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

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9   **Abstract**

10   Contamination of soils with persistent organic pollutants (POPs), such as

11   organochlorine pesticide, polybrominated diphenyl ethers, halohydrocarbon,

12   polycyclic aromatic hydrocarbons (PAHs) is of increasing concern. Microbial

13   degradation is potential mechanism for the removal of POPs, but it is often restricted

14   by low bioavailability of POPs. Thus, it is important to enhance bioavailability of

15   POPs in soil bioremediation. A series of reviews on bioavailability of POPs has been

16   published in the past few years. However, bioavailability of POPs in relation to soil

17   organic matter, minerals and soil microbes has been little studied. To fully understand

18   POPs bioavailability in soil, research on interactions of POPs with soil components

19   and microbial responses in bioavailability limitation conditions are needed. This

20   review focuses on bioavailability mechanisms of POPs in terms of sorption, transport

21   and microbial adaptation, which is particularly novel. In consideration of the

22   significance of bioavailability, further studies should investigate the influence of

23   various bioremediation strategies on POPs bioavailability.

24

25   **Keywords**: POPs; Soil organic matter; Mineral; Microbial adaptation; Soil

26   amendments

Contents

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

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67 microorganisms transfer in. Hence, transport of POPs should also be considered (Hu

68 et al., 2011; Liu et al., 2012). In addition to physicochemical process, understanding

69 the mechanisms of microorganisms to attack POPs is required in bioavailability

70 process. Microorganisms with some special characteristics could increase the

71 bioavailability of POPs under physical limitation conditions. For example,

72 micropore-adsorbed POPs are unable to be attached by microorganisms. In this case,

73 secretion of biosurfactant or hypha structure is important (Fester et al., 2014;

74 Pacwa-Płociniczak et al., 2011). To deal with the problem of deficient solubility of

75 POPs, formation of biofilm, secretion of biosurfactant or change of cell wall

76 properties are possible microbial response (Johnsen and Karlson, 2004;

77 Pacwa-Płociniczak et al., 2011; Wick et al., 2002b).

78   Several reviews have reported biodegradation mechanisms of POPs during

79 bioremediation (Johnsen et al., 2005; Ortega-Calvo et al., 2015; Semple et al., 2007;

80 Stroud et al., 2007). However, the interactions of POPs with soil components and

81 microorganisms associated characteristics to bioavailability have been little studied.

82 Three following aspects were included in this paper: (i) the sorption behavior of soil

83 organic matter (SOM) and minerals to POPs; (ii) transport ways of POPs in soil; and

84 (iii) microbial adaptations to increase bioavailability of POPs under bioavailability

85 restriction conditions. By giving a particular analysis about bioavailability

86 mechanisms of POPs, we want to provide a good research idea of bioavailability in

87 soil bioremediation.

88 **2. Sorption of POPs in soil**

89   It has been reported that bioavailability of POPs was decreased after adsorption

90   by soil. With time increasing, soils form stronger binding with POPs, consequently

91   causing a decline in bioavailability, a process termed as aging. Aging results in three

92   contaminant desorption manners: the 'rapid', 'slow' and 'very-slow domains. The

93   rapid desorption fractions are surface-adsorbed and interchangeable with the

94   pore-water, thus readily bioavailable. However, 'slow' and 'very-slow fractions are

95   strongly bounded or micropore-adsorbed, making it unavailable by microorganisms

96   (Semple et al., 2007). Slow or irreversible desorption of POPs is the the main factors

97   restricting their bioavailability. Although microorganisms can attack adsorbed

98   contaminants, they prefer dissolved fractions (Megharaj et al., 2011). Therefore,

99   sorption and desorption in soil are fundamental processes in controlling susceptibility

100   of POPs to microbial degradation. Sorption of POPs is mostly affected by the content

101   and properties of SOM. Meanwhile, soil minerals also play a role in sorption of POPs,

102   especially when organic matter content is lower than 1% (Cheng et al., 2012).

103   Consequently,, both the properties of SOM and minerals should be considered in

104   sorption of POPs.

2.1. Impacts of soil organic matter

106   It has been well demonstrated that the sequestration capacity of soil to POPs is

107   strongly connected to the proportion of SOM (Lima et al., 2012). However, soils with

108   the same organic matter content may have different sorption potentials for POPs.

109   SOM is a heterogeneous mixture including newly deposited biopolymers (*e.g.*,

110   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

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133 large number of data set was plotted, no specific correlation was found between

134 phenanthrene K_{OC} and the aromaticity of SOM from different sources (Chefetz and

135 Xing, 2009). This was supported by Hur et al. (2009) that aromatic carbon derived

136 from sediment HA served as a partitioning phase to POPs, while that from soil HA

137 functioned as specific adsorption sites. It is therefore concluded that aromaticity and

138 aliphaticity are both important to sorption, and different performances observed are

139 caused by structural complexity and heterogeneity of SOM.

140 2.1.2. Spatial arrangement of SOM

141   Additionally, other factors such as SOM spatial arrangement and surface

142 accessibility to POPs also influence the sorption ability of alkyl-carbon structures

143 (Mitchell and Simpson, 2013; Wang et al., 2011b). Mitchell and Simpson (2013)

144 observed weak correlation between K_{OC} and alkyl-carbon content of SOM. They

145 proposed that alkyl-carbon were absorbed strongly to minerals or buried by other

146 organic matter (*e.g.*, carbohydrates and peptides), which made it not accessible to

147 POPs. Moreover, some researchers attributed the different effect of alkyl domains on

148 sorption to two reasons: (i) condensed domains or O-alkyl components covered the

149 high-affinity alkyl domains and (ii) sorption ability of aromatic domains was

150 strengthened by the introduced black carbon (Han et al., 2014; Jin et al., 2015;

151 Mitchell and Simpson, 2013). Jin et al. (2015) also reported that the enhanced

152 π-acceptor ability of aromatic domains in nonhydrolyzable carbon (NHC) would

153 elevate sorption of phenanthrene but not for phthalate esters. The aromatic ring itself

154 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

177 found that aromaticity in engineered sorbents contributed a lot to the nanopore

178 adsorption.

179 2.1.4. Polarity of SOM

180   On the one hand, polar groups of SOM acted as hydrogen bond acceptor, and

181 water clusters formed on the surface acted as hydrogen bond donor, thereby reducing

182 the accessibility of contaminants to sorption sites by competition effect (Guo et al.,

183 2012; Jin et al., 2015). Also, polar features of HA/FA resulted in less PFOS adsorption

184 due to the increased electrostatic repulsion and decreased hydrophobic effect (Zhang

185 et al., 2015a). On the other hand, polarity of the SOM was positively related to

186 sorption of atrazine (a polar organic compound with mainly aromatic ring), as

187 reported by Wu et al. (2015a). Further, they observed better correlation of K_{OC} with

188 (N+O)/C ratios (polar index) than with H/C ratios (indicator of aliphaticity),

189 indicating that polarity of SOM dominated sorption of atrazine more than its

190 aliphaticity. Unlike the nonpolar organic compounds such as phenanthrene, whose

191 sorption mechanism was controlled by nonspecific hydrophobic partition to the

192 condensed organic matter, sorption of atrazine was attributed to the specific polar

193 interaction *e.g.*, hydrogen bonding between atrazine and polar fractions of SOM

194 (carboxylic and phenolic groups) (Shi et al., 2010; Wu et al., 2015a). Overall, the

195 impact of SOM polarity is dependent on the controlling sorption mechanism. This

196 was also demonstrated in a recent work by Jin et al. (2015) that sorption capacity of

197 phthalate esters was negatively correlated with surface polarity of nonhydrolyzable

198 carbon (NHC) but positively related with polarity of other organic matter (*e.g.* HA,

199   HM) due to dissimilar sorption mechanisms. Hydrophobic interactions regulated NHC

200   sorption affinity but both hydrogen bonding and hydrophobic interactions controlled

201   sorption of other organic matter (Jin et al., 2015).

202   To sum up, structure (aromaticity and aliphaticity), polarity, spatial arrangement

203   and physical conformation of SOM are interactive parameters on sorption of POPs

204   (Fig. 1). For example, the impact of spatial arrangement cannot be ignored when

205   studying the effect of SOM polarity. Guo et al. (2012) found that polyphenyleneoxide,

206   as a polar polymer with substantial O-containing functional groups, showed higher

207   K_{OC} compared with linear polystyrene, a nonpolar polymer. This is contrast to the

208   common notion that polarity of SOM is inversely correlated with its sorption capacity

209   to hydrophobic contaminants (Jin et al., 2015; Zhang et al., 2015a). It could be the

210   result that polar surface was masked in the interior and the hydrophobic sorption

211   domain was exposed outside. Therefore, the interference of different factors on the

212   sorption capacity of SOM should also be considered.

213   **2.2. Impacts of soil minerals**

214   The unique structure of minerals enables it to interact with various compounds,

215   especially highly polar compounds. Sorption of nonpolar 1,3,5-trichlorobenzene

216   decreased by approximately 86% when removal of the whole SOM, while only

217   34-54% for highly polar 1,3,5-trinitrobenzene (Shi et al., 2010). This indicated higher

218   affinity of soil minerals with polar compounds. As shown in Fig. 1, surface hydroxyl

219   group, adsorbed water molecular, hydrophobic Si-O bridged surfaces, hydrated

220   cations and surficial metal of minerals provide possible sorption site for POPs.

221   Phyllosilicate clay mineral and metal oxides are widely studied minerals, both of

222   which are effective sorbent in soil. Meanwhile, considering that soil is a complicated

223   integration, organic and mineral phase are interacting together to form aggregates

224   rather than isolated mixtures. In this case, the sorption behavior of mineral-SOM

225   complex is also important.

226   2.2.1. Pure minerals

227   Kaolinite, smectite and illite are common clay mineral. They are constructed by

228   silicon-oxygen tetrahedral sheets and aluminium-oxygenhydroxyl octahedral sheet

229   with the proportion of 1:1 or 2:1(Deng et al., 2017a). Abundant exchangeable cations

230   were held on the surface of clay minerals, which made them possess high cation

231   exchange capacity (Uddin, 2017). The liner relationship between displaced

232   exchangeable cations from montmorillonite and adsorbed ciprofloxacin indicated the

233   presence of cation exchange interactions (Wang et al., 2011a). Also, in a recent work

234   done by Zhao et al. (2015), cation exchange on the negatively charged surface of

235   kaolinite and montmorillonite dominate sorption of tetracycline rather than surface

236   complexation on the edge site (Si/Al-OH). In addition, the interlayer space of

237   phyllosilicate sheet is often occupied by hydrated cations (*e.g.* Na^+, K^+, Mg^{2+} and

238   Ca^{2+}). Hydrated cations play a significant role in the sorption of contaminants.

239   Hydroxylated metal cations on the mineral surface form the bridge between the

240   silanol or hydroxyl groups of minerals and negative charged perfluoroalkyl acids

241   (Zhao et al., 2014b). Formation of bidentate chelate or bridge inner-sphere complex

242   was also observed in the interaction of picloram with two metal center of

243   montmorillonite (Marco-Brown et al., 2015). Besides, hydrogen bonding is

244   demonstrated to be important mechanisms in clay mineral. Hydrogen bonding is

245   formed between polar groups of contaminants and basal oxygen atoms or adsorbed

246   water on minerals (Wang et al., 2011a; Wu et al., 2015b). Hydroxyl groups on the

247   octahedral sheet and tetrahedral sheet (Si-OH and Al-OH) can act as hydrogen bonds

248   donor to oxygen and nitrogen of amides (e.g. C=O dipole, N–C dipole), and the

249   oxygen of the octahedral sheet and tetrahedral sheet can accept H-bonds from N–H

250   dipoles of amides (Li et al., 2015). Therefore, clay minerals could interact with POPs

251   though different mechanisms. For a particular contaminant, the dominating sorption

252   mechanisms are determined by the type of minerals. For example, carbonyl groups of

253   aflatoxin B1 interact with Si/Al-OH surface of kaolinite by electrostatic attractions

254     $((Si/Al\text{-}OH)_2…(O=C)_2)$, but form Ca^{2+} bridging with hydrophobic silica-oxygen

255   bridged   surfaces   in   smectite $((O=C)_2 …Ca^{2+}… (O\text{-}Si)_4)$,   and   form

256   electron-donor-acceptor interactions with illite coordinated by K^+ $((O=C)_2 …K^+…$

257     $(O\text{-}Al)_3)$ (Kang et al., 2016). This was affected by different properties of clay

258   minerals.

259   Apart from clay mineral, oxides and hydroxides of Al and Fe are also efficient

260   adsorbents for POPs It has been observed that removal of soil iron oxides result in

261   over 85% reduction of pentachlorophenol adsorption in soil (Diagboya et al., 2016).

262   The bulk groups and unique surface structure enables it to form strong interactions

263   with POPs. Ghose et al. (2010) reported the presence of absorbed water, terminal

264   hydroxo group and aquo group on the interface structural of goethite. The adsorbed

265 water or hydroxyl group made great contributions to the adsorption capacity of oxides

266 minerals. Carboxylate group of ciprofloxacin can form hydrogen-bonding with

267 surface hydroxyl group on hydrous aluminum oxides (Gu and Karthikeyan, 2005).

268 Ligand exchange on metal oxides has also been observed in adsorption of glyphosate

269 on hydrous ferric oxides. Phosphonate group of glyphosate replace the adsorbed

270 surface water/ hydroxyl on goethite and interact with iron ions, forming inner-sphere

271 complexes (Sheals et al., 2002). Meanwhile, surficial metal ions play an important

272 role in retention of POPs. Ciprofloxacin interact with hydrous iron oxides by forming

273 six membered ring with surface iron (Gu and Karthikeyan, 2005). Likewise,

274 phosphinic moiety of glufosinate can form stable monodentate complexation with

275 surface Fe(III) centers of goethite (Xu et al., 2016). Zhao et al. (2017) also observed

276 surface bidentate complex and bridging bidentate complex between diclofenac and

277 goethite.

278 In addition to surface adsorption, microstructures of minerals are also important

279 in retention of POPs (Deng et al., 2017a; Diagboya et al., 2016). For montmorillonite,

280 an expandable phase, the interlayer microporosity provide additional adsorption site

281 for benzene, while for kaolinite, the nonexpendable mineral, only external surface was

282 available for benzene (Deng et al., 2017a). This also applies to metal oxides minerals.

283 Micropores of metal oxides provide extra reactive site for adsorption. As a result,

284 amorphous iron oxide had higher sorption capacity than crystalline iron oxides due to

285 higher surface area (Kahle and Stamm, 2007). The nanometer-scale pores of minerals

286 are in the form of interlamellar spaces of layer phyllosilicates/ aluminosilicate clay

287 and cavities/defects in oxides. They take up over 90% of total mineral surface areas

288 (Cheng et al., 2012). In mineral micropores, the sorption capacity is much stronger

289 than the bulk phase, as a result of pore-filling mechanism. However, steric effects

290 inhibit diffusivity in micopores and prevent POPs from accessing sorption site of the

291 micropores (Cheng et al., 2012; Xu et al., 2014; Zhao et al., 2014b). Irregular shaped

292 micropores in minerals further impeded desorption of POPs from micropores

293 (Woignier et al., 2012). Another mechanism contribute to the retention of POPs by

294 mineral micropores is physical shielding, in which the adsorbed POPs are protected

295 from extracellular enzymes degradation (Cheng et al., 2012). Therefore, mineral

296 micropores with steric effects, physical shielding and pore-filling mechanisms also

297 play a significant role in retention of POPs (Fig. 1).

298 2.2.2. Mineral-SOM complexes

299 Mineral are often covered with SOM as mineral-SOM complexes which exhibit

300 different properties from the isolated ones, consequently influencing their adsorption

301 capacity. The accessibility of sorption site on minerals could be blocked by organic

302 matter. In the study of Pils and Laird (2007), clays had higher sorption capacity to

303 tetracyclines than clays-HS complex. Interlayer diffusion of tetracyclines in clays-HS

304 complex was impeded by interlayer adsorbed HS. Similarly, Arroyave et al. (2016)

305 observed a decline in adsorption of glyphosate with increasing adsorbed HA on

306 goethite, which was attributed to the occupation of active site at the goethite surface

307 by the loaded HA, and the existence of electrostatic repulsion between adsorbed HA

308 and glyphosate. However, Wang and Xing (2005) found that aliphatic portion of HA

309 were preferentially adsorbed on minerals than aromatic portion. This selective

310 adsorption could lead to conformation changes of HA, and also enhanced mineral

311 hydrophobicity and adsorption of phenanthrene by minerals. Zhang et al. (2017) also

312 reported the enhanced hydrophobic interaction to phenanthrene and

313 1,2,4,5-tetrachlorobenzene in HSs–clay complexes than the original minerals. In

314 addition, HA may act as bridge linking tetracycline and kaolinite in low pH, which

315 increase the adsorption of tetracycline onto kaolinite (Zhao et al., 2011). Therefore,

316 FA have two different effects on glufosinate adsorption by goethite: on the one hand,

317 FA compete with glufosinate for adsorption site on goethite, which inhibit adsorption

318 of glufosinate; on the other hand, adsorbed FA increase the hydrophobic of goethite,

319 which could promote the hydrophobic interactions of glufosinat. However, the

320 competition effect overwhelmed the enhancement effect due to low octanol-water

321 coefficient of glufosinat, as was observed by Xu et al. (2016).

322 Moreover, it is important to understand the relative contribution of the exposed

323 organic matter in SOM-mineral complex to the overall sorption process. Yang et al.

324 (2012a) found that thickness of organic matter layer rather than minerals in the

325 SOM-mineral complex dominated the bioavailability of phenanthrene. Also, Peng et

326 al. (2015) examined the contribution of coated organic matter in HA-n-Fe$_2$O$_3$

327 complexes on adsorption of ofloxacin and norfloxacin. With 36% surface coverage on

328 Fe$_2$O$_3$, HA take up over 80% of overall adsorption. It should be noticed that minerals

329 determine the adsorption of POPs only when organic matter contents are very low in

330 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

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353   to micelles-associated contaminants (Schaefer and Juliane, 2007). Besides, DOM

354   decreases interception probability of motile bacteria by surrounding soil particles,

355   which contributes to the movement of bacteria (Haftka et al., 2008; Jimenez-Sanchez

356   et al., 2015). Moreover, motile microorganisms are analogous to DOM that act as

357   carriers for POPs (Gilbert et al., 2014). In this sense, both colloid-facilitated transport

358   and motile microorganisms should be considered and the sorption to DOM is

359   fundamental to degradation of adsorbed POPs. Therefore, investigation of their

360   associations in POPs motility is expected to be followed.

361   **4. Microbial adaptations to enhance bioavailability**

362   Commonly, following sorption/desorption, POPs are transported to cellular

363   membrane and are adsorbed by microorganism. This is the full bioavailability process,

364   as described in the National Research Council report (Ehlers and Luthy, 2003).

365   Sorption and transport are essential process for POPs to be available by microbes.

366   However, when POPs are confronted with poor bioavailability conditions (*e.g.*

367   strongly binding by SOM and minerals, steric hindrance between POPs and degrading

368   microorganism, low solubility of POPs), microbial characteristics appear to be

369   particularly important. Therefore, various microbial adaptations to increase

370   bioavailability of POPs should be considered when studying the bioavailability

371   process of POPs in soil. Microorganisms make a series of adjustments to

372   environmental changes (limited bioavailability of chemicals), involving

373   morphological, physiological and behavioral adaptation (Fig. 2) (Fester et al., 2014;

374   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 acrossing 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

397   microbial access to negatively charged n-alkane. It can be seen that cell wall

398   adaptation (composition and surface charge) is important response to poor

399   bioavailable compounds.

400   **4.2. Physiological adaptation of microorganisms**

401   In physiology, microorganisms facilitate POPs transfer either by decreasing

402   transport distance to POPs (e.g. microbial attachment), or by steepening chemical

403   gradient of substrate sources and accelerating diffusive transfer/desorption (Wick et

404   al., 2002a). Formation of biofilm on contaminants-sources is important to get over

405   mass-transfer restrictions in low bioavailability matrix (poorly soluble and strongly

406   adsorbed PAH) (Johnsen and Karlson, 2004; Zhang et al., 2012). The secretion of

407   extracellular polymeric substances, presence of glycolipid or glycopeptidolipid on the

408   mycobacterial cell wall, and a more hydrophobic cell surface potentially facilitate this

409   process (Zhang et al., 2016; Zhang et al., 2015b). The importance and properties of

410   microbial attachment was highlighted by Yang et al. (2010), where phenanthrene was

411   much strongly adsorbed on wax than cellulose, but wax-adsorbed phenanthrene had

412   comparable degradability to cellulose-adsorbed phenanthrene. This was ascribed to

413   more hydrophobic surface of wax (*i.e.*, abundant paraffinic carbons) favorable to

414   bacterial adhesion. The attached bacteria had higher degradation rates due to shorter

415   distance (Yang et al., 2010). They also suggested that association with aromatic

416   moieties of HSs would inhibit immediate bioavailability of phenanthrene, but

417   association with paraffinic carbon domains could be rapidly degraded, due to different

418   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

imcrease 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

441 facilitating redox biotransformation (Van der Zee and Cervantes, 2009; Yang et al.,

442 2012b). Under anaerobic conditions, extracellular respiration bacteria oxidize electron

443 donor (organic matter) and transport electrons to exogenous electron acceptor, from

444 which the microorganisms get energy and growth. There are two ways of extracellular

445 electron transfer: electrons can be directly transported from cell outer membrane

446 cytochromes or bacterial nanowires to extracellular acceptors; moreover, electrons

447 can be indirectly transported by electron shuttles, including microbial secretions and

448 naturally occurring carbon (Peng et al., 2016; You et al., 2015; Yu et al., 2015). The

449 second ways enable microorganisms overcome the limitation of direct contact with

450 POPs, thus increasing POPs bioavailability.

451 **4.3. Behavioral adaptation of microorganisms**

452   Behavioral adaptation include chemotaxis (microbes are apt to access

453 contaminants in the drive of chemical gradient) and swimming modes (enable

454 microbes to move following water and airborne chemical gradients) (Fester et al.,

455 2014). It has been reported that chemotactic movement of bacteria to pollutants

456 increases bioavailability (Krell et al., 2013). Bacterial taxis help to overcome its

457 dispersal limitation of retention by soil particles (Ortega-Calvo et al., 2013).

458 Moreover, microbial movement by self-propulsion accelerated POPs transport, a

459 process called co-transport. Co-transport of POPs with motile microorganisms is

460 extremely important as the high tendency of POPs to be sequestrated in soil, which

461 could also enhance their accessibility to degrading microorganisms (Gilbert et al.,

462 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

485 microorganism accessing the adsorbed POPs. The behaviors of microbial attachment

486 and extracellular enzyme secretion lead to direct degradation of POPs. Besides,

487 biosurfactant contributes to desorption of POPs and facilitate microbial uptake.

488 **5. Conclusions and Future perspectives**

489   This paper reviewed bioavailability related mechanisms of POPs, including

490 molecular-scaled mechanisms governing sorption and transport of POPs and the

491 biological behaviors of microorganisms related to bioavailability. It can be seen that

492 bioavailability of POPs is not only determined by the sorption behavior of SOM and

493 minerals, but also by the DOM/colloid particles/motile microorganisms-facilitated

494 transport. Other than physicochemical factors, this is also affected by microbial

495 adaptations in low bioavailability conditions. Thus, the bioavailability mechanisms of

496 POPs in soil are complicated and different factors should be considered. Following

497 aspects are highlighted in future research:

498   (1) To what extent the POPs are adsorbed in a specific biogeochemical

499 environment needs to be clarified. Most adsorption reactions in soil are spontaneous

500 and exothermic process, and the adsorption extent decrease with higher temperature

501 (Lamichhane et al., 2016). Besides, soil pH determines the surface charge of SOM

502 and minerals, and the existing forms of POPs, which has significant impact on

503 charge-dependent adsorption process (Wang et al., 2013a; Zeng et al., 2014). Under

504 extreme pH conditions, both soil matrix and POPs are positive/negative charged. In

505 such case, the electrostatic repulsion would weaken the sorption interactions. The

506 impact of ionic strength is much more complex. High ionic strength would affect the

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507 electrostatic forces and the hydrophobic interaction or compete for adsorption site

508 with sorbate, but have little impact on surface complexation (Tang et al., 2010; Wang

509 et al., 2013a; Wu et al., 2015b; Zeng et al., 2014). In view of these cases, specific soil

510 conditions, such as temperature, pH and ionic strength should be considered during

511 the sorption studies. Moreover, the microenvironment of SOM or minerals should be

512 taken into account. SOM and minerals interact together to form tortuous and porous

513 soil particles, which make sorption of POPs different from the respective ones.

514 Therefore, it is important to observe the structural characteristics of soil sorbents and

515 spatial distribution of POPs in soil particles at a micrometer scale.

516   (2) Microbial adaptations to increase bioavailability of POPs have been observed.

517 This also has significant implications in soil remediation. For example, Section of

518 biosurfactant is an important microbial response to relieve the bioavailability

519 limitations. Some studies reported that external added surfactants could also enhance

520 biodegradation of PAH and other hydrophobic contaminants (Adrion et al., 2016;

521 Bezza and Chirwa, 2017; Singleton et al., 2016). However, it should be noted that

522 surfactant-enhanced biodegradation is effective only when the POPs are hydrophobic

523 and highly unavailable. As reported by Bezza and Chirwa (2017), addition of

524 lipopeptidal biosurfactant had no apparent effect on the biodegradation of low

525 molecular weight (LMW) PAHs, but significantly increased the biodegradation rate of

526 high molecular weight (HMW) PAHs. LMW PAHs had comparatively high aqueous

527 solubility and were free of bioavailability restrictions to biodegradation. Microbial

528 remediation has been criticized for the low removal rate of HMW POPs. We can

529 therefore combine the surfactants with bioremediation, making all levels of POPs

530 availabile to degrading bacteria.

531 (3) We suggest that studying bioavailability of POPs is a good research idea in

532 soil remediation. Since soil amendments, such as compost, hydroxyapatite (Zeng et al.,

533 2017), nanomaterial (Gong et al., 2009; Xu et al., 2012) and biochar are widely used

534 to remediate soil contamination, it is essential to study how those amendments affect

535 the bioavailability of POPs to allow them to exert best effect on soil remediation. For

536 example, composts with abundant organic matter could decrease bioavailability of

537 POPs due to the increased sorption (Puglisi et al., 2007; Wu et al., 2013). However,

538 the HA-like compounds in the compost could be taken as biosurfactant and increase

539 biodegradation of PAH (Kobayashi et al., 2009; Wu et al., 2013). Soil microbial

540 activity could also be enhanced after addition of compost (Puglisi et al., 2007). The

541 contradictory effect on bioavailability of POPs could be determined by different

542 components and microorganisms in compost.

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548 **References**

549 Adrion, A.C., Nakamura, J., Shea, D., Aitken, M.D., 2016. Screening Nonionic

550 Surfactants for Enhanced Biodegradation of Polycyclic Aromatic

551   Hydrocarbons Remaining in Soil After Conventional Biological Treatment.

552   Environ. Sci. Technol. 50(7), 3838-3845.

553 Arroyave, J.M., Waiman, C.C., Zanini, G.P., Avena, M.J., 2016. Effect of humic acid

554   on the adsorption/desorption behavior of glyphosate on goethite. Isotherms

555   and kinetics. Chemosphere 145, 34-41.

556 Bezza, F.A., Chirwa, E.M.N., 2017. The role of lipopeptide biosurfactant on microbial

557   remediation of aged polycyclic aromatic hydrocarbons (PAHs)-contaminated

558   soil. Chem. Eng. J. 309, 563-576.

559 Chefetz, B., Xing, B.S., 2009. Relative Role of Aliphatic and Aromatic Moieties as

560   Sorption Domains for Organic Compounds: A Review. Environ. Sci. Technol.

561   43, 1680-1688.

562 Chen, B.L, Ding, J., 2012. Biosorption and biodegradation of phenanthrene and

563   pyrene in sterilized and unsterilized soil slurry systems stimulated by

564   Phanerochaete chrysosporium. J. Hazard. Mater. 229, 159-69.

565 Cheng, H.F., Hu, E., Hu, Y.A., 2012. Impact of mineral micropores on transport and

566   fate of organic contaminants: a review. J. Contam. Hydrol. 129, 80-90.

567 Cornelissen, G, Gustafsson, Ö., Bucheli, T.D., Jonker, M.T.O., Koelmans, A.A., Van

568   Noort, P.C.M., 2005. Extensive sorption of organic compounds to black

569   carbon, coal, and kerogen in sediments and soils: Mechanisms and

570   consequences for distribution, bioaccumulation, and biodegradation. Environ.

571   Sci. Technol.. 39, 6881-6895.

572 de Carvalho, C.C.C.R., Wick, L.Y., Heipieper, H.J., 2009. Cell wall adaptations of

27

planktonic and biofilm Rhodococcus erythropolis cells to growth on C5 to C16 n-alkane hydrocarbons. Appl. Microbiol. Biotechnol. 82, 311-320.

Deng, L., Yuan, P., Liu, D., Annabi-Bergaya, F., Zhou, J., Chen, F., Liu, Z., 2017a. Effects of microstructure of clay minerals, montmorillonite, kaolinite and halloysite, on their benzene adsorption behaviors. Appl. Clay Sci. 143, 184-191.

Deng, Y.C., Tang, L., Zeng, G.M., Zhu, Z.J., Yan, M., Zhou, Y.Y., Wang, J.J., Liu, Y.N., Wang, J.J., 2017b. Insight into highly efficient simultaneous photocatalytic removal of Cr(VI) and 2,4-diclorophenol under visible light irradiation by phosphorus doped porous ultrathin g-C_3N_4 nanosheets from aqueous media: Performance and reaction mechanism. Appl Catal B-Environ. 203, 343-354.

Diagboya, P.N., Olu-Owolabi, B.I., Adebowale, K.O., 2016. Distribution and interactions of pentachlorophenol in soils: The roles of soil iron oxides and organic matter. J. Contam. Hydrol. 191, 99-106.

Ehlers, L.J., Luthy, R.G., 2003. Peer Reviewed: Contaminant Bioavailability in Soil and Sediment. Environ. Sci. Technol. 37, 295A-302A.

Fester, T., Giebler, J., Wick, L.Y., Schlosser, D., Kästner, M., 2014. Plant-microbe interactions as drivers of ecosystem functions relevant for the biodegradation of organic contaminants. Curr. Opin. Biotechnol. 27, 168-75.

Furuno, S., Foss, S., Wild, E., Jones, K.C., Semple, K.T., Harms, H., Wick, L.Y., 2012. Mycelia Promote Active Transport and Spatial Dispersion of Polycyclic Aromatic Hydrocarbons. Environ. Sci. Technol. 46, 5463-5470.

595   Garcia, J.M., Wick, L.Y., Harms, H., 2001. Influence of the nonionic surfactant Brij

596   35 on the bioavailability of solid and sorbed dibenzofuran. Environ. Sci.

597   Technol. 35, 2033-2039.

598   Ghose, S.K., Waychunas, G.A., Trainor, T.P., Eng, P.J., 2010. Hydrated goethite

599   (alpha-FeOOH) (100) interface structure: Ordered water and surface

600   functional groups. Geochim. Cosmochim. Ac. 74, 1943-1953.

601   Gilbert, D., Jakobsen, H.H., Winding, A., Mayer, P., 2014. Co-Transport of Polycyclic

602   Aromatic Hydrocarbons by Motile Microorganisms Leads to Enhanced Mass

603   Transfer under Diffusive Conditions. Environ. Sci. Technol. 48, 4368-4375.

604   Gong, J.L., Wang, B., Zeng, G.M., Yang, C.P., Niu, C.G., Niu, Q.Y., Zhou, W.J., Liang,

605   Y., 2009. Removal of cationic dyes from aqueous solution using magnetic

606   multi-wall carbon nanotube nanocomposite as adsorbent. J. Hazard. Mater.

607   164, 1517-1522.

608   Gu, C., Karthikeyan, K.G., 2005. Sorption of the antimicrobial ciprofloxacin to

609   aluminum and iron hydrous oxides. Environ. Sci. Technol. 39, 9166-9173.

610   Guo, X.Y., Wang, X.L., Zhou, X.Z., Kong, X.Z., Tao, S., Xing, B.S., 2012. Sorption

611   of four hydrophobic organic compounds by three chemically distinct polymers:

612   role of chemical and physical composition. Environ. Sci. Technol. 46, 7252-9.

613   Haftka, J.J.H., Parsons, J.R., Govers, H.A.J., Ortega-Calvo, J.J., 2008. Enhanced

614   kinetics of solid-phase microextraction and biodegradation of polycyclic

615   aromatic hydrocarbons in the presence of dissolved organic matter. Environ.

616   Toxicol. Chem. 27, 1526-1532.

617   Han, L.F., Sun, K., Jin, J., Wei, X., Xia, X.H., Wu, F.C., Gao, B., Xing, B.S., 2014.

618   Role of structure and microporosity in phenanthrene sorption by natural and

619   engineered organic matter. Environ. Sci. Technol. 48, 11227-34.

620   Hu, X.J., Wang, J.S., Liu, Y.G., Li, X., Zeng, G.M., Bao, Z.l., Zeng, X.X., Chen, A.W.,

621   Long, F., 2011. Adsorption of chromium (VI) by ethylenediamine-modified

622   cross-linked magnetic chitosan resin: Isotherms, kinetics and thermodynamics.

623   J. Hazard. Mater. 185, 306-314.

624   Hur, J., Lee, D.H., Shin, H.S., 2009. Comparison of the structural, spectroscopic and

625   phenanthrene binding characteristics of humic acids from soils and lake

626   sediments. Org. Geochem. 40, 1091-1099.

627   Jimenez-Sanchez, C., Wick, L.Y., Cantos, M., Ortega-Calvo, J.J., 2015. Impact of

628   dissolved organic matter on bacterial tactic motility, attachment, and transport.

629   Environ. Sci. Technol. 49, 4498-505.

630   Jin, J., Sun, K., Wang, Z.Y., Han, L.F., Pan, Z.Z., Wu, F.C., Liu, X.T., Zhao, Y., Xing,

631   B.S., 2015. Characterization and phthalate esters sorption of organic matter

632   fractions isolated from soils and sediments. Environ. Pollut. 206, 24-31.

633   Johnsen, A.R., Karlson, U., 2004. Evaluation of bacterial strategies to promote the

634   bioavailability of polycyclic aromatic hydrocarbons. Appl. Microbiol.

635   Biotechnol. 63, 452-9.

636   Johnsen, A.R., Wick, L.Y., Harms, H., 2005. Principles of microbial PAH-degradation

637   in soil. Environ. Pollut. 133, 71-84.

638   Kahle, M., Stamm, C., 2007. Time and pH-dependent sorption of the veterinary

639   antimicrobial sulfathiazole to clay minerals and ferrihydrite. Chemosphere 68,

640   1224-1231.

641 Kang, F., Ge, Y., Hu, X., Goikavi, C., Waigi, M.G., Gao, Y., Ling, W., 2016.

642   Understanding the sorption mechanisms of aflatoxin B1 to kaolinite, illite, and

643   smectite clays via a comparative computational study. J. Hazard. Mater. 320,

644   80-87.

645 Keiluweit, M., Kleber, M., 2009. Molecular-Level Interactions in Soils and Sediments:

646   The Role of Aromatic pi-Systems. Environ. Sci. Technol. 43, 3421-3429.

647 Kickham, P., Otton, S.V., Moore, M.M., Ikonomou, M.G., Gobas, F.A.P.C., 2012.

648   Relationship between biodegradation and sorption of phthalate esters and their

649   metabolites in natural sediments. Environ. Toxicol. Chem. 31, 1730-1737.

650 Knappenberger, T., Flury, M., Mattson, E.D., Harsh, J.B., 2014. Does Water Content

651   or Flow Rate Control Colloid Transport in Unsaturated Porous Media?

652   Environ. Sci. Technol. 48, 3791-3799.

653 Kobayashi, T., Murai, Y., Tatsumi, K., Iimura, Y., 2009. Biodegradation of polycyclic

654   aromatic hydrocarbons by *Sphingomonas sp.* enhanced by water-extractable

655   organic matter from manure compost. Sci. Total Environ. 407, 5805-10.

656 Krell, T., Lacal, J., Reyes-Darias, J.A., Jimenez-Sanchez, C., Sungthong, R.,

657   Ortega-Calvo, J.J., 2013. Bioavailability of pollutants and chemotaxis. Curr.

658   Opin. Biotechnol. 24, 451-6.

659 Lamichhane, S., Krishna, K.C.B., Sarukkalige, R., 2016. Polycyclic aromatic

660   hydrocarbons (PAHs) removal by sorption: A review. Chemosphere 148,

661   336-353.

662   Li, K., Xing, B.S., Torello, W.A., 2005. Effect of organic fertilizers derived dissolved

663   organic matter on pesticide sorption and leaching. Environ. Pollut. 134,

664   187-194.

665   Li, Z., Fitzgerald, N.M., Albert, Z., Schnabl, A., Jiang, W.-T., 2015. Contrasting

666   mechanisms of metoprolol uptake on kaolinite and talc. Chem. Eng. J. 272,

667   48-57.

668   Lima, D.L., Schneider, R.J., Esteves, V.I., 2012. Sorption behavior of EE2 on soils

669   subjected to different long-term organic amendments. Sci. Total Environ. 423,

670   120-4.

671   Liu, W.X., Xu, S.S., Xing, B.S., Pan, B., Tao, S., 2010. Nonlinear binding of

672   phenanthrene to the extracted fulvic acid fraction in soil in comparison with

673   other organic matter fractions and to the whole soil sample. Environ. Pollut.

674   158, 566-75.

675   Liu, Y.Y., Zeng, Z.T., Zeng, G.M., Tang, L., Pang, Y., Li, Z., Liu, C., Lei, X.X., Wu,

676   M.S., Ren, P.Y., Liu, Z.F., Chen, M., Xie, G.X., 2012. Immobilization of

677   laccase on magnetic bimodal mesoporous carbon and the application in the

678   removal of phenolic compounds. Bioresour. Technol. 115, 21-26.

679   Marchal, G., Smith, K.E.C., Rein, A., Winding, A., Trapp, S., Karlson, U.G., 2013.

680   Comparing the desorption and biodegradation of low concentrations of

681   phenanthrene sorbed to activated carbon, biochar and compost. Chemosphere.

682   90, 1767-78.

683　Marco-Brown, J.L., Alcira Trinelli, M., Gaigneaux, E.M., Torres Sanchez, R.M., dos

684　　　Santos Afonso, M., 2015. New insights on the structure of the

685　　　picloram-montmorillonite surface complexes. J. Colloid Interface Sci. 444,

686　　　115-122.

687　McGechan, M.B., Lewis, D.R., 2002. SW—Soil and Water: Transport of particulate

688　　　and colloid-sorbed contaminants through soil, part 1: General principles.

689　　　Biosyst. Eng. 83, 255-273.

690　Mechlińska, A., Gdaniec-Pietryka, M., Wolska, L., Namieśnik, J., 2009. Evolution of

691　　　models for sorption of PAHs and PCBs on geosorbents. Trac-Trend. Anal.

692　　　Chem. 28, 466-482.

693　Megharaj, M., Ramakrishnan, B., Venkateswarlu, K., Sethunathan, N., Naidu, R.,

694　　　2011. Bioremediation approaches for organic pollutants: a critical perspective.

695　　　Environ. Int. 37, 1362-1375.

696　Mitchell, P.J., Simpson, M.J., 2013. High affinity sorption domains in soil are blocked

697　　　by polar soil organic matter components. Environ. Sci. Technol. 47, 412-9.

698　Northcott, G.L., Jones, K.C., 2000. Experimental approaches and analytical

699　　　techniques for determining organic compound bound residues in soil and

700　　　sediment. Environ. Pollut. 108, 19-43.

701　Ortega-Calvo, J.J., Harmsen, J., Parsons, J.R., Semple, K.T., Aitken, M.D., Ajao, C.,

702　　　Eadsforth, C., Galay-Burgos, M., Naidu, R., Oliver, R., Peijnenburg, W.J.G.,

703　　　Römbke, J., Streck, G., Versonnen, B., 2015. From Bioavailability Science to

704　　　Regulation of Organic Chemicals. Environ. Sci. Technol. 49, 10255-64.

705   Ortega-Calvo, J.J., Tejeda-Agredano, M.C., Jimenez-Sanchez, C., Congiu, E.,

706   Sungthong, R., Niqui-Arroyo, J.L., Cantos, M., 2013. Is it possible to increase

707   bioavailability but not environmental risk of PAHs in bioremediation? J.

708   Hazard. Mater. 261, 733-45.

709   Otto, S., Banitz, T., Thullner, M., Harms, H., Wick, L.Y., 2016. Effects of Facilitated

710   Bacterial Dispersal on the Degradation and Emission of a Desorbing

711   Contaminant. Environ. Sci. Technol. 50, 6320-6326.

712   Pacwa-Płociniczak, M., Płaza, G.A., Piotrowska-Seget, Z., Cameotra, S.S., 2011.

713   Environmental Applications of Biosurfactants: Recent Advances. Int. J. Mol.

714   Sci. 12, 633.

715   Peng, H., Liang, N., Li, H., Chen, F., Zhang, D., Pan, B., Xing, B., 2015. Contribution

716   of coated humic acids calculated through their surface coverage on nano iron

717   oxides for ofloxacin and norfloxacin sorption. Environ. Pollut. 204, 191-198.

718   Peng, L., Zhang, X.T., Yin, J., Xu, S.Y., Zhang, Y., Xie, D.T., Li, Z.L., 2016.

719   Geobacter sulfurreducens adapts to low electrode potential for extracellular

720   electron transfer. Electrochim. Acta 191, 743-749.

721   Pils, J.R.V., Laird, D.A., 2007. Sorption of tetracycline and chlortetracycline on K-

722   and Ca-saturated soil clays, humic substances, and clay-humic complexes.

723   Environ. Sci. Technol. 41, 1928-1933.

724   Puglisi, E., Cappa, F., Fragoulis, G., Trevisan, M., Del Re, A.A.M., 2007.

725   Bioavailability and degradation of phenanthrene in compost amended soils.

726   Chemosphere. 67, 548-56.

727   Riding, M.J., Doick, K.J., Martin, F.L., Jones, K.C., Semple, K.T., 2013. Chemical

728   measures of bioavailability/bioaccessibility of PAHs in soil: fundamentals to

729   application. J. Hazard. Mater. 261, 687-700.

730   Rončević, S., Spasojević, J., Maletić, S., Jazić, J.M., Isakovski, M.K., Agbaba, J.,

731   Grgić, M., Dalmacija, B., 2016. Assessment of the bioavailability and

732   phytotoxicity of sediment spiked with polycyclic aromatic hydrocarbons.

733   Environ. Sci. Pollut. Res. Int. 23, 3239-46.

734   Schaefer, M., Juliane, F., 2007. The influence of earthworms and organic additives on

735   the biodegradation of oil contaminated soil. Appl. Soil Ecol. 36, 53-62.

736   Schamfuß, S., Neu, T.R., van der Meer, J.R., Tecon, R., Harms, H., Wick, L.Y., 2013.

737   Impact of mycelia on the accessibility of fluorene to PAH-degrading bacteria.

738   Environ. Sci. Technol. 47, 6908-15.

739   Semple, K.T., Doick, K.J., Wick, L.Y., Harms, H., 2007. Microbial interactions with

740   organic contaminants in soil: definitions, processes and measurement. Environ.

741   Pollut. 150, 166-76.

742   Semple, K.T., Riding, M.J., McAllister, L.E., Sopena-Vazquez, F., Bending, G.D.,

743   2013. Impact of black carbon on the bioaccessibility of organic contaminants

744   in soil. J. Hazard. Mater. 261, 808-16.

745   Sharma, P., Mayes, M.A., Tang, G.P., 2013. Role of soil organic carbon and colloids in

746   sorption and transport of TNT, RDX and HMX in training range soils.

747   Chemosphere. 92, 993-1000.

748   Sheals, J., Sjoberg, S., Persson, P., 2002. Adsorption of glyphosate on goethite:

749   Molecular characterization of surface complexes. Environ. Sci. Technol. 36,

750   3090-3095.

751 Shi, X., Ji, L.L., Zhu, D.Q., 2010. Investigating roles of organic and inorganic soil

752   components in sorption of polar and nonpolar aromatic compounds. Environ.

753   Pollut. 158, 319-24.

754 Singh, N., Berns, A.E., Hennecke, D., Hoerner, J., Koerdel, W., Schaeffer, A., 2010.

755   Effect of soil organic matter chemistry on sorption of trinitrotoluene and

756   2,4-dinitrotoluene. J. Hazard. Mater. 173, 343-8.

757 Singleton, D.R., Adrion, A.C., Aitken, M.D., 2016. Surfactant-induced bacterial

758   community changes correlated with increased polycyclic aromatic

759   hydrocarbon degradation in contaminated soil. Appl. Microbiol. Biotechnol.

760   100(23), 10165-10177.

761 Stroud, J.L., Paton, G.I., Semple, K.T., 2007. Microbe-aliphatic hydrocarbon

762   interactions in soil: implications for biodegradation and bioremediation. J.

763   Appl. Microbiol. 102, 1239-1253.

764 Sun, K., Ran, Y., Yang, Y., Xing, B.S., Mao, J.D., 2013. Interaction mechanism of

765   benzene and phenanthrene in condensed organic matter: Importance of

766   adsorption (nanopore-filling). Geoderma. 204, 68-74.

767 Tang, C.Y., Fu, Q.S., Gao, D., Criddle, C.S., Leckie, J.O., 2010. Effect of solution

768   chemistry on the adsorption of perfluorooctane sulfonate onto mineral surfaces.

769   Water Res. 44, 2654-2662.

770 Tang, L., Wang, J.J., Zeng, G.M., Liu, Y.N., Deng, Y.C., Zhou, Y.Y., Tang, J., Wang,

771   J.J., Guo, Z., 2016. Enhanced photocatalytic degradation of norfloxacin in

772   aqueous Bi_2WO_6 dispersions containing nonionic surfactant under visible light

773   irradiation. J. Hazard. Mater. 306, 295-304.

774   Tang, L., Yang, G.D., Zeng, G.M., Cai, Y., Li, S.S., Zhou, Y.Y., Pang, Y., Liu, Y.Y.,

775   Zhang, Y., Luna, B., 2014. Synergistic effect of iron doped ordered

776   mesoporous carbon on adsorption-coupled reduction of hexavalent chromium

777   and the relative mechanism study. Chem. Eng.J. 239, 114-122.

778   Tang, L., Zeng, G.M., Shen, G.L., Li, Y.P., Zhang, Y., Huang, D.L., 2008. Rapid

779   Detection of Picloram in Agricultural Field Samples Using a Disposable

780   Immunomembrane-Based Electrochemical Sensor. Environ. Sci. Technol. 42,

781   1207-1212.

782   Tavakkoli, E., Juhasz, A., Donner, E., Lombi, E., 2015. Characterising the

783   exchangeability of phenanthrene associated with naturally occurring soil

784   colloids using an isotopic dilution technique. Environ. Pollut. 199, 244-52.

785   Uddin, M.K., 2017. A review on the adsorption of heavy metals by clay minerals, with

786   special focus on the past decade. Chem. Eng.J. 308, 438-462.

787   Van der Zee, F.P., Cervantes, F.J., 2009. Impact and application of electron shuttles on

788   the redox (bio)transformation of contaminants: A review. Biotechnol. Adv. 27,

789   256-277.

790   Wang, A., Li, S., Teng, Y., Liu, W., Wu, L., Zhang, H., Huang, Y., Luo, Y., Christie, P.,

791   2013a. Adsorption and desorption characteristics of diphenylarsenicals in two

792   contrasting soils. J. Environ. Sci. (China) 25, 1172-1179.

793   Wang, C.J., Li, Z., Jiang, W.T., 2011a. Adsorption of ciprofloxacin on 2:1 dioctahedral

794   clay minerals. Appl. Clay Sci. 53, 723-728.

795   Wang, H., Yuan, X., Wang, H., Chen, X., Wu, Z., Jiang, L., Xiong, W., Zhang, Y.,

796   Zeng, G., 2015. One-step calcination method for synthesis of mesoporous

797   g-C_3N_4/$NiTiO_3$ heterostructure photocatalyst with improved visible light

798   photoactivity. Rsc Adv. 5, 95643-95648.

799   Wang, H., Yuan, X., Wu, Y., Huang, H., Peng, X., Zeng, G., Zhong, H., Liang, J., Ren,

800   M., 2013b. Graphene-based materials: Fabrication, characterization and

801   application for the decontamination of wastewater and wastegas and hydrogen

802   storage/generation. Adv. Colloid Interfac. 195, 19-40.

803   Wang, H., Yuan, X., Wu, Y., Huang, H., Zeng, G., Liu, Y., Wang, X., Lin, N., Qi, Y.,

804   2013c. Adsorption characteristics and behaviors of graphene oxide for Zn(II)

805   removal from aqueous solution. Appl. Surf. Sci. 279, 432-440.

806   Wang, K.J., Xing, B.S., 2005. Structural and Sorption Characteristics of Adsorbed

807   Humic Acid on Clay Minerals. J. Environ. Qual. 34, 342-349.

808   Wang, X.L., Guo, X.Y., Yang, Y., Tao, S., Xing, B.S., 2011b. Sorption mechanisms of

809   phenanthrene, lindane, and atrazine with various humic acid fractions from a

810   single soil sample. Environ. Sci. Technol. 45, 2124-30.

811   Wick, L.Y., Pasche, N., Bernasconi, S.M., Pelz, O., Harms, H., 2003. Characterization

812   of multiple-substrate utilization by anthracene-degrading Mycobacterium

813   frederiksbergense LB501T. Appl. Environ. Microb. 69, 6133-6142

814   Wick, L.Y., de Munain, A.R., Springael, D., Harms, H., 2002a. Responses of

815   Mycobacterium sp. LB501T to the low bioavailability of solid anthracene.

816   Appl. Microbiol. Biotechnol. 58, 378-85.

817   Wick, L.Y., Wattiau, P., Harms, H., 2002b. Influence of the growth substrate on the

818   mycolic acid profiles of mycobacteria. Environ. Microbiol. 4, 612-616.

819   Woignier, T., Clostre, F., Macarie, H., Jannoyer, M., 2012. Chlordecone retention in

820   the fractal structure of volcanic clay. J. Hazard. Mater. 241-242, 224-30.

821   Wu, G.Z., Kechavarzi, C., Li, X.G., Sui, H., Pollard, S.J.T., Coulon, F., 2013.

822   Influence of mature compost amendment on total and bioavailable polycyclic

823   aromatic hydrocarbons in contaminated soils. Chemosphere. 90, 2240-6.

824   Wu, Q.Q., Yang, Q., Zhou, W.J., Zhu, L.Z., 2015a. Sorption characteristics and

825   contribution of organic matter fractions for atrazine in soil. J. Soil Sediment.

826   15, 2210-2219.

827   Wu, Y., Luo, H., Wang, H., Zhang, L., Liu, P., Feng, L., 2014. Fast adsorption of

828   nickel ions by porous graphene oxide/sawdust composite and reuse for phenol

829   degradation from aqueous solutions. J. Colloid Interf. Sci. 436, 90-98.

830   Wu, Y., Si, Y., Zhou, D., Gao, J., 2015b. Adsorption of diethyl phthalate ester to clay

831   minerals. Chemosphere. 119, 690-696.

832   Xu, H., Qu, X., Li, H., Gu, C., Zhu, D., 2014. Sorption of Tetracycline to

833   Varying-Sized Montmorillonite Fractions. J. Environ. Qual. 43, 2079-2085.

834   Xu, J., Gu, X., Guo, Y., Tong, F., Chen, L., 2016. Adsorption behavior and mechanism

835   of glufosinate onto goethite. Sci. Total Environ. 560, 123-130.

836   Xu, P., Zeng, G.M., Huang, D.L., Feng, C.L., Hu, S., Zhao, M.H., Lai, C., Wei, Z.,

837   Huang, C., Xie, G.X., Liu, Z.F., 2012. Use of iron oxide nanomaterials in

838   wastewater treatment: A review. Sci. Total Environ. 424, 1-10.

839   Yang, Y., Hunter, W., Tao, S., Gan, J., 2009. Microbial Availability of Different Forms

840   of Phenanthrene in Soils. Environ. Sci. Technol. 43, 1852-1857.

841   Yang, Y., Shu, L., Wang, X.L., Xing, B.S., Tao, S., 2012a. Mechanisms regulating

842   bioavailability of phenanthrene sorbed on a peat soil-origin humic substance.

843   Environ. Toxicol. Chem. 31, 1431-7.

844   Yang, Y., Shu, L., Wang, X.L., Xing, B.S., Tao, S., 2010. Effects of Composition and

845   Domain Arrangement of Biopolymer Components of Soil Organic Matter on

846   the Bioavailability of Phenanthrene. Environ. Sci. Technol. 44, 3339-3344.

847   Yang, Y.G., Xu, M.Y., Guo, J., Sun, G.P., 2012b. Bacterial extracellular electron

848   transfer in bioelectrochemical systems. Process. Biochem. 47, 1707-1714.

849   You, L.X., Rao, L., Tian, X.C., Wu, R.R., Wu, X., Zhao, F., Jiang, Y.X., Sun, S.G.,

850   2015. Electrochemical in situ FTIR spectroscopy studies directly extracellular

851   electron transfer of Shewanella oneidensis MR-1. Electrochim. Acta. 170,

852   131-139.

853   Yu, L., Yuan, Y., Tang, J., Wang, Y., Zhou, S., 2015. Biochar as an electron shuttle for

854   reductive dechlorination of pentachlorophenol by Geobacter sulfurreducens.

855   Sci. Rep. 5.

856   Zeng, F., He, Y., Lian, Z., Xu, J., 2014. The impact of solution chemistry of

857   electrolyte on the sorption of pentachlorophenol and phenanthrene by natural

858   hematite nanoparticles. Sci. Total Environ. 466, 577-585.

859   Zeng, G.M., Chen, M., Zeng, Z.T., 2013a. Risks of Neonicotinoid Pesticides. Science.

860   340, 1403-1403.

861   Zeng, G.M., Chen, M., Zeng, Z.T., 2013b. Shale gas: surface water also at risk. Nature.

862   499, 154-154.

863   Zeng G.M., Wan J., Huang D.L., Hu L., Huang C., Cheng M., Xue W.J., Gong X.M,

864   Wang R.Z., Jiang D.N., 2017. Precipitation, adsorption and rhizosphere effect:

865   The mechanisms for Phosphate-induced Pb immobilization in soils—A review.

866   J. Hazard. Mater. 339, 354-367.

867   Zhang, D., Zhu, L., Li, F., 2013. Influences and mechanisms of surfactants on pyrene

868   biodegradation based on interactions of surfactant with a *Klebsiella oxytoca*

869   strain. Bioresour. Technol. 142, 454-461.

870   Zhang, L., Xiang, P., Bao, X., Xiong, M., Liu, F., 2017. The Influence of Humic

871   Substances on the Sorption of Three Organic Contaminants with Different

872   Structure and Polarity to Clay Minerals. Water Air Soil Poll. 228.

873   Zhang, M., Shen, X.F., Zhang, H.Y., Cai, F., Chen, W.X., Gao, Q., Julio Ortega-Calvo,

874   J., Tao, S., Wang, X.L., 2016. Bioavailability of phenanthrene and

875   nitrobenzene sorbed on carbonaceous materials. Carbon. 110, 404-413.

876   Zhang, R.M., Yan, W., Jing, C.Y., 2015a. Experimental and molecular dynamic

877   simulation study of perfluorooctane sulfonate adsorption on soil and sediment

878   components. J. Environ. Sci (China). 29, 131-8.

879   Zhang, Y.L., Ma, X.X., Ran, Y., 2014. Sorption of phenanthrene and benzene on

880   differently structural kerogen: important role of micropore-filling. Environ.

881   Pollut. 185, 213-8.

882 Zhang, Y.P., Wang, F., Bian, Y.R., Kengara, F.O., Gu, C.G., Zhao, Q.G., Jiang, X.,

883   2012. Enhanced desorption of humin-bound phenanthrene by attached

884   phenanthrene-degrading bacteria. Bioresour. Technol. 123, 92-97.

885 Zhang, Y.P., Wang, F., Zhu, X.S., Zeng, J., Zhao, Q.G., Jiang, X., 2015b. Extracellular

886   polymeric substances govern the development of biofilm and mass transfer of

887   polycyclic aromatic hydrocarbons for improved biodegradation. Bioresour.

888   Technol. 193, 274-280.

889 Zhang, Y., Zeng, G.M., Tang, L., Huang, D.L., Jiang, X.Y., Chen, Y.N., 2007. A

890   hydroquinone biosensor using modified core-shell magnetic nanoparticles

891   supported on carbon paste electrode. Biosens. Bioelectron. 22, 2121-2126.

892 Zhao, G., Huang, Q.Y., Rong, X.M., Cai, P., Liang, W., Dai, K., 2014a. Interfacial

893   interaction between methyl parathion-degrading bacteria and minerals is

894   important in biodegradation. Biodegradation. 25, 1-9.

895 Zhao, L., Bian, J., Zhang, Y., Zhu, L., Liu, Z., 2014b. Comparison of the sorption

896   behaviors and mechanisms of perfluorosulfonates and, perfluorocarboxylic

897   acids on three kinds of clay minerals. Chemosphere. 114, 51-58.

898 Zhao, Y., Geng, J., Wang, X., Gu, X., Gao, S., 2011. Tetracycline adsorption on

899   kaolinite: pH, metal cations and humic acid effects. Ecotoxicology. 20,

900   1141-1147.

901 Zhao, Y., Gu, X., Li, S., Han, R., Wang, G., 2015. Insights into tetracycline adsorption

902   onto kaolinite and montmorillonite: experiments and modeling. Environ. Sci.

903   Pollut. 22, 17031-17040.

904   Zhao, Y., Liu, F., Qin, X., 2017. Adsorption of diclofenac onto goethite: Adsorption

905   kinetics and effects of pH. Chemosphere. 180, 373-378.

906   Zhou, Y.Y., Tang, L., Zeng, G.M., Chen, J., Cai, Y., Zhang, Y., Yang, G.D., Liu, Y.Y.,

907   Zhang, C., Tang, W.W., 2014. Mesoporous carbon nitride based biosensor for

908   highly sensitive and selective analysis of phenol and catechol in compost

909   bioremediation. Biosens. Bioelectron. 61, 519-525.

910   Zhu, B.T., Wu, S., Xia, X.H., Lu, X.X., Zhang, X.T., Xia, N., Liu, T., 2016. Effects of

911   carbonaceous   materials   on   microbial   bioavailability   of

912   2,2',4,4'-tetrabromodiphenyl ether (BDE-47) in sediments. J. Hazard. Mater.

913   312, 216-223.

914

Figure captions

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.

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

Fig. 3. Various ways of microorganism accessing POPs.