Abstract

Bioavailability often controls the fate of organic contaminants in surface and subsurface aquatic environments. Bioavailability can be limited by sorption, mass transfer, and intrinsic biodegradation potential and can be further altered by the presence of other compounds. This paper reviews current perspectives on the processes influencing subsurface contaminant bioavailability, how these processes are modeled, and how the relative role of the various processes can be assessed through bioavailability indices. Although these processes are increasingly well understood, the use of sophisticated models and indices often are precluded by an inability to estimate the many parameters that are associated with complex models. Nonetheless, the proper representation of sorption, mass transfer, biodegradation, and co-solute effects can be critical in predicting bio-attenuation. The influence of these processes on contaminant fate is illustrated with numerical simulations for the simultaneous degradation of toluene (growth substrate) and trichloroethylene (nongrowth cometabolite) in hypothetical, aerobic, solid–water systems. The results show how the relative impacts on contaminant fate of the model’s various component processes depends upon system conditions, including co-solute concentrations. Slow biodegradation rates increase the inhibition effects of a cometabolite and suppress the rate enhancement effects of a growth substrate. Irrespective of co-solute effects, contaminant fate is less sensitive to biodegradation processes in systems with strong sorption and slow desorption rates. Bioavailability indices can be used to relate these findings and to help identify appropriate modeling simplifications. In general, however, there remains a need to redefine such indices in order that bioavailability concepts can be better incorporated into site characterization, remediation design, and regulatory oversight.

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1. Introduction

At sites where soils, sediments, and geologic media are contaminated with organic chemicals, in situ bioremediation and monitored natural attenuation are management options that can sometimes achieve acceptable levels of risk reduction at considerably less cost than ex situ or nonbiological alternatives such as pump and treat or continuous injection of chemical additives (NRC, 2003a). Even in cases where nonbiological techniques may be required to remove an imminent threat of contamination, in situ bioremediation or natural attenuation often will be a viable secondary strategy for site maintenance. Natural environments are complex, however, making it difficult to understand, identify, and characterize the underlying processes that control contaminant fate (Sturman et al., 1995; Alexander, 2000; Goltz et al., 2001; NRC, 2003a; Ehlers and Luthy, 2003).

The effectiveness of in situ bioremediation approaches (including natural attenuation) is often dictated by the ability of the native microbial population to take up and metabolize contaminants; however, observed rates of biodegradation in the field are often much lower than would be anticipated based solely on the results of laboratory studies with similar microbial populations and similar water/sediment mixtures (e.g., Rijnaarts et al., 1990; Scow and Hutson, 1992; Bosma et al., 1997; Alexander, 2000; Bogan and Sullivan, 2003; Ahmad et al., 2004). The decreased biodegradation rates in the field can be attributed to both spatial and temporal issues associated with upscaling from a simple batch system to a more complex subsurface domain. In a general sense, the problem arises from both differences in biological activity and decreased availability of the contaminants to microbes (i.e., bioavailability). Consequently, determining the bioavailability of substrates – and not only the intrinsic biodegradation potential – is an
important factor in estimating the feasibility of bioremediation at a site (Röling and van Verseveld, 2002).

Various definitions of bioavailability are used across many disciplines (NRC, 2003a; Madsen, in press; Semple et al., 2004). In this paper, the term bioavailability is applied in the context of the bio-attenuation of compounds found in the subsurface down gradient of a contamination source zone. The primary factors that influence bio-attenuation are sorption, mass transfer, and biological uptake (i.e., “bioavailability processes”; NRC, 2003a; Elhers and Luthy, 2003). Accurately predicting how each process influences contaminant removal is difficult, especially in systems with multiple contaminants (Baveye and Bladon, 1999; Madsen, in press). As a result, bioavailability concepts have yet to be well incorporated into site remediation tools and regulations.

To aid the interpretation and implementation of bioavailability principles, this paper reviews factors influencing contaminant bio-attenuation and the manner in which these factors have been conceptualized and modeled in recent literature. In addition, numerical simulations are conducted for hypothetical, aerobic, solid–water systems that are contaminated with toluene and trichloroethylene. The simulations exemplify the topics discussed in the paper, illustrate the manner in which specific combinations of the bio-attenuation processes can impact contaminant fate, and show how the relative importance of these processes are system dependent. Finally, this paper briefly discusses the need to more explicitly consider bioavailability in field site characterization, remediation design, and regulatory oversight.

2. Processes that affect bioavailability: concepts

In the context of bioremediation, contaminant bioavailability is commonly approached from the premise that chemicals are immediately accessible for microbial uptake only when in aqueous solution that is readily accessible to the advective flow of water—that is, the external aqueous phase of a solid–water batch system or the “mobile” phase of an advective system. The rationale behind this premise is that the small pore spaces (<1 μm) internal to aggregates of soil and sediment particles exclude microbes, such that compounds that are dissolved or sorbed within these “immobile-water” domains must first be transported to the external aqueous phase (i.e., “bulk aqueous phase”) before they can be metabolized (Steinberg et al., 1987; Bosma et al., 1997; Zhang et al., 1998; Ehlers and Luthy, 2003). This premise is supported by several laboratory studies that have found biodegradation to occur only, or predominantly, in the bulk aqueous phase (e.g., Ogram et al., 1985; Scow and Alexander, 1992; Smith et al., 1992; Zhao and Voice, 2000; Bengtsson and Carlsson, 2001). A few other studies have led researchers to conclude that at least some microorganisms are capable of degrading compounds directly from the sorbed phase (Guerin and Boyd, 1992; Tang et al., 1998; Feng et al., 2000). For many of these other studies, however, it is likely that the microbes did not actually metabolize compounds directly from the sorbed domain, but rather facilitated desorption by releasing surfactants or altering the subsurface redox conditions such that aqueous phase concentrations were increased (Alexander, 2000; NRC, 2003a, pp. 153–157 and references therein). Also, for many studies where solid-phase degradation was reported, biodegradation rates were nonetheless observed to decrease with contaminant soil–water contact time (Harms and Bosma, 1997; Alexander, 2000; Feng et al., 2000; Bogan and Sullivan, 2003; Ahmad et al., 2004). Overall, it appears that microbial access to contaminants is increasingly inhibited as solutes migrate deeper into sub-micron pores of impermeable sorption “domains” in soil–water environments.

If microbes only degrade solutes in the “mobile” aqueous phase, then rates of contaminant biodegradation will be reduced by sorption and/or diffusion into impermeable regions, with the
overall rate controlled by the slowest process of desorption or biotransformation (Scow and Hutson, 1992; Fry and Istok, 1994; Ghoshal et al., 1996; Bosma et al., 1997; Ramaswami and Luthy, 1997; Zhang et al., 1998; Braida et al., 2004). For example, in batch systems where the solids have a large sorption capacity, only a small fraction of the contaminant mass may be present in the bulk water. This can lead to a “famine existence” for microbes, even in highly polluted environments (Bosma et al., 1997). Both numerical and batch experiments have shown that sorbent diffusion is often the limiting step, particularly in systems involving contaminants with large organic-carbon partition coefficients ($K_{oc}$) and large fine-pored aggregates with high organic matter content (Scow and Hutson, 1992; Fry and Istok, 1994; Bosma et al., 1997; Zhang et al., 1998; Shor et al., 2003; Sabbah et al., 2004). The rate-limiting step can also change over time. Using numerical simulations that considered diffusion, sorption, and biodegradation in a batch system, Scow and Hutson (1992) demonstrated that the shape of the biodegradation curve (% mineralized vs. time in aqueous concentration) can change from first-order toward zero-order over time, with the contaminants at first being rapidly degraded but slowing as intraparticle diffusion began to limit the replenishment of contaminant concentrations in the bulk aqueous phase. Scow and Alexander (1992) experimentally confirmed these numerical results using phenol and glutamic acid in a batch system with ceramic spheres.

Thus, bioavailability is influenced by a variety of factors, including physical characteristics of the sorbent (e.g., particle shapes, sizes, and internal porosities), chemical properties of the sorbates and sorbents, and biological factors (e.g., microbial abundance and affinity for the contaminant). These simultaneous processes coupled with field-scale complexities make in situ biodegradation rates difficult to isolate and verify by simply showing contaminant disappearance (Sturman et al., 1995; Odencrantz et al., 2003). Another important factor influencing bioavailability that is not as generally considered is the presence of other chemicals. Contamination at any site usually involves multiple contaminants that can compete for adsorption sites and for access to microbial enzymes. The potential impacts that the presence of co-solutes can have on bioavailability are discussed below.

### 3. Effects of solute mixtures on bioavailability

A contaminant’s bioavailability can be influenced by the presence of other compounds. For example, co-solutes might compete for sorption sites, thereby increasing the aqueous concentrations and thus the overall bioavailability of a contaminant of interest. Conversely, they might decrease bioavailability by competing for microbial enzyme sites. This section reviews how the presence of co-solutes can affect bioavailability through altering one or more of the various processes that control overall degradation rates.

#### 3.1. Contaminant mixtures and soil–water partitioning

The presence of multiple organic compounds results in increased competition for adsorption sites. As higher affinity adsorption regions become saturated by the competing solutes, the sorption of any given sorbate will be increasingly confined to lower affinity partitioning domains. This usually linearizes the single-solute sorption isotherms and reduces the sorption affinity for the less strongly sorbed solutes (McGinley et al., 1993, 1996; Schaefer et al., 2000; Xia and Ball, 2000; Graber and Borisover, 2003). The extent of the competition and isotherm linearization with co-contamination will depend on the sorbent material. Materials such as hard carbon, for which surface adsorption is dominant, will exhibit more competitive effects than
“soft” organic matter, for which non-competitive absorption dominates partitioning (McGinley et al., 1996; Allen-King et al., 2002). The degree of co-solute effects on sorption will, of course, also depend on the specific chemicals involved. For example, co-solutes with similar molecular functionality will usually have affinity for similar sorption sites and will show increased competitive effects (e.g., Xing et al., 1996; Xing and Pignatello, 1998; Li and Werth, 2001; Graber and Borisover, 2003).

An exception to this general trend was documented by Martins and Mermoud (1998). These researchers measured sorption isotherms for four nitroaromatic herbicides. All compounds exhibited linear isotherms in the single-solute systems, but in the mixed system, the sorption isotherm of all the herbicides, except 2,4 dinitrophenol (DNP), became strongly nonlinear ($n = 0.55$ to 0.7). The authors reasoned that DNP preferentially filled most of the available strong adsorption sites such that the competitive effects of DNP left only a sparse distribution of weak adsorption sites that led to nonlinear isotherm behavior for the other solutes. This situation is unusual, however, because high affinity adsorption sites will commonly be less abundant.

As an example of competitive sorption causing less retardation, Rivett and Allen-King (2003) observed that the advective transport of PCE at the Borden research site was approximately 3 times greater in a DNAPL dissolution experiment than in an earlier study where solute separation had occurred (e.g., Curtis et al., 1986; MacKay et al., 1986) and that the apparent sorption of PCE was more linear than in the prior study. In the more recent study, the source area concentrations of PCE and other competing solutes (TCE, TCM) were nearly 4000 times greater than in the prior experiment, and the researchers hypothesized that these higher concentrations caused increased competition and decreased solute retardation. This hypothesis was supported by batch sorption studies with single and mixed solutes.

Experiments have also verified that co-solute competition can increase intrasorbent diffusion rates. For example, White and Pignatello (1999) showed that desorption rates for phenanthrene increased in the presence of greater pyrene concentrations. They reasoned that the faster desorption rates were caused by the competing solutes blocking some of the soil micropores and/or swelling the organic matter, thus permitting the phenanthrene to move more rapidly through the intraparticle regions of the soil particles. A similar effect has been reported by Allen-King et al. (2002). They demonstrated that the sorption-based retardation of diffusion in a clay aquitard at Sarnia, Ontario, was less at higher concentrations, and in a manner that was consistent with the known nonlinearity of the solute’s isotherm (in this case the saturation of high affinity sorption sites was caused by the solute itself). Such concentration-based and competitive sorption effects on desorption rates would be expected for retarded intragranular diffusion in any impermeable zone where competitive sorption occurs.

### 3.2. Contaminant mixtures and biodegradation

Excluding effects related to microbial growth (which are discussed subsequently), the presence of multiple substrates will generally reduce the intrinsic (aqueous) biodegradation rates of the individual compounds. This “inhibition” results from more substrate molecules vying for the active enzyme sites. For homologous substrates (compounds with similar catabolic pathways), inhibition is typically competitive – that is, one substrate binds to an enzyme to form an enzyme–substrate complex that blocks another substrate from forming a complex with that enzyme – but noncompetitive or uncompetitive inhibition are also possible. Noncompetitive inhibition occurs when two compounds independently bind to the same enzyme, which decreases the overall utilization rate. Uncompetitive inhibition is similar to noncompetitive
inhibition except that the second substrate (the inhibitor) can bind to an enzyme complex with the first substrate but not to a free enzyme (Copeland, 1996; Reardon et al., 2000; Alvarez-Cohen and Speitel, 2001).

Even with co-solute inhibition, the biodegradation rates for some compounds may increase because of accelerated biomass growth on multiple substrates. For example, Guha et al. (1999) observed that, in a mixed system of naphthalene, phenanthrene, and pyrene, the mineralization rate of the more readily degradable naphthalene slowed, yet the biodegradation rates of more recalcitrant phenanthrene and pyrene were enhanced. The slower naphthalene transformation rate resulted from competitive inhibition while the enhanced rates of the other PAHs were attributed to greater biomass growth.

Enhanced biodegradation rates in co-solute systems can also occur when the solute of interest does not function as a growth substrate. This process, cometabolism, occurs when a growth substrate induces microbes to produce enzymes that “fortuitously” degrade a nongrowth substrate, even though the nongrowth substrate provides little or no growth or energy benefit to the microbes (Criddle, 1993; Semprini, 1997; Alvarez-Cohen and Speitel, 2001). Cometabolism is particularly important in the bioremediation of some otherwise recalcitrant contaminants. Examples of environmentally relevant compounds that have been observed to cometabolically biodegrade include trichloroethylene (TCE), dichloroethylene (DCE) and vinyl chloride (VC) in the presence of aromatic degraders (Schafer and Bouwer, 2000; Alvarez-Cohen and Speitel, 2001; Gandhi et al., 2002; Shingleton et al., 2001; Meza et al., 2003) and methanogenic cultures (e.g., Alvarez-Cohen and Speitel, 2001; Kim et al., 2002); chloroform in the presence of aromatic degraders and methanogens (Gupta et al., 1996; Hamamura et al., 1997); and MTBE in the presence of alkane degraders (Dupasquier et al., 2002; Magar et al., 2002; Smith et al., 2003). Although cometabolism enhances biotransformation of some compounds, the degradation rates for cometabolites are typically slow and subject to inhibition by the primary substrate. For example, the aerobic cometabolic degradation rate of TCE is often observed to be less than an order of magnitude of that of the biodegradation rates of the corresponding growth substrates (Arp et al., 2001).

In addition to the primary substrate effects on cometabolite degradation, cometabolites may suppress the biodegradation rate of the growth substrate through competitive inhibition and due to increased biomass decay rates that may result from toxic effects of cometabolic transformation products (Semprini, 1997; Alvarez-Cohen and Speitel, 2001; Arp et al., 2001). These potential negative impacts necessitate a careful balance between growth substrate and cometabolite concentrations to ensure continued biodegradation at a site.

3.3. Contaminant mixtures and combined processes

Co-solute effects on individual bio-attenuation processes will not necessarily couple through a simple linear superposition of the various processes as modeled in isolation. Interactions of co-solutes with the media, microbes, and other solutes “likely translate into non-linear effects in scaling” and “[as] a consequence, processes need to be understood within the complexity of their natural states.” (NRC, 2003a, pp. 198–199). One example of how the bioavailability constraints imposed by one process can modify the significance of co-solute effects on another process is from the study of the four nitroaromatic compounds by Martins and Mermoud (1998) that was cited earlier. In this study, the researchers monitored the biodegradation of the nitroaromatics in liquid, batches (water with soil suspensions) and in unsaturated solid, batches (repacked soils). They observed that 2, 4-dinitrophenol (DNP) and 2-methyl-4, 6-dinitrophenol (DNOC) were
rapidly biotransformed in the single-solute, liquid batches, but that the transformation rates were significantly reduced when these compounds were combined with 2-sec-butyl-4, 6-dinitrophenol (DNSB) and 2-tert-butyl-4, 6-dinitrophenol (DNTB) due to inhibition and toxicity effects. Conversely, in the solid batches, the multi-solute degradation rates were actually greater than the single-solute rates. The researchers reasoned that greater mass transfer constraints in the solid batches lowered the contaminant-microbe contact and consequently reduced toxicity.

To better predict contaminant fate in single- and multi-solute environments, modeling approaches need to accurately account for the individual and combined effects of the biotic and abiotic processes. The following section reviews traditional and more recent approaches for modeling the sub-component processes that affect bioavailability.

4. Processes that affect bioavailability: models

4.1. Equilibrium sorption

Sorption collectively describes adsorption of solutes onto particle surfaces and absorption (partitioning) of solutes into macromolecular organic phases (Luthy et al., 1997; Allen-King et al., 2002; Huang et al., 2003). Distinguishing between adsorption and absorption mechanisms is difficult, and inferences of microscale sorbate–sorbent interactions are often made through macroscale observations of sorption isotherm characteristics (Luthy et al., 1997; Xia and Pignatello, 2001; Madsen, in press). Isotherm nonlinearity is typically “favorable” (higher sorbed-to-aqueous ratios at low aqueous concentrations) and is often most pronounced at low aqueous concentrations. At higher concentrations, the higher energy sorption sites become saturated, absorption into “soft” organic matter becomes the dominant sorption mechanism, and the isotherm becomes more linear (Xia and Ball, 1999; Xia and Pignatello, 2001; Huang et al., 2003).

Properly delineating the sorption isotherm over the entire concentration range of interest is important because misrepresenting nonlinear sorption behavior with a linear sorption isotherm can lead to overestimations of contaminant bioavailability at low solute concentrations (e.g., Karapanagioti et al., 2001; Sabbah et al., 2004). In addition, separately understanding what fraction of sorption is due to linear partitioning and what fraction is associated with nonlinear processes can also be important because only the latter tend to be competitive (e.g., Xia and Ball, 1999, 2000; Huang et al., 2003). In this context, recently observed sorption isotherms with soils and sediments have been represented as combinations of both linear and nonlinear sorption mechanisms, as more fully reviewed by Allen-King et al. (2002). These dual-mode, combined sorption, or composite models (Weber et al., 1992; Xing et al., 1996; Huang et al., 1997; Xia and Ball, 1999, Huang et al., 2003) have demonstrated particular strength in representing sorption behavior of organic solutes to mixed carbon sources such as sediments or soils that are composed of both natural organic matter and combustion residues or other forms of thermally altered carbon (Allen-King et al., 2002; Huang et al., 2003; Cornelissen and Gustafsson, 2004).

The disadvantage of composite models, however, is the increased number of fitting parameters that complicate the estimation of unique parameter sets (Allen-King et al., 2002; Li and Werth, 2002).

Common sorption isotherms for the nonlinear (adsorption) component are shown in Table 1. (See Hinz, 2001 for a good review of mathematical isotherm expressions.) The Freundlich isotherm model (Eq. (B), Table 1) is perhaps the most widely applied model to describe nonlinear sorption behavior. The observed $n$ values are less than one for sorption onto most
Table 1
Some equilibrium sorption isotherm models commonly applied for soils and sediments

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>Parameters</th>
<th>Example References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>( S = K_d C )</td>
<td>( C ) = aqueous-phase equilibrium concentration [M/L^3]</td>
<td>Karickhoff et al. (1979)</td>
</tr>
<tr>
<td></td>
<td>( S = ) sorbed-phase equilibrium concentration [M/L^3]</td>
<td>( K_d = ) sorption partition coefficient [L^3/M^1]</td>
<td></td>
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<td></td>
<td>[A]</td>
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<tr>
<td>Freundlich</td>
<td>( S = K_f C^n )</td>
<td>( K_f = ) Freundlich sorption coefficient [(L^3/M^1)^n]</td>
<td>Freundlich (1932)</td>
</tr>
<tr>
<td></td>
<td>( n = ) Freundlich exponent [-]</td>
<td></td>
<td>Do (1998)</td>
</tr>
<tr>
<td>Langmuir</td>
<td>( S = \frac{S^{max} b C}{1 + b C} )</td>
<td>( S^{max} = ) maximum sorption capacity [M/L^3], ( b = ) sorption affinity parameter [-]</td>
<td>Langmuir (1918)</td>
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<td></td>
<td></td>
<td></td>
<td>Hinz (2001)</td>
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<tr>
<td></td>
<td>Polanyi–Dubinin–Manes</td>
<td>( S_i = S_{v0} \rho_o \exp \left(-\frac{e_{sw}}{E}\right)^b )</td>
<td>Crittenden et al. (1987)</td>
</tr>
<tr>
<td></td>
<td>( S_i = S_{v0} \rho_o \cdot 10^c e\left(-\frac{e_{sw}}{E}\right)^b )</td>
<td>( e_{sw} = ) available adsorption potential = ( R T \ln(C_{sol}/C_e) ) [L^2 T^{-1}]</td>
<td>Manes (1998)</td>
</tr>
<tr>
<td></td>
<td>( S_i = S_{v0} \rho_o \cdot 10^c e\left(-\frac{e_{sw}}{E}\right)^b )</td>
<td>( C_{sol} = ) aqueous solubility of compound [ML^{-3}], ( C_e = ) equilibrium solute concentration [ML^{-3}]</td>
<td>Kleineidam et al. (2002)</td>
</tr>
<tr>
<td></td>
<td>( S_i = S_{v0} \rho_o \cdot 10^c e\left(-\frac{e_{sw}}{E}\right)^b )</td>
<td>( R = ) ideal gas constant [L^2 T^{-2}], ( T = ) absolute temperature [Kelvin]</td>
<td>Allen-King et al. (2002)</td>
</tr>
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<td></td>
<td>( S_i = S_{v0} \rho_o \cdot 10^c e\left(-\frac{e_{sw}}{E}\right)^b )</td>
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<td></td>
<td>[D.1]</td>
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<tr>
<td></td>
<td>Multi-component Langmuir</td>
<td>( S_i = \frac{S_{v0} \rho_o \cdot 10^c e\left(-\frac{e_{sw}}{E}\right)^b } )</td>
<td>Markham and Benton (1931)</td>
</tr>
<tr>
<td></td>
<td>( S_i = \frac{S_{v0} \rho_o \cdot 10^c e\left(-\frac{e_{sw}}{E}\right)^b } )</td>
<td>( i = ) solute ( i ) (solute of interest) ( j = ) solute ( j ) ( N = ) number of solutes in system</td>
<td>Do (1998)</td>
</tr>
<tr>
<td></td>
<td>( S_i = \frac{S_{v0} \rho_o \cdot 10^c e\left(-\frac{e_{sw}}{E}\right)^b } )</td>
<td></td>
<td>Li and Werth (2002)</td>
</tr>
<tr>
<td></td>
<td>( S_i = \frac{S_{v0} \rho_o \cdot 10^c e\left(-\frac{e_{sw}}{E}\right)^b } )</td>
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<td></td>
<td>[E]</td>
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<td></td>
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<tr>
<td>Ideal Adsorbed Solution Theory (IAST)</td>
<td>( C_i = \left( \frac{S_i}{\sum_{j=1}^{N} S_j} \right) \left[ \frac{K_{fi}}{\sum_{j=1}^{N} \frac{S_j}{n_j}} \right]^{1/2} )</td>
<td>( i = ) solute ( i ) (solute of interest) ( j = ) solute ( j ) ( N = ) number of solutes in system</td>
<td>Radke and Prausnitz (1972)</td>
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<td></td>
<td>( C_i = \left( \frac{S_i}{\sum_{j=1}^{N} S_j} \right) \left[ \frac{K_{fi}}{\sum_{j=1}^{N} \frac{S_j}{n_j}} \right]^{1/2} )</td>
<td></td>
<td>Crittenden et al. (1985)</td>
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<td>( C_i = \left( \frac{S_i}{\sum_{j=1}^{N} S_j} \right) \left[ \frac{K_{fi}}{\sum_{j=1}^{N} \frac{S_j}{n_j}} \right]^{1/2} )</td>
<td></td>
<td>McGinley et al. (1993, 1996)</td>
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<td></td>
<td>( C_i = \left( \frac{S_i}{\sum_{j=1}^{N} S_j} \right) \left[ \frac{K_{fi}}{\sum_{j=1}^{N} \frac{S_j}{n_j}} \right]^{1/2} )</td>
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<td>Schaefer et al. (2000)</td>
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<td></td>
<td>( C_i = \left( \frac{S_i}{\sum_{j=1}^{N} S_j} \right) \left[ \frac{K_{fi}}{\sum_{j=1}^{N} \frac{S_j}{n_j}} \right]^{1/2} )</td>
<td></td>
<td>Li and Werth (2002)</td>
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</table>
sorbents from aqueous solution, indicating the gradual filling of higher energy sorption sites as concentration increases. Although $n$ values are usually only slightly less than one for soils and sediments, recent studies on hard carbon materials, such as combustion residues, have reported $n$ values of 0.6 or less (Kleineidam et al., 2002; Huang et al., 2003; Cornelissen and Gustafsson, 2004; Cornelissen et al., 2004a,b; Nguyen et al., 2005).

Another, useful sorption model is based on the Polanyi–Manes (PM) approach (Manes, 1998; Crittenden et al., 1987; Sontheimer et al., 1988), which, when applied in the form of the Dubinin–Astakov equation, has been referred to as the Polanyi–Dubinin–Manes (PDM) model (Allen-King et al., 2002; Kleineidam et al., 2002). The Dubinin–Astakov equation (or PDM) is shown as Eqs. (D1) and (D2) of Table 1. The PM approach is based on Polanyi’s theory of adsorption potential for a vapor phase system (Allen-King et al., 2002), and can also be applied to aqueous systems based on theory described elsewhere (Wohleber and Manes, 1971a,b; Manes, 1998). The basic assumption of the PM approach is that the available sorption potential, $\varepsilon_{sw}$, decreases as the adsorbed concentration increases—i.e., during filling of micropores in the adsorption domain. The PM approach is particularly suited for situations where the volume available for sorbed molecules is not a function of temperature and is constant for multiple sorbates (Manes, 1998), but the underlying theory is generally applicable to any adsorption process. It is important to recognize that the PM approach does not specify any particular relation between the adsorbed volume and $\varepsilon_{sw}$, such that Eq. (D1) (or equivalently (D2)) is only one convenient mathematical formulation (Manes, 1998).

As previously mentioned, competitive sorption adds complexity to predicting sorbent–water interactions. There are several methods to account for changes in the equilibrium distribution of one solute when in the presence of other sorbates. For example, the single solute Langmuir isotherm is easily extended to a multi-component Langmuir isotherm (Table 1, Eq. (E)). Similar to its single component counterpart, the multi-component Langmuir model assumes a fixed number of sorption sites and no interactions among sorbates (Li and Werth, 2002).

The PDM model also can be modified to account for multiple sorbates by assuming that the adsorbed solution is ideal (or, that the equilibrium sorbed phase activity of an individual solute is proportional to its mole fraction in the sorbed solution; i.e., Raoult’s Law), that the adsorption potential of each solute is the same at equilibrium, and that the total sorption potential of the mixture is the same as the potential of a single sorbate with the same adsorbed volume as the mixture. Modifications of the theory that assume other, less ideal, mixtures of solutes are also available (Manes, 1998). With the ideal solution assumption, the definition of the available sorption potential for the PM approach can be modified for a solute $i$ in a mixture of $n$ components according to the following equations (Xia and Ball, 2000; Li and Werth, 2002):

$$ (\varepsilon_{sw})_i = RT \ln \left( \frac{x \frac{C_i}{C}}{\frac{C_i}{C^*}} \right) $$ (1a)

$$ x_i = \frac{C_i}{C_i^*} $$ (1b)

$$ \sum_{i=1}^{n} x_i = 1 $$ (1c)

where $C_s$ is the solubility of the solute and $C_i^*$ is the aqueous concentration of solute $i$ with the same adsorbed volume as the total adsorbed volume of the mixture at equilibrium.
Table 2
Intraparticle mass transfer and sorption/desorption rate models

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>Parameters</th>
<th>Example References</th>
</tr>
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<tbody>
<tr>
<td>Spherical intraparticle diffusion with surface diffusion to the bulk aqueous phase</td>
<td>$\frac{\partial}{\partial t} \left[ \rho_{im} C_{im} + \rho S \right] = \frac{1}{r^2} \frac{\partial}{\partial r} \left( \rho_{im} D_p r^2 \frac{\partial C_{im}}{\partial r} \right)$</td>
<td>$C_{im}$=aqueous phase solute concentration in intraparticle region $[\text{ML}^{-3}]$ $C_a$=aqueous phase solute concentration at particle surface $[\text{ML}^{-3}]$ $C_b$=bulk aqueous solute concentration $[\text{ML}^{-3}]$ $D_p$=effective pore diffusion coefficient $[\text{L}^2 \text{T}^{-1}]$</td>
<td>Crank (1975) Rao et al. (1980a) Crittenden et al. (1986) Miller and Pedit (1992)</td>
</tr>
<tr>
<td>and</td>
<td>$\frac{\partial C_b}{\partial t} = \frac{3 V_a}{\rho V_w} \left( \frac{C_a - C_b}{a} \right)$</td>
<td>$V_a$=unit soil volume $[\text{L}^3]$ $V_w$=unit water volume $[\text{L}^3]$ $r$=particle radial coordinate $[\text{L}]$ $a$=radial position the particle surface $[\text{L}]$ $\rho$=soil bulk density $[\text{ML}^{-3}]$ $\eta_{im}$=intraparticle porosity $[-]$ $\alpha_s$=surface mass transfer coefficient $[\text{LT}^{-1}]$</td>
<td>[A.2]</td>
</tr>
<tr>
<td>First-order mass transfer</td>
<td>$\frac{\partial C_b}{\partial t} = \alpha_p (C_{im} - C_b)$</td>
<td>$\alpha_p$=first-order mass transfer coefficient $[\text{T}^{-1}]$</td>
<td>van Genuchten and Wierenga (1976)</td>
</tr>
<tr>
<td>One-site desorption</td>
<td>$\frac{\partial S}{\partial t} = -k_d S + \frac{k_s}{R_{s/w}} C$</td>
<td>$C$=aqueous phase concentration $[\text{ML}^{-3}]$ $S$=sorbed phase concentration $[\text{MM}^{-1}]$ $R_{s/w}$=soil/water ratio $[\text{ML}^{-3}]$ $k_s$=desorption rate for slow sorption sites $[\text{T}^{-1}]$</td>
<td>Oddson et al. (1970) Lindstrom et al. (1971)</td>
</tr>
<tr>
<td>and</td>
<td>$\frac{\partial S}{\partial t} = k_d (K_d C - S)$</td>
<td>$K_d = \frac{dS}{dC} = \frac{k_s}{R_{s/w} k_d}$</td>
<td>[C.2]</td>
</tr>
<tr>
<td>Two-site desorption (fast/instantaneous+slow)</td>
<td>$\frac{\partial S}{\partial t} = f K_d \frac{\partial C}{\partial t}$</td>
<td>$S_o$=initial sorbed phase concentration $[\text{MM}^{-1}]$ $f$=fraction of rapid/instantaneous sorption sites $[-]$ $k_s$=desorption rate for slow sorption sites $[\text{T}^{-1}]$</td>
<td>Brusseau et al. (1989) Gamerdinger et al. (1990) Cornelissen et al. (1997)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>and</td>
<td>$\frac{\partial S_o}{\partial t} = (1-f)K_d C - S_o$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S(t) = S_o (1 - f) \exp (- k_s t)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>and</td>
<td>$S(t) = S_o (1 - f) \exp (- k_s t) + (f) \exp (- k_f t)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[D.3]</td>
<td></td>
</tr>
</tbody>
</table>
The sorption model most commonly used to predict adsorption isotherms for solutes in mixtures is derived from the *ideal adsorbed solution theory* (Crittenden et al., 1985; McGinley et al., 1993; Xing et al., 1996; Schaefer et al., 2000; Li and Werth, 2002), which was originally developed for vapor-phase adsorption and later applied to liquid solute systems by Radke and Prausnitz (1972). The main assumptions of the IAST are similar to those of the ideal solution in the PM approach; that is, that solutes in a multi-component system have access to the same sorption sites and that Raoult’s Law applies. Also similar to the competitive PM approach, the IAST assumes that the total spreading pressure – the isothermal difference in interfacial tension between the pure solvent–solid and solution–solid interface – is equivalent for the single- and the multi-solute systems under conditions of equal activity in solution at any given temperature (Xing et al., 1996; Porter et al., 1999). Then, the equilibrium aqueous concentration of each solute in the mixture is equal to the concentration it would have in a single-solute system with the same spreading pressure as in the mixture. An important aspect of both the PM and IAST approaches is that sorption isotherms for multi-component systems can be constructed based on their single-solute isotherms. Eq. (F) of Table 1 shows the IAST equation for the aqueous concentration of a solute \( i \) in a multi-component system based on Freundlich isotherms for the individual solutes.

The IAST has been effectively used to predict multi-solute sorption for numerous sorbents with a variety of organic compounds (e.g., McGinley et al., 1993, 1996; Xing et al., 1996); however, the approach has been less successful predicting competitive sorption in some other cases involving heterogeneous sorption domains (Schaefer et al., 2000; Xing et al., 1996). In addition, multi-component sorption models based on IAST are generally less accurate at high

### Table 2 (continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>Parameters</th>
<th>Example References</th>
</tr>
</thead>
</table>
| Two-site desorption (fast/instantaneous + slow) | \[
\frac{\partial S_k}{\partial t} = \sum_{i=E,X,V} k_i f_i [K C - S_k] 
\]  
\[ [E.1] \]  
\[
S(t) = (f_r) \exp(-k_r t) + (f_s) \exp(-k_s t) + (1 - f_r - f_s) \exp(-k_v t)
\]  
\[ [E.2] \]  
\[ f_r = \text{fraction of rapid sorption sites} [-] \]  
\[ f_s = \text{fraction of slow sorption sites} [-] \]  
\[ f_v = \text{fraction of very slow sorption sites} [-] \]  
\[ k_r = \text{desorption rate for rapid sorption sites} \left[ \text{T}^{-1} \right] \]  
\[ k_s = \text{desorption rate for slow sorption sites} \left[ \text{T}^{-1} \right] \]  
\[ k_v = \text{desorption rate for very slow sorption sites} \left[ \text{T}^{-1} \right] \]  
| [Johnson et al. (2001)] |
| Three-site sorption          | \[
\[ \frac{\partial S_k}{\partial t} = \sum_{i=E,X,V} k_i f_i [K C - S_k] \]
\]  
\[ [E.1] \]  
\[
S(t) = (f_r) \exp(-k_r t) + (f_s) \exp(-k_s t) + (f_v) \exp(-k_v t)
\]  
\[ [E.2] \]  
\[ \eta, \beta = \text{gamma distribution parameters for the probability, } f, \text{ of a domain with desorption rate, } k: \]
\[ f(k) = \frac{\beta^\eta k^{\eta-1} \exp(-\beta k)}{\Gamma(\eta)} \]  
\[ \Gamma(\eta) = \int_0^\infty x^{\eta-1} \exp(-x)dx \]
| [Connaughton et al. (1993)] |  
| Continuum-site sorption (e.g., gamma distribution) | \[
\frac{\partial S_k}{\partial t} = \int k [f_i K C - S_k] dk 
\]  
\[ [F.1] \]  
\[
S(t) = \frac{1}{\beta + t} \left[ \frac{\beta}{\beta + t} \right]^\eta
\]  
\[ [F.2] \]  
\[ C_g(x) = \int_x^\infty x^{\eta-1} \exp(-x) dx \]  
| [Ahn et al. (1996)] |  
| Culver et al. (1997) |  
| Sahoo and Smith (1997) |  
| Johnson et al. (2001) |
solute concentrations and in mixtures with significant solute–solute interactions, where assumptions of ideality are violated (Porter et al., 1999; Li and Werth, 2002). Thus, challenges remain in developing a robust model for simulating sorption behavior in mixed systems across a wide concentration range and with a wide variety of sorbents.

4.2. Rate of mass transfer and desorption

A prominent conceptualization of mass transfer ascribes rate limitations as the physical process of slow diffusion of solutes through intraparticle pores or other intrasorbent regions (Wu and Gschwend, 1986; Brusseau et al., 1989; Ball and Roberts, 1991b). This process is conceptually distinct from sorption–desorption dynamics, a chemical phase-partitioning to solid phases. As both mechanisms affect the rate at which solute mass becomes available in the aqueous phase, however, they can be difficult to distinguish in natural environments. For this reason, and because models of both processes are often mathematically analogous, they are discussed together here.

Several different models are commonly used to describe mass transfer and phase-partitioning rates in environmental systems. Solute mass transfer within a soil or sediment particle is typically thought of as a Fickian diffusion process, assuming, for example, an appropriate average size of spherical particles and radially symmetric transport (see Table 2, Eq (A.1)). In cases where only aqueous pore diffusion is allowed (i.e., sorbed or surface diffusion is negligible or nonexistent), rates of change in the total sorbed concentration will be retarded by sorption along the pore of the intrasorbent diffusion domain. Solute diffusion within a particle is driven by the concentration boundary condition, $C(r=a)=C_a$, which, in turn, is controlled by the solute concentration in the bulk aqueous phase ($C_b$) and an external surface diffusion (Table 2, Eq. (A.2)). In many environmental applications of this approach, the characteristic time for surface diffusion is taken to be much less than the characteristic time for intraparticle mass transfer, such that surface diffusion can be safely neglected and $C_a = C_b$.

In contrast to the uniform sphere assumptions, however, actual solids have heterogeneous sizes, geometries, and internal porosities. Nonetheless, there has been some success in modeling solute mass transfer, or sorption and desorption, by estimating an average spherical diffusion (or sorption–desorption) rate constant and also allowing a fraction of more rapidly (essentially instantaneous) equilibrating sites to exist (e.g., Rao et al., 1980a,b; Addiscott et al., 1983; Nkedi-Kizza et al., 1983; Ball and Roberts, 1991b; Young and Ball, 1994). Other, more recent, investigations have explicitly considered multiple particles sizes, each with its characteristic diffusion rate (Kleineidam et al., 1999; Karapanagioti et al., 2001; Başağaoğlu et al., 2002) and, as will be described subsequently, distributions of rates corresponding to multiple diffusion conditions.

Because definitive characteristics of sorbent physical and chemical characteristics are usually unattainable, and also to simplify the mathematics of modeling, the intraparticle mass transfer is frequently reduced to a first-order rate of solute exchange between mobile and immobile regions (Table 2, Eq. (B)). The first-order mass transfer coefficient is an acknowledged approximation which can never be mechanistically correct, and several investigators have described how the first-order rate must vary over time to simulate a Fickian diffusion process (Rao et al., 1980a; Young and Ball, 1995; Griffioen et al., 1998; Maraqa, 2001). In general, first-order rate models are rarely able to accurately simulate solute concentration histories in either batch or column studies (Young and Ball, 1997; Griffioen, 1998); however, if multiple first-order rate coefficients
are allowed to exist (Table 2, Eqs. C, D, and E) and/or if other system properties (such as the sorption capacity or column dispersivity) are simultaneously fit to experimental data, then reasonable simulations of observed data can sometimes be obtained. Parameter values obtained from such fits, however, should be regarded as case-specific, with little to no direct link to any mechanistic processes of mass transfer.

Another model of desorption rates is based on chemical kinetics under a set of presumed conditions that would cause the rate of desorption to be proportional to the concentration difference between the aqueous and sorbed phases (Table 2, Eq. (C)). Though conceptually distinct, this is mathematically identical to the first-order mass transfer model (Nkedi-Kizza et al., 1984) and, as with the other first-order approaches, two or more first-order rate coefficients are often used to describe desorption/diffusion kinetics from heterogeneous sorbents (Table 2, Eqs. (D)–(E)).

Another well-developed approach for modeling mass transfer and sorption/desorption rates in real soils and sediments is to assume the existence of a diverse distribution of rate constants that are described by a probability density function (pdf). Perhaps the most commonly applied pdf approach, shown in Eq. (F) of Table 2, uses the gamma pdf to simulate a continuum of sorption/desorption rates or diffusion domains (Connaughton et al., 1993; Ahn et al., 1996; Culver et al., 1997; Sahoo and Smith, 1997); although other distribution functions, such as the lognormal density function, have also been applied (Pedit and Miller, 1995; Haggerty and Gorelick, 1998; Li and Brusseau, 2000; Zhang and Brusseau, 2004). Using the gamma distribution model, Culver et al. (1997) achieved significant improvement over the more traditional two-site model in describing long-term desorption behavior for batch and pulse-input column experiments. The rate distribution parameters, however, were sensitive to flow conditions in column experiments and varied between batch and column experiments. A comparison by Johnson et al. (2001) of the gamma distribution model with five other two- or three-compartment desorption models found that the gamma distribution model accurately fit phenanthrene desorption profiles for some soils (Lachine shale and a sandy soil with shale particles accounting for most of the organic matter), but it had difficulty predicting desorption from geologically younger topsoil. They concluded that a two- or three-site model could fit their desorption data as well as or better than the gamma distribution model, argued that the parameters for a two- or three-site model are easier to interpret, and recommended applying a two-site model based on radial diffusion as the best desorption model with three or fewer fitting parameters. Overall, however, this and numerous other studies make it clear that no simply parameterized model can be mechanistically correct for heterogeneous materials of unknown composition, and that any choice of model must be used cautiously with regard to predictions outside of its range of calibration.

As noted previously, because the first-order approach is unable to capture the internal particle solute dynamics, the rate “constants” often need to vary with the experimental time and conditions in order to accurately simulate results (Rao et al., 1980a; Young and Ball, 1995, 1997; Griffioen, 1998; Maraqa, 2001; Haggerty et al., 2004). Moreover, potential errors associated with using a first-order rate model to describe nonequilibrium kinetics are often not apparent from short-term experiments despite the fact that these errors can be substantial over longer times. Generally, good predictions should not be expected for boundary conditions, initial conditions, or time frames different than those with which the first-order parameter was specifically calibrated (Rao et al., 1980a; Young and Ball, 1995; Sabbah et al., 2004). In addition, because a first-order rate cannot capture the intraparticle dynamics during cyclic mass transfer (such as when desorption is onset before sorption is complete), models using first-order
<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>Parameters</th>
<th>Example References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monod Equation</td>
<td>( r_g = \frac{dC_g}{dt} = - \frac{q_{mg}XC_g}{K_{sg} + C_g} )</td>
<td>( K_s ) = half-velocity constant (the aqueous substrate concentration when the growth rate is at one-half of its maximum value) [Mg/L^3] ( X ) = concentration of microorganisms [Mg/L^3] ( Y ) = maximum yield coefficient (mass of microbial cells formed per mass of contaminant substrate consumed) [Mx/g^1] ( b ) = microbial endogenous decay coefficient [T^-1] ( q_{mg} = \mu_{mg} / Y_g ) [Mg/g C^-1 T^-1] ( r_g ) = growth substrate utilization rate [Mg/L^3 T^-1] ( r_x ) = rate of microbial cell growth [Mx/L^3 T^-1] ( l_m ) = maximum specific growth rate [T^-1]</td>
<td>Monod (1949) Tchobanoglous and Burton (1991) Alvarez-Cohen and Speitel (2001)</td>
</tr>
<tr>
<td>First-order</td>
<td>( r_s = -q_1C_s )</td>
<td>( q_1 ) = first-order biodegradation rate coefficient [T^-1]</td>
<td></td>
</tr>
<tr>
<td>Zero-order</td>
<td>( r_s = -q_0 )</td>
<td>( q_0 ) = zero-order biodegradation rate coefficient [Mg/L^3 T^-1]</td>
<td></td>
</tr>
<tr>
<td>Competitive inhibition</td>
<td>( r_g = - \frac{q_{mg}XC_g}{K_{sg}\left(1 + \sum_{j=1}^{n} \frac{C_j}{K_{ic}^j}\right) + C_g} )</td>
<td>( K_i^C ) = competitive inhibition coefficient [Mg/L^3] ( n ) = number of cometabolites in system</td>
<td>Criddle (1993) Alvarez-Cohen (1993) Copeland (1996) Reardon et al. (2000) Alvarez-Cohen and Speitel (2001)</td>
</tr>
<tr>
<td>Noncompetitive inhibition</td>
<td>( r_g = - \frac{q_{mg}XC_g}{(K_{sg} + C_g)\left(1 + \sum_{j=1}^{n} \frac{C_j}{K_{ic}^j}\right)} )</td>
<td>( K_i^N ) = noncompetitive inhibition coefficient [Mg/L^3]</td>
<td>Keenan et al. (1994) Copeland (1996) Reardon et al. (2000) Alvarez-Cohen and Speitel (2001)</td>
</tr>
<tr>
<td>Uncompetitive inhibition</td>
<td>( r_g = - \frac{q_{mg}XC_g}{(K_{sg} + C_g)\left(1 + \sum_{j=1}^{n} \frac{C_j}{K_{ic}^j}\right)} )</td>
<td>( K_i^U ) = uncompetitive inhibition coefficient [Mg/L^3]</td>
<td>Copeland (1996) Reardon et al. (2000)</td>
</tr>
</tbody>
</table>
Cometabolic degradation

\[ r_c = (T_y r_g - q_{mc} X) \left( \frac{C_c}{K_{rc} + C_c} \right) \]

\[ T_y = \text{transformation yield (ratio of the mass of cometabolic substrate transformed to the mass of growth substrate transformed) [M_c M_g^{-1}]} \]

\[ r_c = \text{rate of cometabolic nongrowth substrate utilization [M_c L^{-3} T^{-1}]} \]

Cometabolic degradation with product toxicity

\[ q_{mg}^* = q_{mg} - q_{inact} P_c + q_{rec} P_g \]

\[ P_g = \text{product of the growth substrate [M/L^3]} \]

\[ P_c = \text{product of the cometabolic substrate [M/L^3]} \]

\[ T_c = \text{transformation capacity} = \frac{C_c}{T} \]

\[ q_{mg}^* = \text{modified maximum utilization rate for growth substrate [T^{-1}]} \]

\[ q_{inact} = \text{first-order cell inactivation rate [T^{-1}]} \]

\[ q_{rec} = \text{first-order cell recovery rate [T^{-1}]} \]

Reductant limitation

\[ r_g = -q_{mg} X \left( \frac{K_{sg}}{K_{sg} + C_g} \right) \left( \frac{C_r}{K_{sr} + C_r} \right) \]

\[ C_r = \text{aqueous concentration of reductant [M/L^3]} \]

\[ K_r = \text{half-velocity constant for reductant [ML^{-3}]} \]

\[ \alpha_c = \text{stoichiometric coefficient for reductant consumption from biodegradation of cometabolic substrate [M_c M_r^{-1}]} \]

\[ \alpha_g = \text{stoichiometric coefficient for reductant regeneration from biodegradation of growth substrate [M_r M_g^{-1}]} \]

Haldane–Andrews self-inhibition model

\[ r_g = \frac{q_{mg} X C_g}{K_{sg} + C_g + C_g \left( \frac{C_r}{K_r} \right)^n} \]

\[ K_i = \text{inhibition coefficient [–]} \]

\[ n = \text{order of inhibition (n = 1 for traditional Haldene–Andrews equation)} \]

Alvarez-Cohen and McCarty (1991a,b)

Criddle (1993)

Alvarez-Cohen and Speitel (2001)

Ely et al. (1995)

Alvarez-Cohen and Speitel (2001)


Alvarez-Cohen and Speitel (2001)


Alvarez-Cohen and Speitel (2001)

Edwards (1970)

Neufield et al. (1980)

Gupta et al. (1996)
rates can erroneously predict desorption (and inaccurately imply desorption hysteresis) under such conditions (Griffioen, 1998; Sabbah et al., 2004).

4.3. Biodegradation

Biodegradation models (Table 3) are commonly based on saturation kinetics (Monod, 1949; Copeland, 1996; Kovárová-Kovar and Egli, 1998). The classical Monod expression (Table 3, Eqs. (A.1), (A.2)) models the interdependence of the degradation of a rate-limiting substrate and the biomass growth as functions of a yield coefficient \( Y \) [M\(_x\) M\(_{-1}\)] (biomass formed per mass of contaminant substrate consumed) and a maximum specific microbial growth rate, \( \mu_{mg} \) [T\(^{-1}\)]. (Often \( \mu_m \) and \( Y \) are lumped into a single maximum rate of substrate utilization, \( q_{mg} \) [M\(_g\) M\(_x\) T\(^{-1}\)].) The rate of substrate utilization and biomass growth are influenced by a half-velocity constant, \( K_s \) [ML\(^{-3}\)], which conceptually represents the affinity of the degrading enzyme for the substrate (Copeland, 1996; Kovárová-Kovar and Egli, 1998). When the microbial culture is in the log-growth phase, the biomass growth is reduced by a first-order endogenous decay rate coefficient, \( b \) [T\(^{-1}\)] (Tchobanoglous and Burton, 1991; Kovárová-Kovar and Egli, 1998).

The Haldane–Andrews equation (Table 3, Eq. (K)) modifies the original Monod equation to account for when a substrate (or substrate biotransformation intermediate) is toxic to the degrading population. The effects of this “self-inhibition” are incorporated into the Monod expression with an inhibition term, \( C/K_i \) [–] in the denominator. The Haldane–Andrews equation is similar to the Monod equation at low substrate concentrations, but gives decreased utilization rates as the substrate concentration is increased. A modified form of the Haldane–Andrews equation adds an exponent \( n \) (the order of reaction) to the inhibition term (Gupta et al., 1996).

Further variations to the Monod equation account for co-solute effects, including reductant limitations, co-solute inhibition, and cometabolism with product toxicity. These modifications for co-solutes are shown in Eqs. (D)–(J) of Table 3. (See Copeland, 1996 for a more comprehensive review of models for co-substrate inhibition or Alvarez-Cohen and Speitel, 2001 for a review of these models in the context of cometabolism). Theoretically, the inhibition term, \( K_i \), in the inhibition models (Table 3, Eqs. (D)–(F)) is equivalent to the half-velocity constant, \( K_s \), for that compound (Copeland, 1996). As discussed in Reardon et al. (2000) and Alvarez-Cohen and Speitel (2001), however, this substitution often fails to capture the complexities of intracellular solute interactions, and, consequently, a more nondescript inhibition term is often empirically determined.

A challenge in applying any form of the Monod equation is determining appropriate kinetic parameters. Reported values of \( \mu_m \) and \( K_s \) vary by as much as 3 orders of magnitude, even for the same combination of substrate and microbial culture (Kovárová-Kovar and Egli, 1998). Likely reasons for parameter variations are correlations between \( \mu_m \) and \( K_s \), the history and condition of the degrading population, and experimental data quality and regression technique (Kovárová-Kovar and Egli, 1998). Thus, although there have been a variety of studies to measure \( \mu_m, K_s \), and other parameters, the general applicability of their values is unclear, especially for multi-substrate Monod models that require several additional parameters (Semprini, 1997; Alvarez-Cohen and Speitel, 2001). Consequently, for reasons similar to the use of first-order rate models for mass transfer (i.e., inability to characterize the system and/or for mathematical simplicity), the Monod expression is often reduced to a single rate constant. Making this simplification requires the assumption of zero net biomass growth (\( r_x = 0 \)). Then, if the solute concentration is much less than the half-velocity constant (\( C \ll K_s \)) the Monod equation for substrate degradation reduces to a
first-order equation with a rate constant, \( q_1 \approx q_{mg} X K_s^{-1} [T^{-1}] \) (Table 3, Eq. (B)), or, if \( C \gg K_s \), the Monod equation becomes zero-order with rate constant, \( q_0 \approx q_{mg} X [ML^{-3}T^{-1}] \) (Table 3, Eq. (C)). In modeling solute attenuation in many laboratory experiments and contaminated field sites, a first-order biodegradation rate is the de facto representation, justified by aqueous solute concentrations that are typically low relative to their respective \( K_s \) values (Bjerg et al., 1996). In many cases, the use of a first-order biodegradation rate constant may be necessary because it is infeasible to separate all the biological processes affecting biodegradation in a way needed to parameterize the Monod model. As with the use of a first-order mass transfer constant, however, it should be recognized that an empirically determined first-order biodegradation rate constant is site specific and subject to variations in experimental conditions (including, and especially, when in the presence of co-solutes), and temporal variations in the biomass population. Slight modifications to the first-order approximation, such as including an initial “lag” period of no degradation, can sometimes improve the ability of a first-order model to account for nonideal processes such as microbial adaptation (e.g., Zimdahl et al., 1994; Martins and Mermoud, 1998; Park et al., 2001, 2002). Still, the applicability of a first-order rate model for long-term predictions is hard to validate and should not be extended beyond the specific situation under which it was determined.

5. Evaluation of bioavailability

Bioavailability is often evaluated using dimensionless indices that provide a simple measure of the relative magnitude of mass transfer rates to biodegradation rates with the idea that exceptionally high or low values can provide an indication of the rate limiting mechanism. Table 4 summarizes bioavailability indices used in prior research. For example, one such index is the Damköhler number, \( \omega \), defined as the ratio of the first-order biodegradation rate coefficient to either an overall first-order mass transfer rate coefficient (Table 4, Eq. (A.1)) or an external surface (film) mass transfer coefficient (Table 4, Eq. (A.3)). The Bioavailability Number of Bosma et al. (1997) is the reciprocal of \( \omega \) with the Monod parameters \( K_s \) and \( \mu_m \) used to approximate a first-order biodegradation rate coefficient (Table 4, Eq. (B)). Another bioavailability index, the Thiele Modulus, \( \phi_T \), is the square root of the ratio of the biodegradation rate to the diffusion/desorption rate (Table 4, Eqs. (C.1)–(C.3)). The Thiele Modulus is also used to account for mass transfer rate effects in the Bioavailability Factor of Zhang et al. (1998), which also accounts for effect of equilibrium sorption and the soil–water ratio on the overall rate of biodegradation (Table 4, Eq. (D)).

By identifying the process limiting mass removal, bioavailability indices can assist in the design of remediation strategies. For example, sites with a high bioavailability index (biodegradation rates >mass transfer rates) are likely amenable to bioremediation while sites with a low bioavailability index might require treatments that act to increase aqueous concentrations of the contaminants such as thermal or cosolvent flushing (Zhang et al., 1998).

The utility of a bioavailability index depends on the degree that a value calculated from independently obtained data can reveal the remediation potential at a given site and the ease with which new data can be obtained to adjust the value for new site conditions. This interpretability and transferability will, in turn, depend on the extent to which discernable mechanistic aspects of bioavailability are captured by the index and on whether the assumptions about their inter-relations are valid. In this regard, one limitation of bioavailability indices is that, as single dimensionless coefficients, they only convey relative rates and not the absolute rates for mass transfer and biodegradation. Consequently, a simple bioavailability index alone does not
distinguish a situation where biodegradation and mass transfer rates are mutually rapid from a situation where biodegradation and mass transfer rates are similarly slow (both situations could theoretically have the same bioavailability index).

In the latter regard, it is useful to consider a two-dimensional plot of the mass transfer rate, \( r_{mt} \), versus the biodegradation rate, \( r_{bio} \), as shown in Fig. 1. Such a plot displays both the absolute and relative rates for \( r_{mt} \) and \( r_{bio} \). It also allows a quick assessment of both the limiting processes as well as the overall remediation potential of a site. For example, contaminated sites where the plot of \( r_{mt} \) vs. \( r_{bio} \) lies in regions of the graph near \( r_{bio} = 0 \) (extreme biodegradation rate limitations) or \( r_{mt} = 0 \) (extreme mass transfer rate limitations) are not good candidates for in situ bioremediation or natural attenuation, and the remediation potential increases toward the upper right portion of

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>Parameters</th>
<th>Example references</th>
</tr>
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<tbody>
<tr>
<td>Damköhler number ( \omega )</td>
<td>( \omega = \frac{q_1}{\bar{a}} ) or ( \omega = \frac{q_1}{nv_pA_pk_i} )</td>
<td>( A_p = ) surface area per unit volume of a single particle [ L^{-1} ] ( q_1 = ) first-order biodegradation rate constant [ T^{-1} ]</td>
<td>Ghoshal et al. (1996) Ramaswami and Luthy (1997) Chung et al. (1993)</td>
</tr>
<tr>
<td>Bioavailability number ( B_n )</td>
<td>( B_n = \frac{\omega K_s}{\mu_m} )</td>
<td>( K_s = ) Monod half-velocity constant [ ML^{-3} ] ( \mu_m = ) Monod maximum utilization rate [ T^{-1} ]</td>
<td>Bosma et al. (1997)</td>
</tr>
<tr>
<td>Thiele Modulus ( \phi_T )</td>
<td>( \phi_T = \left( \frac{\alpha}{3} \right)^\frac{1}{2} \left( \frac{q_1}{D_a} \right)^{\frac{1}{2}} ) or ( \phi_T = (a) \left( \frac{\varepsilon_{im} + R(1 - \varepsilon_{im})q_1}{D_a} \right)^{\frac{1}{2}} )</td>
<td>( D_a = ) effective interparticle diffusion coefficient ( (D_p/R) ) [ L^2 T^{-1} ] ( K_d = ) linear soil–water partition coefficient [ L^3 M^{-1} ] ( R = ) retardation factor ([-] ( R_{s/w} = ) soil–water ratio [ ML^{-3} ] ( a = ) particle radius [ L ] ( k_2 = ) first-order desorption rate constant ( q_1 = ) first-order biodegradation rate coefficient [ T^{-1} ] ( \varepsilon_{im} = ) intraparticle porosity ([-]</td>
<td>Myrold and Tiedje (1985) Chung et al. (1993)</td>
</tr>
<tr>
<td>Bioavailability factor ( B_T )</td>
<td>( B_T = \frac{1}{1 + K_d R_{s/w} \left( 1 + \frac{q_1}{k_2 K_d R_{s/w}} \right)} )</td>
<td>( K_d = ) linear soil–water partition coefficient [ L^3 M^{-1} ] ( R = ) retardation factor ([-] ( R_{s/w} = ) soil–water ratio [ ML^{-3} ] ( k_2 = ) first-order desorption rate constant ( q_1 = ) first-order biodegradation rate coefficient [ T^{-1} ] ( \varepsilon_{im} = ) intraparticle porosity ([-)</td>
<td>Zhang et al. (1998)</td>
</tr>
</tbody>
</table>
the graph. A slightly different graphical approach for quantifying bioavailability, recently presented by Braida et al. (2004), was based not directly on rates but rather on the basis of specific experimental endpoints that could be obtained in the laboratory. Although the axis and quadrants of their graph were less clearly defined, the experimental approaches were designed to independently estimate biodegradation rates and thereby isolate mass transfer effects. Generally, such approaches are likely needed to classify sites on the basis of bioavailability.

The interpretability and transferability of bioavailability indices is dependent on the approximations used in their development. Current indices are based on mathematical relationships that are derived from equations for a completely mixed, batch system with homogeneous, spherical solids and rely on simplistic representations of both biodegradation and mass transfer. Also, the current bioavailability indices do not explicitly show the effects of the possible presence of other chemicals. As has been discussed throughout this paper, co-solutes can either increase or decrease mass transfer rates and biodegradation rates—see the numbered arrows in Fig. 1 and the corresponding explanations in Table 5. Consequently, before a bioavailability index can be applied to a given situation, it is important that the index be modified to account for the other solutes in the system. A similar ambiguity in interpreting the current bioavailability indices is that it is unclear how the index incorporates the effects of equilibrium sorption. Because sorption lowers a solute’s aqueous concentration, it will reduce the apparent biodegradation rate. Also, stronger sorption in intraparticle regions will reduce apparent mass transfer rates. Consequently, before a bioavailability index can be correctly interpreted for a given site or transferred from one compound to another, it should be understood whether the biodegradation and mass transfer rates used in the index calculation were measured in the presence of sorption or if they reflect intrinsic rates as would be observed in a system with no sorption.

A further limitation of any bioavailability index is that it can only relate information for a single-time point in the site history. The bioavailability at a site, however, likely changes over

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Fig. 1. Two-dimensional depiction of a bioavailability index, $BI = \frac{r_{mt}}{r_{bio}}$ ($r_{mt} =$ mass transfer rate and $r_{bio} =$ biodegradation rate.). Contaminated sites where $BI$ plots near $r_{bio} = 0$ (extreme biodegradation rate limitations) or $r_{mt} = 0$ (extreme mass transfer rate limitations) are not good candidates for bioremediation or natural attenuation. The feasibility of bioremediation and natural attenuation increases toward the upper right portion of the graph. The numbered arrows represent potential co-solute effects (see Table 5 for explanation).
time. For example, Monod biodegradation kinetics will fluctuate with time depending on changes in both the aqueous solute concentrations and the growth or decay of biomass. Likewise, mass transfer rates will decrease over time as concentration gradients within immobile zones decrease, and this trend will be magnified in materials with nonlinear sorption isotherms. The dependence of mass transfer rates on the solute distribution makes even a single-time bioavailability index difficult to estimate at a site if the prior system history and initial contaminant profiles within the immobile zones are unknown.

It is uncertain whether site and process characterization can ever be sufficient to allow the development of more robust bioavailability indices that account for site-specific conditions of sorption equilibrium, mass transfer rates, biodegradation kinetics, initial spatial distributions of contaminants, and solution chemistry. This does not mean, however, that simpler bioavailability indices can be of no practical value. Rather, a bioavailability index can aid in site characterization and remediation if the time and condition-specific nature of the indicators is appropriately acknowledged. For example, time varying bioavailability indices could be used as part of an adaptive management approach that includes both initial field-scale testing and periodic recalibration of indices over time based on occasional field-scale perturbations and measurements (NRC, 2003b). The potential usefulness and limitations of bioavailability indices can be illustrated through some specific example calculations based on numerical simulations in

Table 5
Possible co-solute effects on bioavailability

<table>
<thead>
<tr>
<th>No.</th>
<th>Co-solute effect on bioavailability</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Increased $r_{mt}$: competitive sorption reduces retardation. Unchanged $r_{bio}$: biomass growth is at steady-state and the biodegradation rate is a zero-order process (high substrate concentration). No cometabolic, inhibitive, or toxicity effects.</td>
<td>Sorption $n &lt; 1$ Biodegradation $K_e &lt; C$ $K_i \gg C$ $T_c \rightarrow \infty$</td>
</tr>
<tr>
<td>2</td>
<td>Unchanged $r_{mt}$: noncompetitive sorption Increased $r_{bio}$: increased biomass and or cometabolism outweigh any toxic or inhibitive effects.</td>
<td>Sorption $n = 1$ Biodegradation $T_c \rightarrow \infty$ $T_y &gt; 0$</td>
</tr>
<tr>
<td>3</td>
<td>Unchanged $r_{mt}$: noncompetitive sorption Decreased $r_{bio}$: toxic and/or inhibitive effects outweigh biomass growth or cometabolic effects.</td>
<td>Sorption $n = 1$ Biodegradation $K_i \ll C$ $T_c \rightarrow 0$</td>
</tr>
<tr>
<td>4</td>
<td>Increased $r_{mt}$: as in case (1) Increased $r_{bio}$: as in case (2)</td>
<td>Sorption $n &lt; 1$ Biodegradation $T_c \rightarrow \infty$ $T_y &gt; 0$</td>
</tr>
<tr>
<td>5</td>
<td>Increased $r_{mt}$: as in case (1) Decreased $r_{bio}$: as in case (3)</td>
<td>Sorption $n &lt; 1$ Biodegradation $K_i \ll C$ $T_c \rightarrow 0$</td>
</tr>
</tbody>
</table>

The numbered scenarios correspond to the numbered arrows shown in Fig. 1. The last column indicates likely values of the principal sorption and biodegradation parameters for the given scenario. ($r_{mt}$=mass transfer rate and $r_{bio}$=biodegradation rate).
a well defined batch system. Such simulations and associated discussions are provided in the remaining sections of this paper. Additional exemplary calculations and alternative methods of rate comparison (to directly illustrate effects from the variability of biodegradation rates over time) are provided elsewhere (Haws et al., in press).

6. Illustration of bioavailability concepts

To illustrate how co-solute and mass transfer constraints influence contaminant bioavailability, numerical simulations were conducted for hypothetical cases studies of the fate of a primary growth substrate (toluene) and a cometabolically degraded non-growth substrate (trichloroethylene) in single and dual substrate systems. Toluene and trichloroethylene (TCE) were chosen because of their environmental relevance as both individual contaminants and as cometabolic substrates and because of the availability of reported aerobic biodegradation parameters for these compounds.

6.1. Model development

The numerical model used in this work incorporates fully reversible and linear sorption and simple, lumped mass transfer/desorption with Monod biodegradation kinetics for solutes in a well-mixed batch system of a water-saturated sorbent. The forward and reverse mass transfer is represented by a one-site sorption domain:

\[ C \xrightarrow{k_a} S \xleftarrow{k_d} \]

where \( C \) [ML\(^{-3}\)] is the aqueous-phase solute concentration, \( S \) [MM\(^{-1}\)] is the sorbed-phase concentration, and \( k_a \) and \( k_d \) [T\(^{-1}\)] are the respective first-order sorption and desorption rate constants. Accordingly, the equilibrium soil–water partitioning coefficient, \( K_d \) [L\(^3\)M\(^{-1}\)], for a given soil–water ratio, \( R_{s/w} \) [ML\(^{-3}\)], is defined by the following equation:

\[ K_d = \frac{k_a}{R_{s/w}k_d} \] (2)

The linear sorption model does not include competitive sorption effects and assumes that an effective intraparticle diffusion rate parameter can be lumped into the sorption and desorption rate coefficients. Though certainly not realistic for actual soil/sediment systems, this representation is useful to explore some of the basic processes that influence bioavailability and to establish some baseline cases against which other, more complex, modeling results might be compared. Similarly, the well-mixed batch conditions are not realistic for most environmental systems but can be considered to represent an endpoint of behavior that might be observed in the laboratory or under certain special cases of controlled remediation.

Single component biodegradation is modeled using the Monod expressions given in Eqs. (A.1)–(A.2) of Table 3. Co-contaminant inhibition is incorporated with the competitive inhibition representation given by Eq. (D) of Table 3. Cometabolism and product toxicity are simulated using Eqs. (G) and (I) of Table 3. Nutrients and energy substrates are assumed to be non-limiting.

The numerical solution for coupling mass transfer and biodegradation was programmed using MS Excel/Visual Basic. Aqueous and sorbed concentrations, as well as the microbial growth or decay, were updated at each time step using a central-weighted, finite-difference scheme. The
numerical algorithm first solved for the contaminant distribution between aqueous and sorbed phases, and then used this result to calculate the mass of substrate degraded and the change in the biomass concentration.

6.2. Parameterization

All case studies were for a 1 L, completely mixed, aerobic batch domain with $R_{s/w} = 4.4$. This $R_{s/w}$ corresponds to the solid and water ratios that would exist in saturated aquifers with soil bulk densities, $\rho$, in the range of 1.5 to 1.9 g/cm$^3$ and water contents, $\theta$, in the range of 0.34 to 0.43. Two hypothetical soils were investigated. The first, a weaker sorbent (Type I), was representative of aquifer sands in Borden, Ontario with an organic carbon fraction of 0.00023 (D’Adamo, 2003). The second, a stronger sorbent (Type II), was typical of silt loam aquitard material in Dover, Delaware with an organic carbon fraction of 0.015 (D’Adamo, 2003). Although sorption in the Borden material has been found to be slightly nonlinear and in excess of that estimated from typical correlations with organic matter (Ball and Roberts, 1991a; Rivett and Allen-King, 2003; Ran et al., 2003), the simulations in this work for both Borden and Dover materials are simplified to be based on linear partition coefficients, $K_d$, that were estimated from partition coefficients, $K_{oc}$, normalized to the fraction of organic carbon, $f_{oc}$:

$$K_d = f_{oc}K_{oc}$$  (3)

The $K_{oc}$ values were approximated from reported octanol–water partition coefficients, $K_{ow}$, with the relationship used by Schaerlaekens et al. (1999) and based on the long-standing correlation of Karickhoff (1981):

$$\log K_{oc} = 0.95\log K_{ow} - 0.2$$  (4)

As recently reviewed by Allen-King et al. (2002), this correlation is but one of many empirical correlations that give similar results to within approximately 0.3 to 1.0 log units for various nonpolar organic chemicals. Recently published equations (see Allen-King et al., 2002) provide more accurate techniques to estimate sorption strength. Correlations of $K_{oc}$ with $K_{ow}$ are still in common use, however, and Eq. (3) is sufficient for the illustrative purposes of this work.

First-order desorption rate coefficients, $k_d$, were approximated from the computed $K_d$ values using the regression relationship of Brusseau et al. (1991):

$$\log k_d = -0.7\log K_d - 1.67$$  (5)

As with Eq. (4), the $k_d - K_d$ regression in Eq. (5), is used here for simplicity and as a crude means of approximating a first-order constant that includes some of the effects of increased retardation and slowed mass transfer that are expected to occur under conditions of diffusion-limited desorption with intraparticle sorption (Ball et al., 1991).

The specific log $K_{ow}$ value for TCE, 2.32, was taken from the averages of several literature values assembled by Schaerlaekens et al. (1999). The log $K_{oc}$ value for toluene, 2.18, was obtained directly from values reported by E.P.A. (1995). The $K_d$ and $k_d$ values used in each simulation are reported in Table 6.

Selecting representative values for the aerobic biodegradation parameters of each contaminant was difficult because of the large number of parameters and the large variation of reported values within a given parameter class (see Section 4.3). However, toluene and/or TCE biodegradation parameter values compiled by Semprini (1997), Alvarez-Cohen and Speitel (2001), Alagappan and Cowan (2003), Arp et al. (2001), as well as other individual studies (see
footnotes to Table 7) provided a suitable dataset from which to estimate average biodegradation parameter values. TCE biodegradation parameters were taken only from experiments of TCE cometabolism where toluene or phenol was used as the primary growth substrate.

The reported biodegradation rates from studies using pure-strain microbial cultures were generally greater than those reported for studies using mixed microbial cultures. To highlight the effects of biodegradation rate, two biodegradation parameter sets were compiled for toluene and TCE: one using average values from the pure culture studies (termed “fast”) and one using average values from the mixed culture studies (termed “slow”). The value of the “fast” $K_s$ was also used for both the “fast” and “slow” $K_i$ values. (Recall that the validity of substituting $K_s$ values for $K_i$ values is still under debate; however, a lack of reported $K_i$ values necessitated this assumption.) For each simulation, the initial biomass concentration, $X$, was set at 5 mg/l, which is within the range of reported values for batch biodegradation studies (McCarty et al., 1998; Schafer and Bouwer, 2000; Alagappan and Cowan, 2003; Kim et al., 2002).

To show the effects of the initial contaminant concentrations, two different scenarios of initial contaminant mass were also explored: one at a higher initial contaminant mass (high $M_o$) and one at a lower initial mass (low $M_o$). For TCE, the high $M_o$ was 100 μmol and the low $M_o$ was 1 μmol. The $M_o$ for toluene was set at 10 times the $M_o$ for TCE. The $M_o$ values were selected to provide initial high/low concentrations that bounded typical values used in biodegradation studies and bioremediation scenarios (McCarty et al., 1998; Cupples et al., 2004; Schafer and Bouwer, 2000; Alvarez-Cohen and Speitel, 2001). The initial solute distributions between

### Table 6
Equilibrium sorption partition coefficients ($K_d$) and first-order desorption rate coefficients ($k_d$) used in the simulations with the Borden-like solids (Type I) and the Dover-like solids (Type II)

<table>
<thead>
<tr>
<th></th>
<th>Toluene</th>
<th>TCE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type I soil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_d$ (L kg$^{-1}$)</td>
<td>0.035</td>
<td>0.024</td>
</tr>
<tr>
<td>$k_a$ (d$^{-1}$)</td>
<td>0.83</td>
<td>0.77</td>
</tr>
<tr>
<td>$k_d$ (d$^{-1}$)</td>
<td>5.4</td>
<td>7.3</td>
</tr>
<tr>
<td><strong>Type II soil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_d$ (L kg$^{-1}$)</td>
<td>2.2</td>
<td>1.6</td>
</tr>
<tr>
<td>$k_a$ (d$^{-1}$)</td>
<td>2.8</td>
<td>2.7</td>
</tr>
<tr>
<td>$k_d$ (d$^{-1}$)</td>
<td>0.29</td>
<td>0.39</td>
</tr>
</tbody>
</table>

### Table 7
Aerobic biodegradation parameters used for “fast” and “slow” biodegradation rates

<table>
<thead>
<tr>
<th></th>
<th>Toluene</th>
<th>TCE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fast (pure cultures)</strong></td>
<td><strong>Slow (mixed cultures)</strong></td>
<td><strong>Fast (pure cultures)</strong></td>
</tr>
<tr>
<td>$q_m$ (μmol mg$^{-1}$ d$^{-1}$)</td>
<td>200</td>
<td>130</td>
</tr>
<tr>
<td>$K_s$ (mol L$^{-1}$)</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>$K_i$ (μmol L$^{-1}$)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>$Y$ (mg$_x$ μmol$^{-1}$)</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>$T_y$ (μmol μmol$^{-1}$)</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>$T_c$ (μmol mg$^{-1}$)</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

---


aqueous and sorbed phases were set to the equilibrium value for the given \( R_{s/w} \) and \( K_d \). In order to evaluate the effects of co-solutes, additional simulations were also conducted for systems with only a single component, toluene or TCE, at high and low \( M_o \).

The different scenarios for the Type I and Type II soils, the fast and slow biodegradation parameters, the high and low \( M_o \) values, and the single and dual solute scenarios combined for a total of 16 simulations. Fig. 2 shows the conditions assumed for the various scenarios and provides identification numbers for cross-reference use in subsequent figures.

### 6.3. Results

The relative mass remaining (\( M/M_o \)) for toluene and TCE is plotted against time for each simulation in Figs. 3 and 4, respectively. Because toluene has consistently greater relative mass reduction than TCE, a semi-log scale is used in Fig. 3 and a linear scale is used in Fig. 4. For the dual contaminant system with the “fast” biodegradation parameters, toluene degradation is fairly

<table>
<thead>
<tr>
<th>Type I Soil</th>
<th>Fast Biodeg.</th>
<th>Low ( M_o ) 1. Tol, 1000 +TCE, 100 (Type I Soil, Fast Bio)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slow Biodeg.</td>
<td>High ( M_o ) 2. Tol, 10 +TCE, 1 (Type I Soil, Fast Bio)</td>
</tr>
<tr>
<td>Dual Substrate</td>
<td></td>
<td>Low ( M_o ) 3. Tol, 1000 +TCE, 1 (Type I Soil, Slow Bio)</td>
</tr>
<tr>
<td>Single Substrate</td>
<td></td>
<td>High ( M_o ) 4. Tol, 10 +TCE, 1 (Type I Soil, Slow Bio)</td>
</tr>
<tr>
<td>Fast Biodeg.</td>
<td></td>
<td>Low ( M_o ) 5. Tol,1000 or TCE, 100 (Type I Soil, Fast Bio)</td>
</tr>
<tr>
<td>Slow Biodeg.</td>
<td></td>
<td>High ( M_o ) 6. Tol,10 or TCE, 1 (Type I Soil, Fast Bio)</td>
</tr>
<tr>
<td>Type II Soil</td>
<td></td>
<td>Low ( M_o ) 7. Tol,1000 or TCE, 100 (Type I Soil, Slow Bio)</td>
</tr>
<tr>
<td>Fast Biodeg.</td>
<td></td>
<td>High ( M_o ) 8. Tol,10 or TCE, 1 (Type I Soil, Slow Bio)</td>
</tr>
<tr>
<td>Slow Biodeg.</td>
<td></td>
<td>Low ( M_o ) 9. Tol,1000 +TCE, 100 (Type II Soil, Fast Bio)</td>
</tr>
<tr>
<td>Dual Substrate</td>
<td></td>
<td>High ( M_o ) 10. Tol, 10 +TCE, 1 (Type II Soil, Fast Bio)</td>
</tr>
<tr>
<td>Slow Biodeg.</td>
<td></td>
<td>Low ( M_o ) 11. Tol, 1000 +TCE, 100 (Type II Soil, Slow Bio)</td>
</tr>
<tr>
<td>Type II Soil</td>
<td></td>
<td>High ( M_o ) 12. Tol, 10 +TCE, 1 (Type II Soil, Slow Bio)</td>
</tr>
<tr>
<td>Fast Biodeg.</td>
<td></td>
<td>Low ( M_o ) 13. Tol, 1000 or TCE, 100 (Type II Soil, Fast Bio)</td>
</tr>
<tr>
<td>Single Substrate</td>
<td></td>
<td>Low ( M_o ) 14. Tol, 10 or TCE, 1 (Type II Soil, Fast Bio)</td>
</tr>
<tr>
<td>Slow Biodeg.</td>
<td></td>
<td>High ( M_o ) 15. Tol, 1000 or TCE, 100 (Type II Soil, Slow Bio)</td>
</tr>
<tr>
<td>Slow Biodeg.</td>
<td></td>
<td>Low ( M_o ) 16. Tol, 10 or TCE, 1 (Type II Soil, Slow Bio)</td>
</tr>
</tbody>
</table>

Fig. 2. Outline of scenarios for simulations of toluene and TCE biodegradation. \( M_o \) refers to the initial mass of toluene or TCE in the batch system.
insensitive to the presence of TCE (Fig. 3A and C). There is no perceptible difference between the toluene degradation in the dual contaminant scenario and the toluene-only scenario for the low $M_o$ cases; however, for the high $M_o$ case in the Type I soil, the presence of TCE noticeably inhibits toluene degradation.

In contrast to toluene, the mass removal of TCE in the TCE-only scenario is significantly less than in the dual contaminant scenario (Fig. 4). This is expected because TCE consumption does not aid in biomass growth and because the toxic product formation from TCE degradation results in increased biomass decay. When TCE exists as the single solute and at low $M_o$, the TCE mass is removed at rates only slightly less than those of the dual solute scenario at low $M_o$. For the TCE-only scenario at high $M_o$, however, the biomass is depleted before any substantial amount of degradation can occur (Fig. 4, all plots).

The relative effect that the presence of a co-solute has on mass removal also depends on the biodegradation rate. Simulations using the “slow” biodegradation parameters tend to accentuate co-solute effects for the degradation of toluene, but suppress differences for TCE. Slower TCE degradation allows TCE to persist and continue to inhibit the toluene degradation for a longer duration than in the “fast” degradation cases. Conversely, slower toluene biodegradation rates suppress the cometabolic biodegradation rate enhancement of TCE (see Eq. (G) in Table 3).

At both low and high $M_o$, toluene and TCE mass removals are significantly influenced by the soil type. Greater mass transfer constraints imposed by the Type II soil relative to the Type I soil result in overall 5-day mass reductions for toluene that are several orders of magnitude less for toluene in the Type II soil versus the corresponding scenario in the Type I soil (full dataset not shown in Fig. 3). Likewise, for all TCE scenarios, except TCE at high $M_o$, mass fractions of
TCE remaining after 5 days are less than 0.01 for the Type I soil with “fast” biodegradation parameters and only between 0.2 and 0.4 for the corresponding scenarios in the Type II soil. The mass transfer constraints imposed by the different soil types also control the sensitivity to changes in biodegradation parameters, changes in $M_o$, and presence or absence of a cometabolite. In regard to all three factors, sensitivity decreases as the contaminant bioavailability is reduced by stronger sorption and slower desorption (Type II soil).

To more clearly illustrate the influences of soil type, co-contamination, and $M_o$, the ratio of mass remaining for the dual contaminant scenario to the mass remaining for the corresponding single solute case are plotted against time in Fig. 5. Ratios for toluene are always greater than unity (biodegradation inhibition by a nongrowth substrate) and the ratios for TCE are always less than one (biodegradation enhancement by a growth substrate). Ratios are more clustered around 1 for the Type II soils versus the Type I soils (reduced co-solute effects with greater sorption/mass transfer limitations; Fig. 5C and D vs. Fig. 5A and B) and for cases of low $M_o$ compared to cases of high $M_o$ (reduced effects of competitive inhibition and transformation capacities; dashed vs. solid lines). Finally, for Type I soils (rapid mass transfer), ratios for toluene tend to increase for the “slow” biodegradation parameters, especially at low $M_o$ (slower TCE degradation means higher TCE concentrations and greater competitive inhibition; Fig. 5B dashed line), but they remain closer to 1 for TCE at all times for low $M_o$ and at early times for high $M_o$ (slower toluene degradation suppresses the cometabolic rate enhancement of TCE; Fig. 5B).

The case studies demonstrate that the presence of co-solutes generally decreases the degradation rate of growth substrates relative to a single-solute system and that this inhibition effect is more pronounced at higher initial solute concentrations. In contrast, the degradation rate
of a cometabolic nongrowth substrate will be significantly increased in the presence of a growth substrate. When the initial concentration of the nongrowth substrate is low, an appreciable fraction of the nongrowth substrate mass can be transformed without the concurrent presence of the growth substrate (assuming that the biomass is expressing the proper enzymes). There is substantially less fractional degradation of a nongrowth substrate at higher initial concentrations, however, because transformation capacities are quickly exceeded and the biomass is depleted.

6.4. Discussion

The simplistic representation of sorption and mass transfer used in these simulations limit their applicability to actual field sites. Even slightly more complex numerical models such as those that might account for nonlinear sorption or diffusion-limited mass transfer must impose idealistic assumptions on the sorbent properties (e.g., homogeneous particles), the microbial composition and activity, and on the nature and effect of chemical composition (co-solutes) on both sorption and biodegradation. Furthermore, batch system models cannot account for the added complexities that occur in advective systems, where solutes are transported at different rates, thus altering the species competition over time.

Consideration of all these varied complexities of real systems requires models that are likely too complicated to be practical for field applications. Fortunately, however, fully mechanistic representations of both biodegradation and sorption/mass transfer may not always be required. For instance, the simulations presented here show that in systems where bioavailability is controlled by sorption and mass transfer, mass removal is insensitive to the biodegradation component. In these systems, co-solute effects on biodegradation might reasonably be neglected.
and the biodegradation kinetics simplified to a first-order rate without the loss of significant accuracy in the simulation results. Conversely, it is reasonable to assume that in systems with low sorption and rapid mass transfer, such as the Type I soil, the consideration of both microbial growth kinetics and co-solute effects on biodegradation become more critical, but the representation of sorption and mass transfer might justifiably be simplified to linear, first-order processes. It should be recognized, however, that the impact of co-solutes on one component process might increase or decrease the relative degree that another process limits contaminant removal and the sensitivity to that process component.

Bioavailability indices can serve as preliminary guides for determining appropriate modeling simplifications to insensitive model components. For example, bioavailability indices for the numerical case studies conducted here are listed for both toluene and TCE in Table 8, under the BI heading. These indices are computed as $BI = \frac{r_{mt}}{r_{bio}}$ based on the initial solute concentrations and biomass density (i.e., computed for the known condition at time = 0). Comparing these BI values with Figs. 3, 4, and 5 shows that as the BI decreases (meaning that the bioavailability is more limited by sorption/mass transfer), the relative sensitivity to the influence of co-solutes and concentration differences on biodegradation also decreases (Fig. 5).

Further insight on process sensitivity and the overall remediation potential of a particular case study can be gained by translating the BI of Table 8 into the two dimensional bioavailability indicator plot (BI plot) of $r_{mt}/C_0^*$ vs. $r_{bio}/C_0^*$, which are computed as shown on the axes labels of Fig. 6 with $C_0^* = \text{(initial solute mass)}/(\text{volume of water})$. Note that in scaling by $C_0^*$, the parameters are representative of pseudo first-order rate constants. Fig. 6 gives four examples of such plots. Fig. 6A illustrates that an increase in the initial solute mass causes mass removal to become more biodegradation limited (horizontal shift toward left). Also, points located further toward the upper-right of the plot correspond to greater remediation potential and therefore to a decreased sensitivity to both biodegradation and mass transfer processes. Future work is needed to more rigorously investigate which simplifications to the component process models can be justified on the basis of bioavailability limitations. Future investigations also need to better quantify the definition of “high” and “low” index values for which such simplifications are justified. Some of these concepts have been further explored through additional simulations that are presented elsewhere (Haws et al., in press). This companion paper also explores the issue of how the relative rates of biodegradation and mass transfer vary over time for selected systems, including consideration of the effects of changes in average sorbed-phase solute concentration.

<table>
<thead>
<tr>
<th>Case Study</th>
<th>Toluene (high $M_o$)</th>
<th>TCE (high $M_o$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BI</td>
<td>BI&lt;sub&gt;R&lt;/sub&gt;</td>
</tr>
<tr>
<td>T1, F — low $M_o$</td>
<td>0.039</td>
<td>0.043</td>
</tr>
<tr>
<td>T1, S — low $M_o$</td>
<td>0.138</td>
<td>0.155</td>
</tr>
<tr>
<td>T2, F — low $M_o$</td>
<td>0.014</td>
<td>0.090</td>
</tr>
<tr>
<td>T2, S — low $M_o$</td>
<td>0.050</td>
<td>0.440</td>
</tr>
<tr>
<td>T1, F — high $M_o$</td>
<td>1.81</td>
<td>1.82</td>
</tr>
<tr>
<td>T1, S — high $M_o$</td>
<td>2.87</td>
<td>2.89</td>
</tr>
<tr>
<td>T2, F — high $M_o$</td>
<td>0.66</td>
<td>0.74</td>
</tr>
<tr>
<td>T2, S — high $M_o$</td>
<td>1.05</td>
<td>1.44</td>
</tr>
</tbody>
</table>

The index BI does not account for equilibrium sorption effects on $r_{bio}$; whereas BI<sub>R</sub> does account for sorption effects and BI<sub>co</sub> includes both sorption and co-solute effects (compare Fig. 6). For all cases, the indices are computed as $r_{mt}/r_{bio}$ for time = 0 as given in the axis definition in Fig. 6.
on biodegradation rate and mass transfer, with the latter related to changes in diffusion retardation that occur as a result of sorption nonlinearity. Neither this work nor the companion paper, however, account for changes over time in concentration gradients at the mobile–immobile interface, which will affect diffusion fluxes. Such changes are highly case specific and also depend on the initial concentration distribution in the system at the onset of diffusion (Sabbah et al., 2004). Because the initial solute concentrations can rarely, if ever, be determined a priori for real systems, additional research should evaluate the degree that changes in the effective diffusion flux can have on the overall prediction of solute bioavailability.

To better evaluate the effects of equilibrium sorption on bioavailability, Fig. 6B shows the BI plot when $r_{bio}$ is computed using initial aqueous concentrations that assume equilibrium sorption to the solids in the batch reactor (as opposed to initial concentrations assuming no sorption in Fig. 6A). As expected, the impact of including sorption effects on bioavailability is most dramatic (more of a leftward shift) for points representing the Type 2 soil. Also, bioavailability points for the low $M_o$ cases ($C_o < K_s$) are more left-shifted than the high $M_o$ cases ($C_o > K_s$). The corresponding increased BI values after accounting for sorption on $r_{bio}$ are shown in Table 8 under the BI_R heading.

Co-solute effects on BI_R and the BI_R plot are evaluated for the case studies by redefining the equations for $r_{bio}$ to consider co-solutes (see x-axis labels for Fig. 6C and 6D). The impact of competitive inhibition by TCE on toluene biodegradation is reflected in the increased BI values.

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Fig. 6. Bioavailability plots for the case studies used in the numerical simulations. The points in Graph A do not consider sorption effects on $r_{bio}$, whereas, the sorption effects in $r_{bio}$ are considered in graph B. In Graphs C and D the arrows indicate the magnitude and direction of the effects of the co-solute on $r_{bio}$. In all cases, $r_{mt}$ and $r_{bio}$ are estimated for time=0 using the equations shown on the axes label. All rates are normalized to the theoretical initial aqueous concentration assuming no sorption ($C_o^* = \text{initial solute mass/volume of water}$).
in Table 8 (compare BI\textsubscript{R} and BI\textsubscript{R}^{co} columns) and the leftward pointing arrows in Fig. 6C. The BI\textsubscript{R}^{co} values for TCE (Table 8) slightly decrease and the BI\textsubscript{R}^{co} plot points for TCE (Fig. 6D) nudge to the right for most cases relative to their corresponding single solute values, reflective of a rate enhancement by toluene on TCE that is slightly greater than the competitive inhibition for these cases. Because co-solute effects were only included in the model’s biodegradation component, the presence of a co-solute only shifts the points in the BI plot horizontally, with the magnitude of the shift directly proportional to the change in the BI. If co-solute effects on \( r_{mt} \) were also considered, the points on the BI\textsubscript{R}^{co} plots might also have a vertical shift (see Fig. 1) and the BI would not necessarily be a proportional indicator of the magnitude of the changes to bioavailability caused by the presence of a co-solute.

The BI\textsubscript{R}^{co} values and the co-solute BI plots also reveal some fundamental inadequacies of a single-time bioavailability index. The BI plot computed at \( t = 0 \) suggests that the presence of toluene provides little, if any, enhancement to the biodegradation rate for TCE (Fig. 6D). The dual vs. single simulation comparisons (Fig. 5) show, however, that the overall 5-day mass removal of TCE is always enhanced in the presence of toluene and sometimes dramatically. Similarly, the dual vs. single comparisons show a much greater inhibition by TCE on toluene removal than what is indicated in the BI plot (Fig. 6C). The BI values and plotted points for \( t = 0 \) cannot show the effects of a growth substrate and cometabolite toxicity on the biomass dynamics, nor can they capture how inhibition is reduced as concentrations decrease over time. Consequently, estimations of bioavailability made from the single index values computed at \( t = 0 \) becomes increasingly unreliable at times different than that for which they were computed. Time and concentration effects on the \( r_{mt} \) component of a bioavailability index would also be expected if the numerical model used a more mechanistic representation of desorption and considered isotherm nonlinearity. Some of the temporal effects on bioavailability are more explicitly evaluated and discussed in a companion paper (Haws et al., in press). In that work, additional simulations are also used to explore modeling sensitivity to the choice of sorption, mass transfer, or biodegradation model, and bioavailability plots are used to show how bioavailability indices can change over time.

7. Implications of bioavailability for field-scale bioremediation

Understanding the bioavailability constraints at a contaminated site is an essential part in determining the effectiveness of bioremediation at the field-scale. Unfortunately, site characterization and monitoring are difficult to conduct in the specific context of trying to better identify bioavailability limitations. Nonetheless, this issue may be among the most important for understanding the ultimate potential of a remediation plan to meet the treatment objectives. With better site characterization that focuses on bioavailability constraints, it is possible to incorporate some understanding of bioavailability issues into the design and prediction of remediation and treatment processes (Stroo et al., 2000; NRC, 2003a, p. 357). For example, Harms and Bosma (1997) suggested that site remediation might often be undertaken in two steps, in accordance with expected changes in the limiting process. Initially, when the site is biodegradation rate limited, biostimulation (such as the addition of substrates and nutrients) can be used to increase the biodegradation rate of contaminants in mobile water. Then, as the contaminant removal rate begins to decrease due to mass transfer limitations, a policy of monitored natural attenuation can be implemented to evaluate pollutant removal as solutes diffuse and desorb into bioavailable regions. More generally, contaminant bioavailability will almost always need to be addressed in determining the feasibility of any remediation alternative as well as the final remediation endpoints.
For natural attenuation to be an acceptable alternative, contaminants need to be either sufficiently well sequestered (nonavailable) as to pose negligible risk or sufficiently bioavailable as to sustain a microbial population that can transform the contaminants as rapidly as they desorb, thus maintaining a steady-state or shrinking contaminant plume. As contaminants become less bioavailable to microorganisms, they will also have reduced availability to other receptors, including humans (Alexander, 2000; NRC, 2003a, p. 366). Consequently, decreased bioavailability over time is not necessarily disadvantageous to long term risk control. In fact, it can be argued that reduction in contaminant bioavailability, more than mass removal, is perhaps the more appropriate remediation goal in many circumstances (Einarson and Mackay, 2001). A better understanding between bioavailability as defined for bioremediation potential and bioavailability as defined for human health and ecosystem risks would facilitate improved regulatory procedures. For example, current site characterization regulations require vigorous extraction of compounds in both soil and water phases, without accounting for the decreased bioavailability of sorbed-phase concentrations. As a result, site remediation or natural attenuation measures may be deemed unsuccessful even though the risk to contaminant exposure has been significantly reduced (Alexander, 2000). Conversely, it is also possible that long-term slow rates of contaminant release will not be great enough to support biodegradation processes but nonetheless be of cumulative harm to environmental receptors. Clear identification of these different scenarios will be an important regulatory challenge.

8. Conclusions

Although the natural attenuation of organic compounds is mediated by microbial processes, the overall rates of contaminant removal often are limited by sorption and mass transfer. There is, therefore, a growing awareness that contaminant bioavailability, and not just the intrinsic biodegradation potential, must be addressed in order to accurately evaluate the feasibility of natural attenuation or bioremediation as remediation alternatives at a given polluted site. In order for bioavailability to be better understood, there is need for improved means of characterizing and modeling the combined effects of the bio-attenuation processes (i.e., sorption, mass transfer, biodegradation). A particular challenge in this regard is properly accounting for site complexities, including heterogeneous sorption domains, a multiplicity of particle sizes, and spatially variable microbial populations. As emphasized throughout this report, the effects of co-contamination on bioavailability also need to be more thoroughly incorporated into numerical models and site remediation plans.

A challenge with developing more sophisticated models for contaminant fate is that the models can become so highly parameterized as to be impractical for field-scale applications. Consequently, efforts to better model various component processes should also identify where simplifications are justified. As was demonstrated in the numerical case studies, model simplifications to the non-limiting processes can be justified in some cases. With appropriate site characterization techniques, it is possible that such simplifications can be made on a site-by-site basis. Before making simplifications, however, the potential effects of co-solutes on bioavailability should be considered. For example, the simulations conducted in this study showed that although slower biodegradation rates increase the inhibition effects of a nongrowth cometabolite (TCE) on the fate of the primary growth substrate (toluene), they suppress the enhancement effects of the primary substrate on the fate of the cometabolite.

Bioavailability indices are potentially useful as a practical guide for estimating the feasibility of bioremediation and targeting the process that limits contaminant removal. As shown in the
numerical simulations, bioavailability indices can also be useful in determining appropriate modeling simplifications by indicating which process is non-limiting and therefore less sensitive to a precise representation of its underlying mechanism. As with the models themselves, however, more work is needed to develop robust bioavailability indices that include more complex process representations and account for potential co-solute effects.

Numerical models and bioavailability indices will also find greater practical value for field-scale remediation when site characterization techniques and regulatory requirements are developed that more directly address remediation in the context of bioavailability. In order for this to occur, more field-scale data are needed that specifically evaluate how the various processes of sorption, mass transfer, and intrinsic biodegradation affect bioremediation efficiency under different field conditions.

There have been noteworthy accomplishments towards better quantifying, modeling, and interpreting bioavailability of organic contaminants in subsurface environments; however, there is still much uncertainty in understanding and predicting bioavailability effects and their implications at specific field sites. Moreover, additional theoretical and mechanistic complexities of contaminant bioavailability will undoubtedly continue to be uncovered, even at the laboratory scale. In this context, the objective of this paper has been to identify some of the existing issues that need to be resolved and to hopefully provide a better basis of understanding from which these on-going challenges can continue to be addressed.

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