halohydrocarbon, polycyclic aromatic hydrocarbons (PAHs) (Wang et al., 2011b; Zeng et al., 2013a; Zhang et al., 2007; Zhou et al., 2014). Most of those compounds are toxic to human health even at low concentrations (Deng et al., 2017b; Tang et al., 2016; Tang et al., 2014; Tang et al., 2008). Microbial degradation, as an important mechanism for the removal of POPs, is restricted by the low bioavailability (Chen and Ding, 2012). Therefore, increasing the bioavailability of POPs to degrader is important in soil bioremediation.

The National Research Council report defines “bioavailability processes” as the individual physical, chemical, and biological interactions that determine the exposure of organisms to chemicals associated with soils and sediments (Ehlers and Luthy, 2003). From the soil to the microorganism, bioavailability of contaminants involves a full process of adsorption and desorption, transport, and uptake by microorganisms (Rončević et al., 2016). Sorption process limit the substrate supplement and mass transfer of pollutants to microorganisms (Kickham et al., 2012; Wang et al., 2015; Wang et al., 2013c). Therefore, contaminants that adsorb strongly on soil are recalcitrant to degradation, and remain in soil for a long term (Riding et al., 2013; Semple et al., 2013; Wang et al., 2013b; Wu et al., 2014). As for POPs that are bound on the inner domain of soil aggregate or micropore-adsorbed, only by the way of transport can they be accessed by microorganisms, either POPs transfer out or microorganisms transfer in. Hence, transport of POPs should also be considered (Hu et al., 2011; Liu et al., 2012). In addition to physicochemical process, understanding the mechanisms of microorganisms to attack POPs is required in bioavailability process. Microorganisms with some special characteristics could increase the bioavailability of POPs under physical limitation conditions. For example, micropore-adsorbed POPs are unable to be attached by microorganisms. In this case, secretion of biosurfactant or hypha structure is important (Fester et al., 2014; Pacwa-Płociniczak et al., 2011). To deal with the problem of deficient solubility of POPs, formation of biofilm, secretion of biosurfactant or change of cell wall properties are possible microbial response (Johnsen and Karlson, 2004; Pacwa-Płociniczak et al., 2011; Wick et al., 2002b).

Several reviews have reported biodegradation mechanisms of POPs during bioremediation (Johnsen et al., 2005; Ortega-Calvo et al., 2015; Semple et al., 2007; Stroud et al., 2007). However, the interactions of POPs with soil components and microorganisms associated characteristics to bioavailability have been little studied. Three following aspects were included in this paper: (i) the sorption behavior of soil organic matter (SOM) and minerals to POPs; (ii) transport ways of POPs in soil; and (iii) microbial adaptations to increase bioavailability of POPs under bioavailability restriction conditions. By giving a particular analysis about bioavailability mechanisms of POPs, we want to provide a good research idea of bioavailability in soil bioremediation.

2. Sorption of POPs in soil

It has been reported that bioavailability of POPs was decreased after adsorption by soil. With time increasing, soils form stronger binding with POPs, consequently causing a decline in bioavailability, a process termed as aging. Aging results in three contaminant desorption manners: the ‘rapid’, ‘slow’ and ‘very-slow domains. The rapid desorption fractions are surface-adsorbed and interchangeable with the porewater, thus readily bioavailable. However, ‘slow’ and ‘very-slow fractions are strongly bounded or micropore-adsorbed, making it unavailable by microorganisms (Semple et al., 2007). Slow or irreversible desorption of POPs is the main factors restricting their bioavailability. Although microorganisms can attack adsorbed contaminants, they prefer dissolved fractions (Megharaj et al., 2011). Therefore, sorption and desorption in soil are fundamental processes in controlling susceptibility of POPs to microbial degradation. Sorption of POPs is mostly affected by the content and properties of SOM. Meanwhile, soil minerals also play a role in sorption of POPs, especially when organic matter content is lower than 1% (Cheng et al., 2012). Consequently, both the properties of SOM and minerals should be considered in sorption of POPs.

2.1. Impacts of soil organic matter

It has been well demonstrated that the sequestration capacity of soil to POPs is strongly connected to the proportion of SOM (Lima et al., 2012). However, soils with the same organic matter content may have different sorption potentials for POPs. SOM is a heterogeneous mixture including newly deposited biopolymers (*e.g.*, proteins, polysaccharides, and lipids), moderately aged humic substances (HSs), well matured kerogen and black carbon, each of which are potential sorbents for POPs (Mechlińska et al., 2009). In the study of Liu et al. (2010), sorption coefficient (K_{OC}) of phenanthrene followed the descending order of humin (HM), humic acid (HA) and fulvic acid (FA). Zhu et al. (2016) recently found that desorbing fraction and microbial debromination ratio of PBDEs were weakly related to total organic carbon but strongly related to content of black carbon. It has been reported that structure characteristics (aromaticity and aliphaticity), spatial arrangement, physical conformation and polarity of SOM could affect its sorption capacity.

2.1.1. Structure characteristics of SOM

Whether aliphatic or aromatic domain of SOM is more important to sorption of POPs has been much studied. It is emphasized that aromatic structures of SOM are responsible for its high sorption affinity to POPs because of the specific π–π interactions (Keiluweit and Kleber, 2009). Yang et al. (2010) also proved that phenanthrene would be adsorbed preferentially by aromatic carbon rich lignin than paraffinic carbon-rich wax, thus lowering its bioavailability. However, neither aliphatic nor aromatic domains alone could be used to predict the sorption capacity of SOM (Chefetz and Xing, 2009). Sorption of the nitroaromatic is closely correlated with the aliphatic carbon rather than the aromatic carbon (Singh et al., 2010). This is consistent with the observation from Sun et al. (2013) that aliphatic carbon of natural organic matter was responsible for the high sorption capacity to benzene and phenanthrene. There is no consensus on which domain of SOM dominates sorption, probably caused by different type of SOM used in different experiments. When a large number of data set was plotted, no specific correlation was found between phenanthrene K_{OC} and the aromaticity of SOM from different sources (Chefetz and Xing, 2009). This was supported by Hur et al. (2009) that aromatic carbon derived from sediment HA served as a partitioning phase to POPs, while that from soil HA functioned as specific adsorption sites. It is therefore concluded that aromaticity and aliphaticity are both important to sorption, and different performances observed are caused by structural complexity and heterogeneity of SOM.

2.1.2. Spatial arrangement of SOM

Additionally, other factors such as SOM spatial arrangement and surface accessibility to POPs also influence the sorption ability of alkyl carbon structures (Mitchell and Simpson, 2013; Wang et al., 2011b). Mitchell and Simpson (2013) observed weak correlation between K_{OC} and alkyl carbon content of SOM. They proposed that alkyl carbon were absorbed strongly to minerals or buried by other organic matter (*e.g.*, carbohydrates and peptides), which made it not accessible to POPs. Moreover, some researchers attributed the different effect of alkyl domains on sorption to two reasons: (i) condensed domains or O-alkyl components covered the high-affinity alkyl domains and (ii) sorption ability of aromatic domains was strengthened by the introduced black carbon (Han et al., 2014; Jin et al., 2015; Mitchell and Simpson, 2013). Jin et al. (2015) also reported that the enhanced π-acceptor ability of aromatic domains in nonhydrolyzable carbon (NHC) would elevate sorption of phenanthrene but not for phthalate esters. The aromatic ring itself on phthalate esters would act as π-acceptors, consequently inhibiting its sorption by NHC, which highlighted the influence of microenvironment in aromatic carbon on sorption process. All these results further revealed the significance of sorption domains spatial arrangement.

2.1.3. Physical conformation of SOM

SOM can be described as two distinct physical conformation, "soft/rubbery/amorphous phase [*i.e.*, amorphous organic matter (AOM)]" and "hard/glassy/condensed phase [*i.e.*, carbonaceous geosorbent (CG)]" (Cornelissen et al., 2005). AOM is gel-like matrix, consisting of partly degraded and/or reconstituted biopolymers, and humic/fulvic acids, while CG is a relatively rigid and porosity phase, such as black carbon, kerogen and HM (Semple et al., 2013). Partitioning of contaminants mainly occurred in rubbery fraction of SOM while hole-filling primary occurred in the condensed fraction. In kerogen samples, micropore adsorption volumes to phenanthrene and benzene made up 23–46% and 36–65% of its total sorption volumes respectively, suggesting hole-filling as an indispensable mechanism (Zhang et al., 2014). Moreover, it was suggested that amorphous domains of aliphaticity rather than the total level was strongly related with sorption capacity of SOM (Chefetz and Xing, 2009). Amorphous aliphatic domains generally contribute to partitioning of nonpolar chemicals, while rigid aliphatic domains, comparable to aromatic moieties, are linked to nonliner sorption (hole-filling) (Chefetz and Xing, 2009). In the study of Han et al. (2014), aliphaticity of SOM was enhanced with increasing surface area, which validated that the aliphatic moieties were partially responsible for the formation of nanopores in natural sorbents. Interestingly, they found that aromaticity in engineered sorbents contributed a lot to the nanopore adsorption.

2.1.4. Polarity of SOM

On the one hand, polar groups of SOM acted as hydrogen bond acceptor, and water clusters formed on the surface acted as hydrogen bond donor, thereby reducing the accessibility of contaminants to sorption sites by competition effect (Guo et al., 2012; Jin et al., 2015). Also, polar features of HA/FA resulted in less PFOS adsorption due to the increased electrostatic repulsion and decreased hydrophobic effect (Zhang et al., 2015a). On the other hand, polarity of the SOM was positively related to sorption of atrazine (a polar organic compound with mainly aromatic ring), as reported by Wu et al. (2015a). Further, they observed better correlation of K_{OC} with $(N + O)/C$ ratios (polar index) than with H/C ratios (indicator of aliphaticity), indicating that polarity of SOM dominated sorption of atrazine more than its aliphaticity. Unlike the nonpolar organic compounds such as phenanthrene, whose sorption mechanism was controlled by nonspecific hydrophobic partition to the condensed organic matter, sorption of atrazine was attributed to the specific polar interaction *e.g.*, hydrogen bonding between atrazine and polar fractions of SOM (carboxylic and phenolic groups) (Shi et al., 2010; Wu et al., 2015a). Overall, the impact of SOM polarity is dependent on the controlling sorption mechanism. This was also demonstrated in a recent work by Jin et al. (2015) that sorption capacity of phthalate esters was negatively correlated with surface polarity of nonhydrolyzable carbon (NHC) but positively related with polarity of other organic matter (*e.g.* HA, HM) due to dissimilar sorption mechanisms. Hydrophobic interactions regulated NHC sorption affinity but both hydrogen bonding and hydrophobic interactions controlled sorption of other organic matter (Jin et al., 2015).

To sum up, structure (aromaticity and aliphaticity), polarity, spatial arrangement and physical conformation of SOM are interactive parameters on sorption of POPs (Fig. 1). For example, the impact of spatial arrangement cannot be ignored when studying the effect of SOM polarity. Guo et al. (2012) found that polyphenyleneoxide, as a polar polymer with substantial O-containing functional groups, showed higher K_{OC} compared with linear polystyrene, a nonpolar polymer. This is contrast to the common notion that polarity of SOM is inversely correlated with its sorption capacity to hydrophobic contaminants (Jin et al., 2015; Zhang et al., 2015a). It could be the result that polar surface was masked in the interior and the hydrophobic sorption domain was exposed outside. Therefore, the interference of different factors on the sorption capacity of SOM should also be considered.

2.2. Impacts of soil minerals

The unique structure of minerals enables it to interact with various compounds, especially highly polar compounds. Sorption of nonpolar 1,3,5-trichlorobenzene decreased by approximately 86% when removal of the whole SOM, while only 34–54% for highly polar 1,3,5-trinitrobenzene (Shi et al., 2010). This indicated higher affinity of soil minerals with polar compounds. As shown in Fig. 1, surface hydroxyl group, adsorbed water molecular, hydrophobic Si-O bridged surfaces, hydrated cations and surficial metal of minerals provide possible sorption site for POPs.

Phyllosilicate clay mineral and metal oxides are widely studied minerals, both of which are effective sorbent in soil. Meanwhile, considering that soil is a complicated integration, organic and mineral phase are interacting together to form aggregates rather than isolated mixtures. In this case, the sorption behavior of mineral-SOM complex is also important.

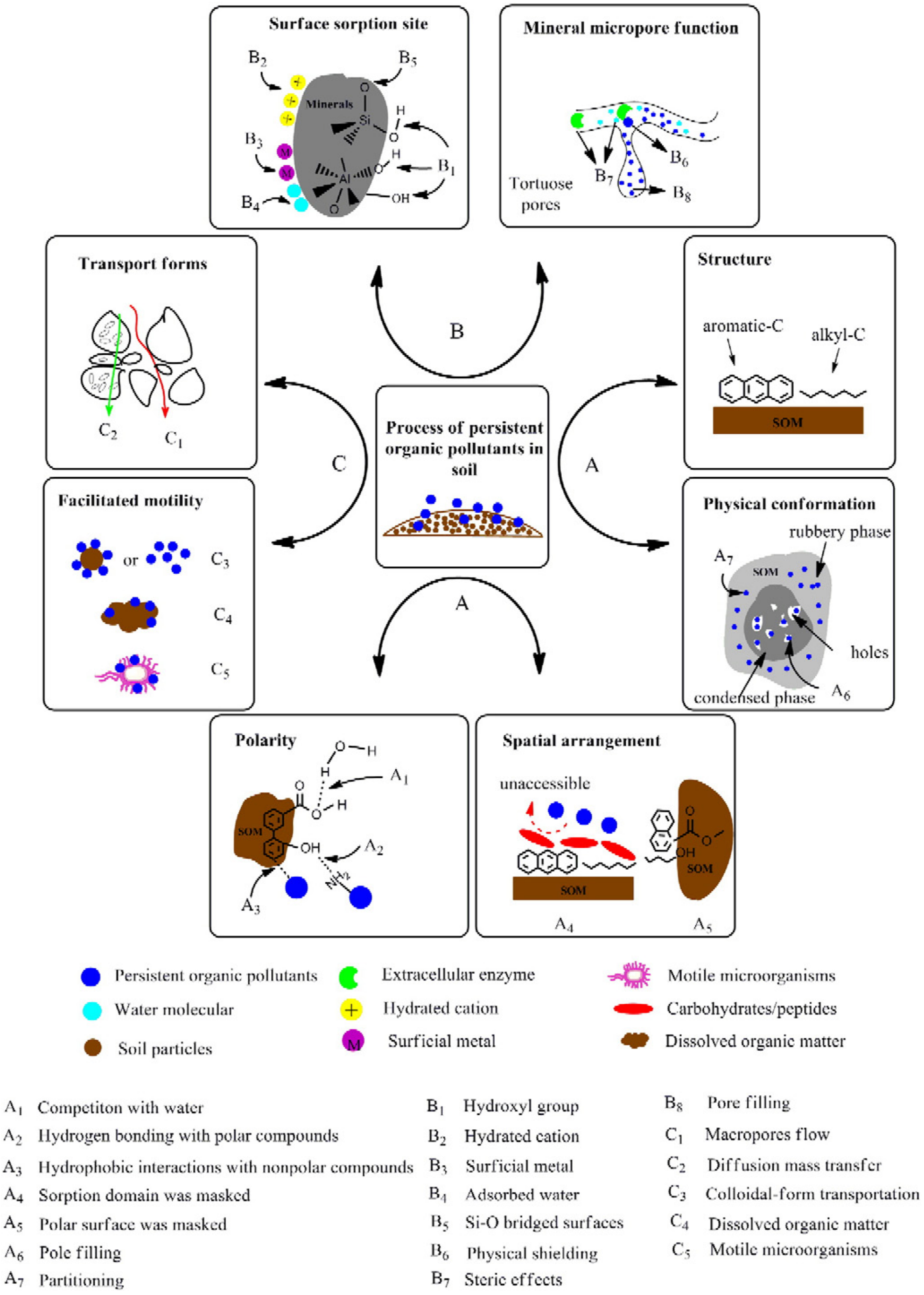

Fig. 1. Sorption and transport process of POPs in soil. (A) Sorption of POPs by SOM, influenced by structure (aromaticity and aliphaticity), polarity, spatial arrangement and physical conformation of SOM. (B) Sorption of POPs by soil minerals due to surface reaction and micropore sorption. (C) Transport of POPs in soil, including macropore flow, diffusion mass transfer as well as facilitated mobility.

2.2.1. Pure minerals

Kaolinite, smectite and illite are common clay mineral. They are constructed by silicon oxygen tetrahedral sheets and aluminum oxygenhydroxyl octahedral sheet with the proportion of 1:1 or 2:1 (Deng et al., 2017a). Abundant exchangeable cations were held on the surface of clay minerals, which made them possess high cation exchange capacity (Uddin, 2017). The liner relationship between displaced exchangeable cations from montmorillonite and adsorbed ciprofloxacin indicated the presence of cation exchange interactions (Wang et al., 2011a). Also, in a recent work done by Zhao et al. (2015), cation exchange on the negatively charged surface of kaolinite and montmorillonite dominate sorption of tetracycline rather than surface complexation on the edge site (Si/Al-OH). In addition, the interlayer space of phyllosilicate sheet is often occupied by hydrated cations (*e.g.* Na^+, K^+, Mg^{2+} and Ca^{2+}). Hydrated cations play a significant role in the sorption of contaminants. Hydroxylated metal cations on the mineral surface form the bridge between the silanol or hydroxyl groups of minerals and negative charged perfluoroalkyl acids (Zhao et al., 2014b). Formation of bidentate chelate or bridge inner-sphere complex was also observed in the interaction of picloram with two metal center of montmorillonite (Marco-Brown et al., 2015). Besides, hydrogen bonding is demonstrated to be important mechanisms in clay mineral. Hydrogen bonding is formed between polar groups of contaminants and basal oxygen atoms or adsorbed water on minerals (Wang et al., 2011a; Wu et al., 2015b). Hydroxyl groups on the octahedral sheet and tetrahedral sheet (*Si*-OH and Al-OH) can act as hydrogen bonds donor to oxygen and nitrogen of amides (*e.g.* C═O dipole, N—C dipole), and the oxygen of the octahedral sheet and tetrahedral sheet can accept H-bonds from N—H dipoles of amides (Li et al., 2015). Therefore, clay minerals could interact with POPs though different mechanisms. For a particular contaminant, the dominating sorption mechanisms are determined by the type of minerals. For example, carbonyl groups of aflatoxin B1 interact with Si/Al-OH surface of kaolinite by electrostatic attractions ($(\text{Si/Al-OH})_2\ldots(\text{O}{=}\text{C})_2$), but form Ca^{2+} bridging with hydrophobic silica oxygen bridged surfaces in smectite ($(\text{O}{=}\text{C})_2 \ldots \text{Ca}^{2+}\ldots (\text{O—Si})_4$), and form electron-donor-acceptor interactions with illite coordinated by K^+ ($(\text{O}{=}\text{C})_2 \ldots\text{K}^+\ldots (\text{O—Al})_3$) (Kang et al., 2016). This was affected by different properties of clay minerals.

Apart from clay mineral, oxides and hydroxides of Al and Fe are also efficient adsorbents for POPs It has been observed that removal of soil iron oxides result in over 85% reduction of pentachlorophenol adsorption in soil (Diagboya et al., 2016). The bulk groups and unique surface structure enables it to form strong interactions with POPs. Ghose et al. (2010) reported the presence of absorbed water, terminal hydroxo group and aquo group on the interface structural of goethite. The adsorbed water or hydroxyl group made great contributions to the adsorption capacity of oxides minerals. Carboxylate group of ciprofloxacin can form hydrogen-bonding with surface hydroxyl group on hydrous aluminum oxides (Gu and Karthikeyan, 2005). Ligand exchange on metal oxides has also been observed in adsorption of glyphosate on hydrous ferric oxides. Phosphonate group of glyphosate replace the adsorbed surface water/hydroxyl on goethite and interact with iron ions, forming inner-sphere complexes (Sheals et al., 2002). Meanwhile, surficial metal ions play an important role in retention of POPs. Ciprofloxacin interact with hydrous iron oxides by forming six membered ring with surface iron (Gu and Karthikeyan, 2005). Likewise, phosphinic moiety of glufosinate can form stable monodentate complexation with surface Fe(III) centers of goethite (Xu et al., 2016). Zhao et al. (2017) also observed surface bidentate complex and bridging bidentate complex between diclofenac and goethite.

In addition to surface adsorption, microstructures of minerals are also important in retention of POPs (Deng et al., 2017a; Diagboya et al., 2016). For montmorillonite, an expandable phase, the interlayer microporosity provide additional adsorption site for benzene, while for kaolinite, the nonexpendable mineral, only external surface was available for benzene (Deng et al., 2017a). This also applies to metal oxides minerals. Micropores of metal oxides provide extra reactive site for adsorption. As a result, amorphous iron oxide had higher sorption capacity than crystalline iron oxides due to higher surface area (Kahle and Stamm, 2007). The nanometer-scale pores of minerals are in the form of interlamellar spaces of layer phyllosilicates/aluminosilicate clay and cavities/defects in oxides. They take up over 90% of total mineral surface areas (Cheng et al., 2012). In mineral micropores, the sorption capacity is much stronger than the bulk phase, as a result of pore-filling mechanism. However, steric effects inhibit diffusivity in micopores and prevent POPs from accessing sorption site of the micropores (Cheng et al., 2012; Xu et al., 2014; Zhao et al., 2014b). Irregular shaped micropores in minerals further impeded desorption of POPs from micropores (Woignier et al., 2012). Another mechanism contribute to the retention of POPs by mineral micropores is physical shielding, in which the adsorbed POPs are protected from extracellular enzymes degradation (Cheng et al., 2012). Therefore, mineral micropores with steric effects, physical shielding and pore-filling mechanisms also play a significant role in retention of POPs (Fig. 1).

2.2.2. Mineral-SOM complexes

Mineral are often covered with SOM as mineral-SOM complexes which exhibit different properties from the isolated ones, consequently influencing their adsorption capacity. The accessibility of sorption site on minerals could be blocked by organic matter. In the study of Pils and Laird (2007), clays had higher sorption capacity to tetracyclines than clays-HS complex. Interlayer diffusion of tetracyclines in clays-HS complex was impeded by interlayer adsorbed HS. Similarly, Arroyave et al. (2016) observed a decline in adsorption of glyphosate with increasing adsorbed HA on goethite, which was attributed to the occupation of active site at the goethite surface by the loaded HA, and the existence of electrostatic repulsion between adsorbed HA and glyphosate. However, Wang and Xing (2005) found that aliphatic portion of HA were preferentially adsorbed on minerals than aromatic portion. This selective adsorption could lead to conformation changes of HA, and also enhanced mineral hydrophobicity and adsorption of phenanthrene by minerals. Zhang et al. (2017) also reported the enhanced hydrophobic interaction to phenanthrene and 1,2,4,5-tetrachlorobenzene in HSs–clay complexes than the original minerals. In addition, HA may act as bridge linking tetracycline and kaolinite in low pH, which increase the adsorption of tetracycline onto kaolinite (Zhao et al., 2011). Therefore, FA have two different effects on glufosinate adsorption by goethite: on the one hand, FA compete with glufosinate for adsorption site on goethite, which inhibit adsorption of glufosinate; on the other hand, adsorbed FA increase the hydrophobic of goethite, which could promote the hydrophobic interactions of glufosinat. However, the competition effect overwhelmed the enhancement effect due to low octanol-water coefficient of glufosinat, as was observed by Xu et al. (2016).

Moreover, it is important to understand the relative contribution of the exposed organic matter in SOM-mineral complex to the overall sorption process. Yang et al. (2012a) found that thickness of organic matter layer rather than minerals in the SOM-mineral complex dominated the bioavailability of phenanthrene. Also, Peng et al. (2015) examined the contribution of coated organic matter in HA-n-Fe_2O_3 complexes on adsorption of ofloxacin and norfloxacin. With 36% surface coverage on Fe_2O_3, HA take up over 80% of overall adsorption. It should be noticed that minerals determine the adsorption of POPs only when organic matter contents are very low in soil.

3. Transport of POPs in soil

The transport of POPs in soil is believed to be a combination of diffusion processes and medium-flow processes (Mechlińska et al., 2009) (Fig. 1). Diffusion is strongly related to the bioavailability of POPs (Johnsen et al., 2005). On the one hand, diffusion mass transfer of intraparticulate diffusion (IPD) and intraorganic matter diffusion (IOMD) are the primary process contributing to POPs sequestration in soil (Northcott and Jones, 2000). On the other hand, when POPs are too remote to be accessible by microorganism, diffusion process increases their bioavailability. Soil pores are the principal passway of medium-flow process, especially macropores which allow rapid and unrestricted movement of particle contaminants. Particulate or colloidal-form transport exists under two circumstances: contaminants are inherently particulates due to low solubility or the contaminants attach to otherwise harmless mobile particles (McGechan and Lewis, 2002; Sharma et al., 2013). The high specific surface areas enable colloids to effectively sorb low solubility and hydrophobic contaminants (Tavakkoli et al., 2015). Unlike sorption in static components that restrict movement of POPs, sorption onto mobile soil particles are demonstrated to be promotive in POPs transport not only at water-saturated media but also water unsaturated porous media in despite of some limitations, but in turn, this process is more likely to aggravate pollution (Knappenberger et al., 2014; Zeng et al., 2013b).

Dissolved organic matter (DOM) is important to the transport of POPs. Organic amendment-derived DOM was documented to promote pesticides transport (Li et al., 2005). Bacteria may be physically connected to DOM and facilitate its direct contact to micelles-associated contaminants (Schaefer and Juliane, 2007). Besides, DOM decreases interception probability of motile bacteria by surrounding soil particles, which contributes to the movement of bacteria (Haftka et al., 2008; Jimenez-Sanchez et al., 2015). Moreover, motile microorganisms are analogous to DOM that act as carriers for POPs (Gilbert et al., 2014). In this sense, both colloid-facilitated transport and motile microorganisms should be considered and the sorption to DOM is fundamental to degradation of adsorbed POPs. Therefore, investigation of their associations in POPs motility is expected to be followed.

4. Microbial adaptations to enhance bioavailability

Commonly, following sorption/desorption, POPs are transported to cellular membrane and are adsorbed by microorganism. This is the full bioavailability process, as described in the National Research Council report (Ehlers and Luthy, 2003). Sorption and transport are essential process for POPs to be available by microbes. However, when POPs are confronted with poor bioavailability conditions (*e.g.* strongly binding by SOM and minerals, steric hindrance between POPs and degrading microorganism, low solubility of POPs), microbial characteristics appear to be particularly important. Therefore, various microbial adaptations to increase bioavailability of POPs should be considered when studying the bioavailability process of POPs in soil. Microorganisms make a series of adjustments to environmental changes (limited bioavailability of chemicals), involving morphological, physiological and behavioral adaptation (Fig. 2) (Fester et al., 2014; Johnsen et al., 2005).

4.1. Morphological adaptation of microorganisms

In morphology, microbes develop multi-dimensional structure to increase the contact area with POPs, a typical example of which is fungal mycelia (Furuno et al., 2012). The formation of mycelia enables efficient mobilization of chemicals in soil, by the advantage of hyphal long-distance transport and also the possibility for hypha crossing air-filled pores (Fester et al., 2014; Schamfuß et al., 2013). Furuno et al. (2012) confirmed active transport of vesicles-associated PAH within hyphal pipelines with the help of cytoplasmic streaming, leading to a more efficient distribution than diffusion mechanisms. This is consistent with the observation of Schamfuß et al. (2013), who further proved that mycelia-transported fluorene were bioavailable to bacteria, and proposed that this process was directed by passive uptake from PAH sources, active transfer within hyphae and diffusion-driven release. More recently, Otto et al. (2016) demonstrated that fungal mycelia-promoted dispersal and spatial arrangement of microbial populations did enhance contaminant degradation.

In addition, it has been reported that anthracene-grown mycobacteria adapt to low solubility anthracene substrate by modifying cell surface properties, and show up to 70-fold higher attachment efficiency than glucose-grown mycobacteria (Wick et al., 2002a). Mycobacteria exhibit substrate-specific cell wall composition, with more mycolic acids in hydrophobic substrates (Wick et al., 2002b). Mycolic acids are hydrophobic fatty acid, and are believed to increase microbial adhesion to poor solubility substrate (Wick et al., 2003). Moreover, de Carvalho et al. (2009) observed cell surface charges change from negative to positive, which obviously stimulate microbial access to negatively charged n-alkane. It can be seen that cell wall adaptation (composition and surface charge) is important response to poor bioavailable compounds.

4.2. Physiological adaptation of microorganisms

In physiology, microorganisms facilitate POPs transfer either by decreasing transport distance to POPs (*e.g.* microbial attachment), or by steepening chemical gradient of substrate sources and accelerating diffusive transfer/desorption (Wick et al., 2002a). Formation of biofilm on contaminants-sources is important to get over mass-transfer restrictions in low bioavailability matrix (poorly soluble and strongly adsorbed PAH) (Johnsen and Karlson, 2004; Zhang et al., 2012). The secretion of extracellular polymeric substances, presence of glycolipid or glycopeptidolipid on the mycobacterial cell wall, and a more hydrophobic cell surface potentially facilitate this process (Zhang et al., 2016; Zhang et al., 2015b). The importance and properties of microbial attachment was highlighted by Yang et al. (2010), where phenanthrene was much strongly adsorbed on wax than cellulose, but wax-adsorbed phenanthrene had comparable degradability to cellulose-adsorbed

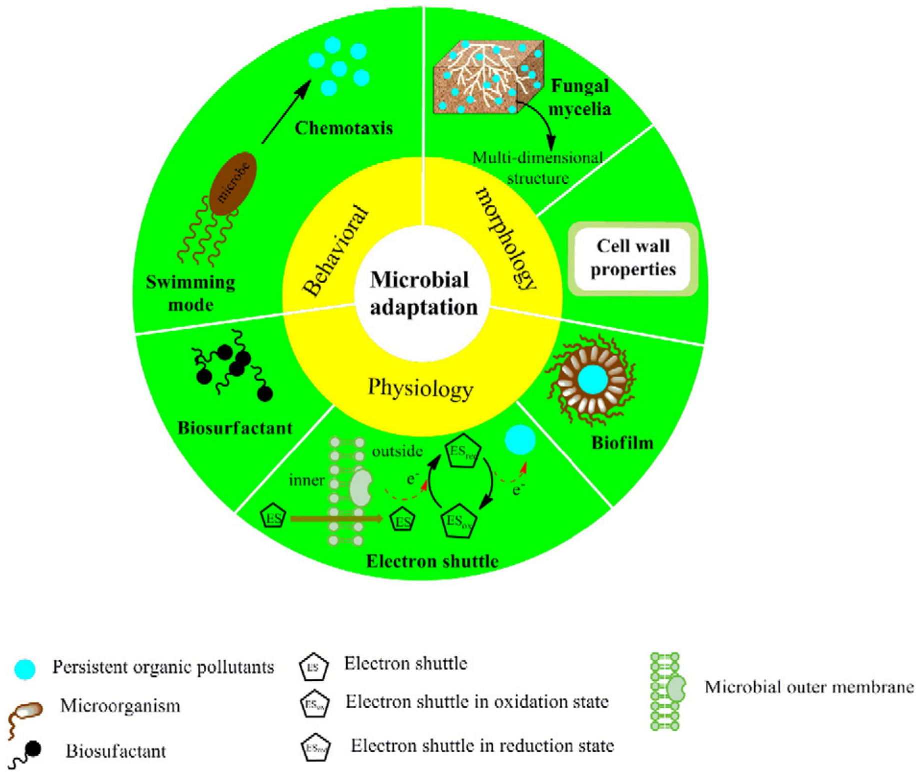

Fig. 2. Microbial adaptations to increase POPs bioavailability. Microbes adjust to unfavorable conditions by making morphological, physiological and behavioral adaptations.

phenanthrene. This was ascribed to more hydrophobic surface of wax (*i.e.*, abundant paraffinic carbons) favorable to bacterial adhesion. The attached bacteria had higher degradation rates due to shorter distance (Yang et al., 2010). They also suggested that association with aromatic moieties of HSs would inhibit immediate bioavailability of phenanthrene, but association with paraffinic carbon domains could be rapidly degraded, due to different potency of sorption domains to be microbial attachment (Yang et al., 2012a). As is the same case with SOM, POPs interaction with different minerals show different tendency to be available by microorganism. In a recent work done by Zhao et al. (2014a), metabolic activities of *Pseudomonas putida* and biodegradation of methyl parathion were enhanced by kaolinite but suppressed by goethite. Interfacial interactions of cellular surfaces with mineral particles were responsible for this phenomenon. Bacteria cells were loosely attached to larger particles of kaolinite, and this kind of interactions facilitated use of adsorbed substrate and then stimulated bacterial activity. By contrast, bacterial cells were tightly bound to small particles of goethite, which limited diffusion of adsorbed substrates, thereby inhibiting biodegradation (Zhao et al., 2014a). It can be seen that the promotive effect of microbial attachment to bioavailability is sorbent structure dependent.

Besides, microorganisms release surface active molecules (*e.g.* biosurfactants) to increase bioavailability (Zhang et al., 2013). On the one hand, biosurfactant decrease interfacial tensions of contaminant and promote its solubility and mobility. This is realized by micellar solubilization of POPs or direct modification of the contaminant matrix (*i.e.* decrease of soil-water interfacial tension) (Adrion et al., 2016; Bezza and Chirwa, 2017; Garcia et al., 2001; Singleton et al., 2016). On the other hand, hydrophobicity of the cell surface and its association with hydrophobic substrates are enhanced by biosurfactants (Pacwa-Płociniczak et al., 2011).

In addition, electron shuttles (*e.g.*, riboflavin, flavin mononucleotide, phenazines) secreted by some microorganisms, especially those with extracellular respiration pattern, are able to transfer electrons between the cell surface and POPs, thus facilitating redox biotransformation (Van der Zee and Cervantes, 2009; Yang et al., 2012b). Under anaerobic conditions, extracellular respiration bacteria oxidize electron donor (organic matter) and transport electrons to exogenous electron acceptor, from which the microorganisms get energy and growth. There are two ways of extracellular electron transfer: electrons can be directly transported from cell outer membrane cytochromes or bacterial nanowires to extracellular acceptors; moreover, electrons can be indirectly transported by electron shuttles, including microbial secretions and naturally occurring carbon (Peng et al., 2016; You et al., 2015; Yu et al., 2015). The second ways enable microorganisms overcome the limitation of direct contact with POPs, thus increasing POPs bioavailability.

4.3. Behavioral adaptation of microorganisms

Behavioral adaptation include chemotaxis (microbes are apt to access contaminants in the drive of chemical gradient) and swimming modes (enable microbes to move following water and airborne chemical gradients) (Fester et al., 2014). It has been reported that chemotactic movement of bacteria to pollutants increases bioavailability (Krell et al., 2013). Bacterial taxis help to overcome its dispersal limitation of retention by soil particles (Ortega-Calvo et al., 2013). Moreover, microbial movement by self-propulsion accelerated POPs transport, a process called co-transport. Co-transport of POPs with motile microorganisms is extremely important as the high tendency of POPs to be sequestrated in soil, which could also enhance their accessibility to degrading microorganisms (Gilbert et al., 2014).

4.4. Microbial access to adsorbed POPs

Given the adaptation of microorganisms, more than just in dissolved phase, POPs in adsorbed state can be available to microorganisms. Two possible ways are offered concerning bioavailability of adsorbed POPs (Chen and Ding, 2012): (i) soil-adsorbed POPs should be released to aqueous phase with the help of biosurfactant before biodegradation; and (ii) adsorbed POPs can be degraded directly by attached cell or by extracellular enzyme. It seems from above that desorption is not a limiting factor to bioavailability. Marchal et al. (2013) proved that phenanthrene adsorbed to compost, activated carbon and charcoal was desorbed to different extent but with similar degradation amount, in the presence of abundant bacteria and/or the production of biosurfactant or biofilms. Nevertheless, compared with the adsorbed contaminant, the dissolved form in pore water is considered to be more bioavailable (Megharaj et al., 2011), which is in accordance with a recent study where carbonaceous amendments strongly adsorb 2,2′,4,4′-tetrabrominated biphenyl ether and reduce its bioavailability to degrading microorganisms (Zhu et al., 2016). Moreover, it was reported that not until the exhaustion of readily available forms (dissolved fraction and reversibly adsorbed fraction) could the adsorbed phenanthrene be available to microbes (Yang et al., 2009). Various ways of microorganism accessing to POPs can be seen in Fig. 3. The dissolved fractions of POPs are readily available to microorganisms. However, due to microbial adaptations, POPs that are absorbed in soil can also be utilized by microorganisms. Direct adhesion to adsorbed POPs, production of extracellular enzyme and biosurfactant are possible ways of microorganism accessing the adsorbed POPs. The behaviors of microbial attachment and extracellular enzyme secretion lead to direct degradation of POPs. Besides, biosurfactant contributes to desorption of POPs and facilitate microbial uptake.

5. Conclusions and future perspectives

This paper reviewed bioavailability related mechanisms of POPs, including molecular-scaled mechanisms governing sorption and transport of POPs and the biological behaviors of microorganisms related to bioavailability. It can be seen that bioavailability of POPs is not only determined by the sorption behavior of SOM and minerals, but also by the DOM/colloid particles/motile microorganisms-facilitated transport. Other than physicochemical factors, this is also affected by microbial adaptations in low bioavailability conditions. Thus, the bioavailability mechanisms of POPs in soil are complicated and different factors should be considered. Following aspects are highlighted in future research:

(1) To what extent the POPs are adsorbed in a specific biogeochemical environment needs to be clarified. Most adsorption reactions in soil are spontaneous and exothermic process, and the adsorption extent decrease with higher temperature (Lamichhane et al., 2016). Besides, soil pH determines the surface charge of SOM and minerals, and the existing forms of POPs, which has significant impact on charge-dependent adsorption process (Wang et al., 2013a; Zeng et al., 2014). Under extreme pH conditions, both soil matrix and POPs are positive/negative charged. In such case, the electrostatic repulsion would weaken the sorption interactions. The impact of ionic strength is much more complex. High ionic strength would affect the electrostatic forces and the hydrophobic interaction or compete for adsorption site with sorbate, but have little impact on surface complexation (Tang et al., 2010; Wang et al., 2013a; Wu et al., 2015b; Zeng et al., 2014). In view of these cases, specific soil conditions, such as temperature, pH and ionic strength should be considered during the sorption studies. Moreover, the microenvironment of SOM or minerals should be taken into account. SOM and minerals interact together to form tortuous and porous soil particles, which make sorption of POPs different from the respective ones. Therefore, it is important to observe the structural characteristics of soil sorbents and spatial distribution of POPs in soil particles at a micrometer scale.

(2) Microbial adaptations to increase bioavailability of POPs have been observed. This also has significant implications in soil remediation. For example, Section of biosurfactant is an important microbial response to relieve the bioavailability limitations. Some studies

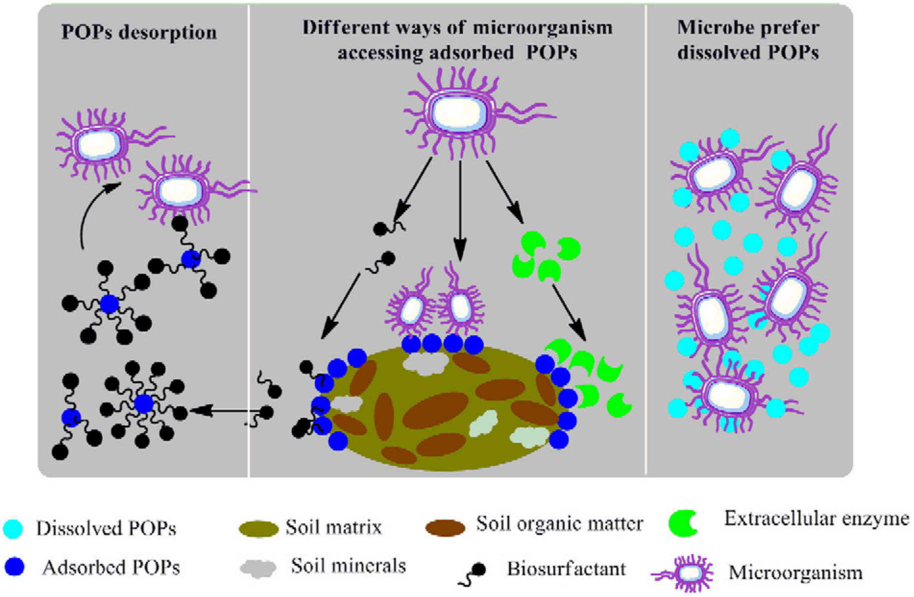

Fig. 3. Various ways of microorganism accessing POPs.

reported that external added surfactants could also enhance biodegradation of PAH and other hydrophobic contaminants (Adrion et al., 2016; Bezza and Chirwa, 2017; Singleton et al., 2016). However, it should be noted that surfactant-enhanced biodegradation is effective only when the POPs are hydrophobic and highly unavailable. As reported by Bezza and Chirwa (2017), addition of lipopeptidal biosurfactant had no apparent effect on the biodegradation of low molecular weight (LMW) PAHs, but significantly increased the biodegradation rate of high molecular weight (HMW) PAHs. LMW PAHs had comparatively high aqueous solubility and were free of bioavailability restrictions to biodegradation. Microbial remediation has been criticized for the low removal rate of HMW POPs. We can therefore combine the surfactants with bioremediation, making all levels of POPs available to degrading bacteria.

(3) We suggest that studying bioavailability of POPs is a good research idea in soil remediation. Since soil amendments, such as compost, hydroxyapatite (Zeng et al., 2017), nanomaterial (Gong et al., 2009; Xu et al., 2012) and biochar are widely used to remediate soil contamination, it is essential to study how those amendments affect the bioavailability of POPs to allow them to exert best effect on soil remediation. For example, composts with abundant organic matter could decrease bioavailability of POPs due to the increased sorption (Puglisi et al., 2007; Wu et al., 2013). However, the HA-like compounds in the compost could be taken as biosurfactant and increase biodegradation of PAH (Kobayashi et al., 2009; Wu et al., 2013). Soil microbial activity could also be enhanced after addition of compost (Puglisi et al., 2007). The contradictory effect on bioavailability of POPs could be determined by different components and microorganisms in compost.

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