

1 **Interactions Between Nonpolar Compounds and Soil Organic Carbon Under Low Redox**

2 **Potentials: Implications for Bioavailability**

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Jessica E. Sharpe and Andrew Ogram\*

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Soil and Water Sciences Department, University of Florida, Gainesville, FL USA

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Jessica Sharpe

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PO Box 110290

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Soil and Water Sciences Department

9

University of Florida

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Gainesville, FL 32611-0290

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[JessicaElaineSharpe@gmail.com](mailto:JessicaElaineSharpe@gmail.com)

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805-338-2259

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\*Corresponding author:

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Andrew Ogram

16

PO Box 110290

17

Soil and Water Sciences Department

18

University of Florida

19

Gainesville, FL 32611-0290

20

USA

21

[aogram@ufl.edu](mailto:aogram@ufl.edu)

22

Phone: 352-294-3138

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### **Abstract**

The association between redox potential in soils and sediments, and availability of nonpolar compounds may play an important role in bioavailability of these compounds for microbial degradation; however, this aspect of bioavailability is poorly understood. This review aims to summarize the literature concerning the impacts that low redox environments have on sorption and desorption, and on the concentrations of dissolved organic carbon and its role in contaminant bioavailability. Multiple models of sorption have been used to predict contaminant behavior, including a dual-mode model to explain nonideal sorption tendencies. Laboratory studies have shown that environments with low redox potentials brought about by microbial activity may cause sequestered nonpolar compounds to be released. This increase in dissolved organic carbon allows for greater bioavailability, increasing the potential for the compound to be metabolized by microorganisms. The formation of a previously proposed hemi-micelle model may be used as a model to explain the transfer of the contaminant to a degrading cell for uptake and metabolism. A clearer understanding of this relationship will aid in prediction and control of the biodegradation of pollutants and toxic compounds found in low redox environments.

### **Introduction**

Hydrophobic Organic Contaminants (HOCs), including polyaromatic hydrocarbons (PAH), are often toxic and carcinogenic, and may be released into the environment from both human activities and from natural sources. Although the total amounts of PAHs in soils and sediments are unknown, a U.S Geological Survey study indicated that PAH concentrations tend to increase with population, energy consumption, and land use (Van Metre and Van Der See 1997). HOCs range from pesticides to by-products of fossil fuel combustion, and may persist for long periods of time in the environment (Sorensen et al. 2005). Due to their low aqueous solubilities, HOCs become sorbed by soil particles and may resist extraction and biodegradation (Mao et al. 2002); however, the impacts of an HOC's interactions with dissolved organic carbon (DOC) may be more complex with respect to bioavailability. Most research on this issue has focused on sorption under aerobic conditions, although much contaminated soil is found in anaerobic settings under

54 reduced conditions (i.e., low redox potentials). The structure and concentrations of DOC are strongly  
55 influenced by redox potential (Pravecek et al. 2005), which may play a significant role in the solubility and  
56 potential bioavailability of HOCs. Assessing the fate of these compounds in anoxic soils and sediments is  
57 essential for accurate prediction of the exposure of humans and wildlife. This paper will address molecular  
58 models of the interaction between HOC and Soil Organic Matter (SOM), the impacts of redox potentials  
59 on the solubility and molecular structures of DOC, and the availability and biodegradation of HOCs under  
60 low redox potentials.

61

## 62 **Interactions Between HOCs and Organic Matter**

### 63 **The importance of polarity**

64 The sorption and desorption of HOCs is controlled by many factors; however, the polarity of Soil  
65 Organic Matter (SOM) and DOC typically exhibits an inverse relationship with the sorption of HOCs  
66 (Pedersen et al. 1999). Some research has suggested that the hydrophobic fraction of DOC harbors a  
67 greater number of sorption sites for HOCs (Pan et al. 2008) than does the more polar fractions; however,  
68 recent data have indicated a high sorption rate for aliphatic rich SOM. This complicates the previous notion  
69 that sorption coefficients are directly associated with the aromatic C content (Pfaender and Kim 2005).  
70 Kang and Xing (2005) found that HOC sorption is directly linked to aliphatic material in SOM, as  
71 supported by his research showing humin fractions with the greatest aliphatic carbon contents had  
72 increased sorption ability in comparison to humic acids. Humin is the portion of humic material that is not  
73 soluble at any pH value in an aqueous solution (Stevenson 1994). Pan et al. (2008) suggested that aromatic  
74 and aliphatic carbons contribute to HOC-SOM sorption, and polarity could be utilized to understand SOM  
75 sorption mechanisms.

76 As recognition of the importance of SOM to sorption, the sorption of non-ionic compounds to soil is  
77 frequently described by the carbon-normalized distribution coefficient ( $K_{oc}$ )(Smernik and Kookana 2015).  
78 The  $K_{oc}$  is the ratio of the chemical mass adsorbed to the soil versus the amount dissolved at equilibrium,  
79 normalized to the mass of carbon in the soil, and can be incorporated into models for predicting the mobility

80 of HOCs in soil. A high  $K_{oc}$  indicates a less mobile HOC, and may vary dependent on the structure of the  
81 SOM (Smernik and Kookana 2015). Binding degrees are represented by  $K_{oc}$  and are dependent on the  
82 physiochemical composition of SOM for individual HOCs. A significant amount of data have suggested  
83 that aromaticity has the greatest influence on  $K_{oc}$ , although this relationship may be complex. Smernik and  
84 Kookana (2015) found that  $K_{oc}$  increased with aromatic C content and decreased with O-alkyl C and alkyl  
85 C content, which may be due to sorption sites being obstructed by organic matter high in these functional  
86 groups.

87 In the case of DOC, HOC partitioning between DOC and water is typically described by a linear  
88 sorption isotherm (Suffet and Belton 1985); however, certain types of binding results in nonlinear sorption  
89 isotherms. Pan et al. (2007) used two PAHs (peranthene and pyrene) to demonstrate that occupation of  
90 competitive binding sites can result in nonideal binding behavior. Due to this reasoning, isotherm  
91 nonlinearity is invoked to explain HOC binding behaviors (Hur et al. 2011).

92

### 93 **Conceptual Models for HOC Sorption**

94 A critical step in the interaction between HOCs and SOM may be the diffusion of the HOC into the  
95 SOM matrix. Humic substances are known to swell during absorption of nonpolar molecules (Marschner  
96 and Kalbitz. 2003), which may provide clues to the mechanism of sorption. Lyon (1995) showed that during  
97 the sorption process, some nonpolar molecules react with peat with a resulting change in volume. A  
98 noteworthy change was the volume shrinkage of one peat by 26% after reacting with propyl sulfone for 8  
99 weeks. Heating or swelling of SOM results in increased linearity of sorption, as predicted from the behavior  
100 of “glassy” (discussed below) polymers. The increase in linearity of sorption with swelling has been shown  
101 in recent studies; after addition of swelling solvents to organic soils, swelling was noted and the respective  
102 isotherms became more linear (Pravecek et al. 2006). A similar study noted isotherm linearity of phenyl  
103 ureas with a soil mixed with a known swelling solvent (dimethyl sulfoxide) (Xing and Pignatello 1997). A  
104 possible explanation for the increased linearity with swelling was introduced by Huang and Weber (1997):  
105 Sorbing molecules are able to diffuse through swollen SOM regions. The pores in these swollen regions

106 can stretch or shrink with HOC changes in aqueous-phase concentrations. The flexible SOM areas work in  
107 pseudo-aqueous partitioning phases for hydrophobic solutes, displaying almost linear and no hysteretic  
108 sorption. Under reducing conditions, SOM domains are more rigid and follow a Langmuir-type adsorption,  
109 thus resulting in nonlinear sorption likely due to exclusion of the molecules from access to binding  
110 functional groups. As condensed regions increase in reduced SOM, nonlinearity should also increase, and  
111 increase sorption for hydrophobic solutes. This is due to increased affinity between SOM and hydrophobic  
112 solutes and an increase in ability for hydrophobic molecules to penetrate highly condensed SOM or expand  
113 the SOM matrix.

114         The concepts of “glassy” and “rubbery” domains within SOM have been used to describe sorption  
115 and desorption kinetics (Pravecek et al. 2006). The glassy phase, composed of aromatic carbon, is proposed  
116 to contribute to both linear and nonlinear sorption. This glassy condensed phase is characterized by char or  
117 soot with high affinity adsorption sites, and is also considered to be more aromatic and less polar. High  
118 molecular weights, cross linking, and unsaturated bonds reduce flexibility in molecular SOM and so a  
119 glassy state will take shape (Pan et al. 2008). The so-called rubbery phase, dominated by aliphatic regions,  
120 contributes to linear sorption and is responsible for partitioning (mobility of compound). These multiple  
121 domains ultimately effect sorption rates (Pravecek et al. 2006). Rubbery domains play a dominant role in  
122 linear sorption whilst glassy domains contribute to both linear and also nonlinear sorption (Pan et al. 2008).

123         The dual-mode model features SOM having both partition and adsorption domains (Xing and  
124 Pignatello 1996). The glassy rigid phase includes sorption sites made of somewhat permanent nanopore  
125 structures and can be subject to co-solute competition. White et al. (1999) showed that there is a direct  
126 correlation between bioavailability and desorption rates of HOCs in respect to aging. It has been proposed  
127 that because of condensed structure of the glassy domain, HOCs sorbed into this fraction are poorly  
128 bioavailable in comparison to the rubbery phase (Cuypers et al. 2002). The linear components of the rubbery  
129 phase allow for HOCs to be the most bioavailable due to its prompt equilibrium with interstitial waters,  
130 while the non-linear attributes of the glassy phase impede bioavailable fractions (Burgess et al. 2003).

131 These mechanisms work together to determine bioavailability of HOC's dependent upon the respective  
132 domains (Fig 1).

### 133 **The impacts of diagenesis on SOM molecular structure and sorption**

134 To understand the nature of organic matter and its interaction with HOC, the system should be  
135 viewed as a complex, dynamic system of diagenesis, and not only in terms of static molecular properties.  
136 A critical driver in diagenesis is microbial activity (Schmidt et al. 2011). The initial phases of SOM  
137 formation and humification processes are highly influenced by microbial reactions (Pfaender et al. 2005).  
138 Soil factors that increase microbial metabolic activity will correspondingly increase desorption of PAHs or  
139 increase PAH aqueous concentration, and potentially escalate degradation rates (Pravecek et al. 2006).  
140 Increases in nonlinear sorption are consistent with increases in diagenetic maturity and condensed regions.  
141 A study by Gunasekara et al. (2003) reported that linear isotherms were produced after aromatic carbon  
142 was removed by bleaching or hydrolysis of humic acid. Advanced diagenesis results in aromatization and  
143 condensation of fractions of the molecule that are linked to nonlinear and hysteretic sorption-desorption.  
144 Geosorbents that have undergone a substantial amount of diagenesis are reported to exhibit a higher degree  
145 of sequestration of PAHs. Furthermore, nonpolar compounds have been shown to release slowly from  
146 geosorbent material. Desorption rates are slower with high degrees of SOM condensation (a reaction where  
147 two molecules combine to create a larger one) (Käcker et al 2002). The lower rate of desorption may be  
148 observed with higher condensation due to the molecules' chemical properties becoming more nonpolar and  
149 rigid. This phenomenon raises the issue of biostabilization or the formation of bound residues (discussed  
150 below), and if the residual HOC remaining in soil is being addressed in bioremediation efforts. Additionally,  
151 the formation of pores within SOM may directly increase sorption nonlinearity as well as sorption-  
152 desorption hysteresis (Pan et al. 2008). The kinetics of HOC desorption reflects these domain phases. The  
153 initial desorption is a fast release through the macro-mesopore network, which is then followed by a slow  
154 desorption rate due to entrapment along hydrophobic pore walls (Zhu et al. 2008).

155 Nonlinear sorption may result in nonideal transport through soil (as predicted by the two-domain  
156 model), which would yield erroneous retardation estimates if not accounted for. In models for prediction

157 of the fate and transport of HOC, nonlinear sorption would more accurately depict the fact that retardation  
158 will be lower and contaminant plumes would be larger. In addition, breakthrough curves may be more  
159 asymmetrical due to nonlinear sorption (Hu and Brusseau 1998). Transport of HOCs through a soil column  
160 depends on both position and time. Contaminants move through a soil medium as they fill up available  
161 sorption sites. That movement will increase the overall adsorption through time as more sites become  
162 available at the boundary. As sites become less available (potential volume of available sites decreases in  
163 a soil medium) the rate of sorption decreases through time.

164         Recent research has suggested that molecular characteristics of SOM may play only a part in  
165 overall partitioning (Smernik and Kookana 2015). Environmental influences such as aeration, pH,  
166 temperature, and soil structure have all been found to play a significant part in defining the sorption of  
167 HOCs (Pravecek et al. 2006). This information is vital to biodegradation research because the aqueous  
168 phase concentration of HOCs is determined by SOM and HOC interactions. This in turn determines the  
169 mobilization and reactivity of HOCs in the soil (Kim et al 2008).

170         It has been well established that sorption processes vary dependent upon the available organic  
171 matter fraction due to its reactivity with the respective HOC. Diagenetic processes may include the  
172 alteration of biopolymers to humic substances by both biotic and abiotic processes. Shale materials,  
173 subsurface materials with extremely high diagenetic alteration, have been found to have both the highest  
174 isotherm nonlinearity and sorption capacity (Young et al. 1995). Similarly, another study found that the  
175 glassy and rubbery domains were dependent on the origin and nature of the soil organic matter. Condensed  
176 domains in organic matter with little diagenetic alteration contain elevated amounts of aliphatic C, while  
177 condensed domains with high diagenesis harbored higher amounts of aromatic C (Cuypers et al. 2002). It  
178 can then be inferred using the dual-mode model that nonlinear sorption tendencies are related to binding of  
179 the condensed regions that were formed during diagenesis.

180

## 181 **Formation of Bound Residues**





208 be due to enhancement of hydrophobic interactions due to the conversion of chlorophenols to neutral forms  
209 (Kim and Pfaender 2005).

210 The mobility and bioavailability of bound HOCs are influenced by redox conditions and, as such,  
211 are controlled by the terminal acceptor for microbial activities. Kim et al. (2008) reported that microbes  
212 utilizing sulfate as a terminal electron acceptor increased soluble SOM concentrations and thus increased  
213 PAH binding with DOC. The researchers concluded that sulfate reduction increased DOC due to the  
214 lowering of redox conditions and consequential H<sup>+</sup> utilization, allowing for SOM partitioning and leading  
215 to increased binding between PAH and DOC. They also concluded that properties of SOM are changed  
216 under microbially-mediated redox conditions. Thus, DOC liberated under anaerobic incubation was more  
217 aromatic, more condensed, and had a greater sorption capacity for PAHs.

218

#### 219 **Production of DOC under low redox potentials**

220 DOC originates from decomposed biota and microbial byproducts (Richnow et al. 2000). Two main  
221 factors contribute to formation of DOC: microbial activity; and pH. These two influences are largely  
222 interrelated. Most studies show that disassociation of DOC is directly correlated with high pH (Kalbitz et  
223 al. 2000). With changes in pH, humic substances exhibit shifts in degree of protonation (Marschner and  
224 Kalbitz 2003). After aerobic and facultative microbes respire the available dissolved oxygen, the redox  
225 potential ( $E_h$ ) begins to drop. As anaerobic microorganisms begin to reduce available soil minerals, pH  
226 rises due to consumption of H<sup>+</sup> ions. When pH is increased, adsorption capacity of DOC is limited and  
227 therefore DOC solubility increases (Kalbitz et al. 2000). Several authors have found a relationship between  
228 the rise in pH due to reduced conditions and a rise in DOC dissolution (Huang et al. 2003, Kalbitz et al.  
229 2000). It has been shown that in elevated pH conditions, more SOM is released and PAH binding with DOC  
230 was greater (Kim et al. 2008).

231 While most research has indicated that DOC release is directly linked to pH (Kalbitz et al. 2000),  
232 another line of research indicated that low pH can contribute to DOC formation. Lower pH values can  
233 cause the dissolution of organo-metal complexes, which may then contribute to release of SOM from the

234 solid matrix (Hu and Brusseau, 1998). Other studies suggest that increasing pH produces an increase in  
235 DOC concentration (Kalbitz et al. 2000). Microbes control the redox potential of soils and also aid in  
236 diagenetic SOM development (Pfaender and Kim 2005). Anaerobic microbes are known to alter soil  
237 conditions such as pH which would then lead to increases in DOC (Pravecek et al. 2005). DOC solubility  
238 can usually be increased by addition of  $\text{Na}^+$  or  $\text{K}^+$ , which expands DOC molecules (Marschner and Kalbitz  
239 2003).

240

### 241 **Chemical alteration of DOC under low redox potentials**

242 DOC increases solubility of organic compounds (Marschner et al. 2003). There is research showing  
243 that supplementation of DOC increases mineralization of HOCs with respect to four to six-ring PAHs  
244 (Bengtsson and Zerhouni 2003). Kim et al. (2008b) reported that anoxic environments created by  
245 microbial activity help dissolve soil-bound OM; and DOC helps to aid in desorption of PAHs through  
246 sorption. The DOC produced under anaerobic incubation has a significant aromatic component and has a  
247 higher affinity for PAHs, resulting in an increase in concentration found in the aqueous phase.

248 Pfaender and Kim (2005) found that DOC with increased humic acid content exhibited higher sorption  
249 affinities for pyrene. They concluded that reduced conditions result in “humification-like alteration” of  
250 DOC and in greater sorption affinities for the PAH(s). DOC has also been reported to have higher sorption  
251 with pyrene in anaerobic conditions than when compared to aerobic conditions (D’Angelo and Reddy  
252 2003). It has also been found that humin has relatively high aromaticity, and became more nonpolar under  
253 low redox potentials, which caused an increase in pyrene sorption rates compared to biocide treated humin  
254 (Pfaender and Kim 2005). Humin fractions are usually more aliphatic and tend to have higher  $K_{OC}$  values.  
255 Due to anaerobic incubation increasing SOM humification, which is similar to diagenesis, the higher  
256 sorption capacity for pyrene has been reported to be more nonlinear and hysteric. Similar effects were also  
257 found for DDT. DOC increases desorption rates of soil-bound DDT. The sediment-water partition  
258 coefficient showed a large decrease when humic matter was added to the aqueous phase DOC (Caron et  
259 al. 1985).

260

## 261 **DOC Under Reduced Conditions**

262           The main content of SOM and DOC is humic substances, and this fraction is what controls sorption  
263 tendencies of HOCs (Pan et al. 2008).  $K_{OC}$  of fulvic acids is usually lower than humic and humin fractions.  
264  $K_{OC}$  increases with aromaticity in humic acids. Humin is usually more aliphatic and tend to exhibit higher  
265  $K_{OC}$  values (Smernik and Kookana 2015).  $K_{OC}$  for HOCs is proportional to the aromatic C content of humic  
266 acids (Pedersen et al. 1999). Pan et al. (2008) reported that sorption/desorption hysteresis follows the order  
267 of FA (fulvic acid)<HA(humic acid)<HM(humin). Burgess et al. (2003) found that PAH-colloid sorption  
268 tendencies increased with depth of soil, which is assumed to have a lower redox potential. They also  
269 observed higher PAH concentrations in the aqueous phase under these reduced conditions (Pravecek et al.  
270 2005).

271

## 272 **Chemical properties of DOC under reduced conditions related to sorption**

273           DOC released under reduced conditions usually exhibits the following chemical properties: 1) the DOC  
274 tends to be more aromatic and polydispersed; 2) it has higher molecular weights; and 3) it is less polar  
275 and oxygenated (Pfaender and Kim 2005, Zhu et al. 2008). Pfaender et al. (2005) also reported witnessing  
276 an increase in humic acid content and a decrease in the O:C ratios under low redox potentials. Due to these  
277 molecular changes, the sorption capacity for contaminants may change. Both Pfaender et al. (2005) and  
278 Zhu et al. (2008) found that DOC under reduced conditions exhibited a high sorption capacity for pyrene  
279 compared to sorption under oxic conditions. It is postulated that anoxic degradation of SOM polar  
280 constituents aid in diagenesis of DOC, which yields increased amounts of nonpolar OM. It has also been  
281 reported that OM from reduced conditions (deep layer pore water) had a higher molecular weight and that  
282 the molecular weight is linked to increased aromaticity of OM. Under reduced conditions, microbial  
283 activity could alter polar or “oxygenated function group-rich” DOC, creating more humified OM (Pfaender  
284 et al. 2005). The consequence of more humified material is a change in physicochemical and biochemical  
285 properties of soil to represent that of diagenesis.

286

287 **Bioavailability of nonpolar compounds under low redox potentials**

288 Due to the fact that microbial uptake mechanisms typically necessitate that solutes be dissolved in the  
289 aqueous phase (Ogram et al. 1985), DOC may be the most bioavailable part of soil. Bioavailability is a  
290 requirement for degradation and is limited if DOC is in unreachable areas of pores in soil. The dynamics  
291 that influence DOC biodegradability are: fundamental DOC features; soil and solution constraints; and  
292 external factors. Research has shown some correlation between denitrification rates and amounts of DOC  
293 available in soils. This parallel could indicate that the accessibility of biodegradable DOC could be a  
294 necessary environmental condition for producing reduced conditions (Marschner and Kalbitz 2003). A  
295 three-phase model proposed by Mitra et al. (1999) illustrated the behavior of hydrophobic substances in a  
296 freely dissolved phase, DOC, and suspended solids. The authors stated that greater PAH pore water  
297 concentrations are a direct outcome from PAH-DOC interactions due to DOC having a high affinity for  
298 HOCs.

299 Many contaminants can be found in soils with varying redox potential due to microbial utilization  
300 of diverse electron acceptors (e.g.,  $O_2$ ,  $NO_3^-$ ,  $Fe^{3+}$ ). Thus, microbial redox activities have a strong impact  
301 on soil solid phase and aqueous chemical properties. Because of this, it is expected that microbial redox  
302 activities will have a large impact on the fate of soil contaminants (D'Angelo Reddy 2003). Previous  
303 research has shown that the amount of PAH in aqueous phases increases under anaerobic conditions, and  
304 (as discussed above) that microbial activity alters pH and DOC, thus resulting in PAH release (Zhu et al.  
305 2008). In addition to biodegradation, microbes influence PAH concentrations in solution by changing the  
306 pH and DOC alteration. In a study by Pravecek et al. (2005), the PAH was transferred from the solid into  
307 the aqueous phase at a higher rate under anaerobic incubation than under aerobic conditions (Pravecek et  
308 al. 2005). This study also confirmed that with SOM release came release of high molecular weight PAHs  
309 (Pfaender and Kim 2005). Moeckel et al. (2014) showed a strong correlation between molecular weight of  
310 PAHs and organic carbon concentration. They found that concentrations of PAHs with five or more  
311 aromatic rings increase with greater organic carbon concentration. Pravecek et al. (2005) found that soil

312 under anaerobic incubation with nitrate or sulfate amendment had an increase of extractable pyrene at 365  
313 d when compared to controls. The authors postulate it resulted from oxidation–reduction potential and pH  
314 changes caused by microbial activity. They concluded that the available terminal electron acceptor will  
315 produce the most energetically favorable microbes to control this niche (Pravecek et al. 2005).

316

### 317 **Biological Degradation Rates Under Reduced Conditions Relative to Oxidic Conditions**

318 If the increase in DOC under anoxic conditions is taken into account, it is likely that biological  
319 degradation of HOCs under reduced conditions will be higher than when compared to oxidic conditions due  
320 to increased bioavailability. Some research has shown this in different contaminants. Kim et al. (2008)  
321 found that anaerobic incubation of contaminated soils can increase desorption of HOCs, increasing  
322 degradation. Some PAHs were also shown to degrade under denitrifying conditions (Hutchins et al. 1991).  
323 Fermentative degradation is also known to occur with denitrification in reduced environments. It is  
324 postulated that aromatic compounds ferment with low molecular weight organic matter due to the local  
325 microbial species acting as denitrifiers or using H<sub>2</sub> as the electron donor. Some PAHs, such as  
326 phenanthrene and naphthalene, have been shown to be degraded by sulfate-reducing microbes (Ambrosoli  
327 et al. 2005). Lu et al. (2011) also found that, under anoxic conditions, denitrification is a useful solution  
328 for some areas contaminated with PAHs.

329

### 330 **Micelle/Pseudomicelle Formation**

331 The mechanisms for interactions between soluble HOC:DOC complexes and the cell surfaces of  
332 degrading microorganisms is not fully understood at this time; however, models to describe this interaction  
333 have been proposed. Humic substances possess both hydrophobic and hydrophilic properties. This  
334 amphiphilic quality allows for it to act as the main carrier in solubilization of HOCs. DOC has been shown  
335 to produce surfactant-like properties (Cho et al. 2002) which could allow for enhanced mobility of nonpolar  
336 compounds under reduced conditions. The idea of a pseudomicelle has been proposed using fluorescence-  
337 polarization. Morra et al. (1990) reported that naphthalene and 1-naphthol interact with humic acid by

338 creating a loose cage without binding. Other studies refer to humic acid solutions as true micelles because  
339 they have similar characteristics with critical micelle concentrations (CMC) (Chiou et al. 1986). Also, once  
340 the CMC is reached, the humic acid micellar solution will solubilize PAHs (Vacca et al. 2005). This  
341 proposed “true” micelle of humic acids has been observed in concentrated alkaline aqueous solutions  
342 (Guetzloff and Rice 1994). According to this possible model, humic acid surfactants could greatly increase  
343 partitioning of HOCs into the aqueous phase after the CMC has been reached (Pan et al. 2008). The actual  
344 uptake of contaminants by the cell has little supporting evidence, but Guhu et al. (1996) proposed a model  
345 using a hemi-micelle. Their hypothesis suggested that filled micelles (with the PAH partitioned in the  
346 hydrophobic core) come into contact with cells by mixing. At this point, the cells/enzymes are surrounded  
347 by a hemi-micellar layer containing the PAH (Fig 2). This allows for the PAH to diffuse into the cell to be  
348 degraded. This phenanthrene-based model assumes that the system is completely mixed, equilibrium is  
349 established, and degradation kinetics are not affected by the surfactant.

350

351

### **Conclusions**

352 The fate of organic contaminants is influenced by many factors. Ecological influences as well as  
353 intrinsic physical properties determine sorption/desorption rates and thus bioavailability. Yet, DOC has  
354 been shown to be a key player in desorption mechanisms by aiding in the change of physiochemical  
355 properties under anaerobic or anoxic incubation. Under such conditions, microbial metabolism causes an  
356 increase in pH. This increase results in a drop in redox conditions, which in turn encourages a humification-  
357 like change in organic soil that causes an increase in aromaticity in SOM. This alteration increases the  
358 release of with DOC and contaminants from the solid matrix. The surfactant-like properties in DOC has led  
359 to the proposal of a micelle model for interaction between DOC, HOC, and degrading bacterial cells, in  
360 which a hemi-micelle transports the HOC to the soil microorganism for degradation. Understanding the  
361 relationship between reduced soil conditions and contaminants is critical for biodegradation and ecological  
362 health studies.

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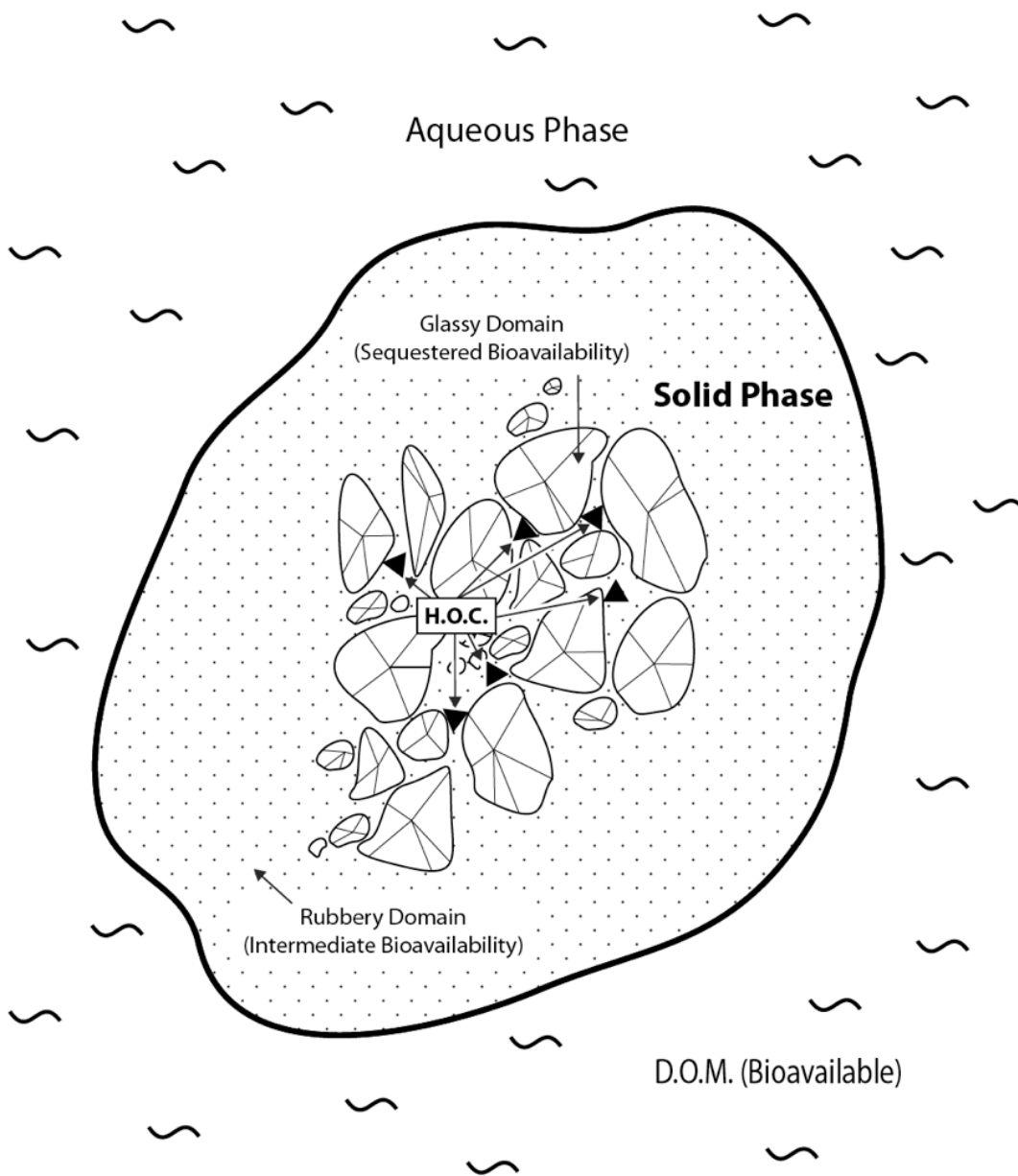
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### Figure Legends

Figure 1. Bioavailability of Hydrophobic Organic Contaminants. Dual-mode influence determines the bioavailability of the contaminant within the soil complex. After Mao J. D. and K. Schmidt-Rohr (2006).

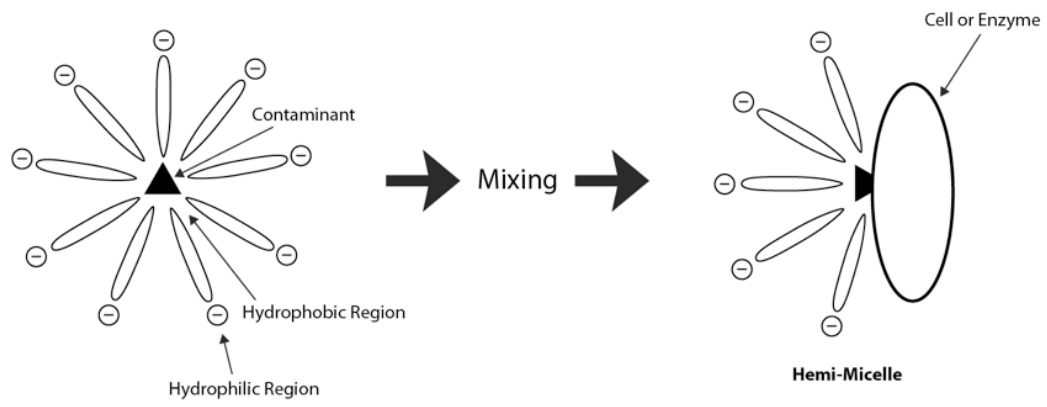
Figure 2. Humic Acid Micelle Formation and Pseudosolubilization. Micelle formation is first formed in reduced conditions. After mixing, the contaminant is available to be transferred to the cell. After Guhu et al. (1996).



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498 Figure 1.

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501 Figure 2