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EVALUATING POTENTIAL EXPOSURES TO ECOLOGICAL RECEPTORS DUE TO TRANSPORT OF HYDROPHOBIC ORGANIC CONTAMINANTS IN SUBSURFACE SYSTEMS

by

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NOTICE

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ABSTRACT

The occurrence of substantial concentrations of hydrophobic organic contaminants (HOCs) such as polychlorinated biphenyls (PCBs) or dioxin in ground water presents a conundrum in that HOCs are generally immobile in subsurface systems. For systems in which there is hydraulic connection between the contaminated aquifer and downgradient surface water bodies, assessment of ecological exposure to HOCs may be required. Mechanisms that may enhance subsurface HOC migration include increases in solubility due to cosolvency with other mobile organic constituents in the plume, and the association of HOCs with mobile colloids within the aquifer. HOC transport by either mechanism can be affected by the site-contaminant source composition, the geophysical characteristics of the hydrologic system, and the dynamics of subsurface chemistry, which can affect sorption of the HOC (chemical partitioning) to mobile (e.g., colloidal) or immobile subsurface solids. This technical paper recommends several types of screening assessments to evaluate site conditions for the potential to enhance transport of HOCs, as well as site artifacts that result from inadequate well installation and sampling procedures within a ground-water monitoring network. These assessments are incorporated into a suggested three-tiered decision analysis process that provides a summarized view of the upland, contaminant source characteristics that need evaluation in order to establish if facilitated transport of HOCs may occur at a given site. The decision analysis process attempts to address all potential mechanisms that can result in HOC transport to surface water. The potential transport pathways (tiers) considered in the decision analysis process are (1) nonaqueous phase liquid (NAPL) as primary transport medium, (2) ground water as primary transport medium, and (3) mobile colloids as primary transport medium.

Visual inspection of site conditions within surface water bodies that are located along the flow path originating from upgradient source areas can support estimates of plume discharge locations based on screening evaluations of aquifer conditions. Along with subsequent examination of HOC concentrations in sediment solids and pore water from suspect locations, this preliminary site assessment provides the basis for establishing a monitoring network to map out the dimensions of the migrating plume and the zone of impact within the surface water body. Delineation of the spatial extent and magnitude of contaminant flux migrating across the GW/SW transition zone will ultimately help target approaches to estimate the extent of

bioaccumulation and/or ecological risk that more accurately capture realistic exposure scenarios for biota in the surface water body.

A process for using HOC exposure information to estimate risks to ecological receptors is summarized below. A general assumption for assessing the extent of biological uptake is that the dissolved form of the HOC is the primary source of bio-uptake for the biological receptor. Evaluation of the distribution of HOCs between the dissolved, NAPL, and/or colloidal/particulate phases, and the influence of this phase distribution on exposure/toxicity to ecological receptors, is particularly important where facilitated transport occurs. Where a complete exposure pathway exists from ground water to surface water, several methodologies may be used to estimate risks to ecological receptors:

- Compare chemical concentrations in ground water, interstitial water or overlying water to water-only toxicity values (i.e., effect concentrations) such as final chronic values (FCVs) or secondary chronic values (SCVs).

- Compare organic carbon normalized sediment concentrations to equilibrium partitioning sediment benchmarks (ESBs) derived from water-only effects concentrations and respective organic carbon-water partition coefficients.

- Compare concentrations derived through the use of chemical uptake models or bioaccumulation studies to risk-based concentrations. Chemical uptake models utilizing HOC distributions in sediments, pore water and overlying surface water may employ laboratory-derived bioconcentration factors (BCFs), field-derived bioaccumulation factors (BAFs), or biota sediment accumulation factors (BSAFs).

- Compare results from toxicity and bioaccumulation tests (in situ preferred) to those from a reference site.

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LIST OF ABBREVIATIONS

BAF	bioaccumulation factor
BCF	bioconcentration factor
BSAF	biota sediment accumulation factor
CSM	conceptual site model
DNAPL	dense nonaqueous phase liquid
DOC	dissolved organic carbon
EPA	U.S. Environmental Protection Agency
EPI	Estimation Programs Interface
ERASC	Ecological Risk Assessment Support Center
ESB	equilibrium partitioning sediment benchmark
FCV	final chronic value
GW/SW	ground-water/surface-water
HOC	hydrophobic organic contaminant
HPCD	hydroxypropyl-β-cyclodextrin
IFT	interfacial tension
IUPAC	International Union for Pure and Applied Chemistry
MTBE	methyl tert-butyl ether
NAPL	nonaqueous phase liquid
NIST	National Institute of Standards and Technology
OC	organic carbon
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
S	solubility limit
SCV	secondary chronic value
TOC	total organic carbon

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1. INTRODUCTION

The Office of Research and Development's Ecological Risk Assessment Support Center (ERASC) received a request from the Ecological Risk Assessment Forum relating to the mechanisms by which hydrophobic organic contaminants (HOCs) may transport via a ground-water pathway to downgradient media, and how these mechanisms affect exposures, bioaccumulation and toxic effects on ecological receptors. Hydrophobic organic contaminants comprise a wide array of compounds, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans, and polychlorinated dibenzo-*p*-dioxins. These contaminants commonly enter into the environment in nonaqueous phase liquids (NAPLs), or more specifically in dense nonaqueous phase liquids (DNAPLs) such as creosote, coal tar, PCB oils and chlorinated solvents (U.S. EPA, 1991a; Pankow and Cherry, 1996; Environment Agency, 2003).

Hydrophobic organic contaminants may transport through ground water via several mechanisms, including (1) direct transport as a NAPL, (2) partial dissolution into and transport as a dissolved component in ground water, and (3) enhanced transport via interaction with cosolvents or surfactants originating from contaminant source zones or mobile colloidal phases derived from contaminant sources or the native aquifer solids. In general, completion of an exposure pathway from the subsurface to surface water bodies by direct NAPL transport or NAPL dissolution into ground water will depend on the proximity of contamination to the surface water body. Detailed discussion of enhanced transport mechanisms is the focus of this document. For detailed information on the first two transport mechanisms, several comprehensive reference sources are available for review (e.g., Environment Agency, 2003; ITRC, 2003; U.S. EPA, 2009).

Sites with HOC contamination frequently show the presence of NAPLs consisting of mixtures of various organic compounds that possess a range of solubility in water. The solubility of a given HOC may increase due to interactions with comingled organic solvents that have greater water solubility. Therefore, HOC transport may increase via a cosolvency mechanism in the presence of an additional organic solvent(s) of higher aqueous solubility. Moreover, transport of HOCs may increase by partitioning to mobile (carrier) colloids in ground water, which have a high surface-area-to-volume ratio. HOCs have a tendency to "escape" the water due to their hydrophobicity (Mackay, 1991) and partition to solid-phase materials such as carrier colloids that can migrate with ground water.

The focus of this document is to provide a critical review of the current state of knowledge concerning enhanced transport mechanisms for HOC in ground water with particular emphasis on sites in which a complete pathway exists for transport from ground water to surface water. Elaboration of the role of cosolvents, surfactants and mobile colloids towards facilitating subsurface HOC transport is emphasized, including discussion of sampling and measurement approaches employed to delineate and characterize the influence of these components. Following detailed discussion of the potential mechanisms for enhanced HOC transport, we present: (1) a decision framework for assessing the potential for facilitated transport of HOCs to surface water bodies, and (2) a process for using exposure information to estimate risks to ecological receptors. In addition, the reader is directed to existing published guidance for detailed discussion of methods that may be employed to assess exposure and risk to ecological receptors (e.g., U.S. EPA, 1997, 2002a, 2002b, 2002c, 2008).

2. GENERALIZED CONCEPTUAL SITE MODEL

Developing the framework for evaluating potential downgradient exposures from subsurface release of HOCs into ground water depends on understanding the mass transport processes that control HOC migration from source to receptor (Environment Agency, 2003). Transport processes may vary depending on the specific nature of HOCs, the hydrogeological and biogeological characteristics of the site, and the physical characteristics and age of the contaminant release. Consequently, it is important to develop a conceptual site model (CSM) based on site-specific characterization data that describe the dominant transport processes as accurately as possible.

In general, CSMs begin with the consideration of one or more fluid phases, such as water, air, or NAPL, within the void space of an assumed immobile solid porous matrix. There are situations where it may be inappropriate to assume an immobile solid porous matrix, and, as will be discussed later, mobile solids may serve as an important vector for HOC transport. These mobile solids may originate from the immobile porous matrix, or they may derive from upgradient sources and, thus, represent a special component of the transported fluid. Transport processes associated with each fluid may include advection, diffusion, and dispersion. For source areas in close proximity to a surface water body, advective transport of the NAPL may represent the predominant HOC transport process. Chemical processes that influence HOC-phase partitioning may also be important and may include dissolution, volatilization, and sorption. These transport and partitioning processes may in turn be linked to abiotic and biotic degradation processes, both from the standpoint of contaminant loss (i.e., degradation of a parent compound) and contaminant gain (i.e., production of a daughter product in those cases where the daughter product is also a contaminant of concern). Finally, subsurface contaminant transport may lead to contamination of overbank soils/sediments susceptible to physical erosion into the surface water body under the influence of heavy rain events or daily tidal fluctuations.

Given the nature of HOC contamination sites, it is likely that the subsurface distribution of HOC mass will initially be controlled by subsurface NAPL migration and partitioning between NAPL and ground water. In general, introduction of HOCs to the subsurface will result from a surface release (or near-surface release for underground storage tanks) followed by gravity-induced infiltration through the unsaturated zone and, potentially, into saturated portions of an unconsolidated or underlying consolidated aquifer. The migration and ultimate distribution of NAPL is important not only because it is a contaminant itself, but also because it may act as a carrier for other HOC contaminants (e.g., Han et al., 2008; Serralde et al., 2008; Weber et al., 2008). Factors that impact the movement and distribution of NAPL in the subsurface include fluid properties such as interfacial tension, density, and viscosity; porous media properties such as permeability and grain-size distribution; and fluid/porous media properties such as wettability and capillary pressure (e.g., Mercer and Cohen, 1990; U.S. EPA, 1991a; Pankow and Cherry, 1996). Moreover, these factors may change with time due to other NAPL component properties such as volatility and solubility (e.g., Roy et al., 2002).

It is also important to recognize that NAPL migration may proceed for a long time after release into the subsurface. For example, Gerhard et al. (2007) investigated the time to reach stable distributions for six different DNAPLs, and reported a strong relationship to DNAPL density, DNAPL viscosity, and the aquifer permeability. Low density, high viscosity DNAPLs (e.g., PCB and coal tar) were reported to take two or more orders of magnitude longer to reach stable distributions compared to high density, low viscosity DNAPLs (e.g., chlorinated solvents). Results from their simulations, based on an unconsolidated aquifer with fine- to medium-grained sand of moderate heterogeneity, indicated that it would require more than 100 years for a 20-drum release of coal tar to reach a steady-state mass distribution. Jackson et al. (2006) also reported long-term migration associated with coal tars and creosotes.

Ultimately, NAPL released into the subsurface will become trapped either in the pore space at residual saturations or as "pools" of higher saturation above capillary barriers. In either case, trapped NAPL may remobilize under certain conditions, which may constitute facilitated transport if the NAPL contains HOCs. Pennell et al. (1996) and Li et al. (2007) introduced and tested a dimensionless number, called the total trapping number, to characterize the potential for tetrachloroethylene mobilization based on the balance between capillary, aqueous viscous, and gravity forces at the pore scale. A NAPL becomes trapped in porous media when capillary forces are sufficiently large to inhibit displacement by aqueous viscous or gravity forces. Facilitated transport through the remobilization of trapped NAPL may therefore occur if conditions are imposed to disrupt the force balance. Examples include an increase in the aqueous viscous force due to increased ground-water velocity or reductions in the capillary forces due to reductions in interfacial tension. Changes in interfacial tension may result from codisposal of waste material or subsequent disposal of waste material (e.g., Moody and Field, 2000; Hsu and Demond, 2007; Nellis et al., 2009). Partitioning of dissolved phase contaminants from up-stream contaminant sources into downgradient trapped NAPL may also result in mobilization (Serralde et al., 2008). Moreover, dissolution of components from a multicomponent DNAPL may produce changes in the DNAPL properties that result in remobilization (Roy et al., 2002; Roy et al., 2004; Birak and Miller, 2009).

Other factors that may promote mobilization of trapped NAPL include a reduction in NAPL viscosity due to seasonal variability in temperature (McLinn and Stolzenburg, 2009), at least for locations adjacent to surface water bodies. Finally, under certain conditions, the ebullition of gas bubbles may promote the upward migration of NAPL. For example, McLinn and Stolzenburg (2009) reported that the upward migration of methane and carbon dioxide, produced from anaerobic biodegradation, entrained coal tar and facilitated its transport from sediment to surface water.

To illustrate the complexity of characteristics such as site hydrogeology and plume architecture, a hypothetical CSM is illustrated in Figure 1. For this particular scenario, the NAPL containing HOCs has penetrated into both the saturated, unconsolidated aquifer, as well as the underlying consolidated, fractured bedrock aquifer. In both aquifer types, the contaminant is present in both the NAPL and as a dissolved component in ground water. Potential exposure pathways for HOC transport are illustrated, including human health receptors that may ingest ground water from either the unconsolidated or consolidated portions of the subsurface system, or ecological receptors that may occur in aquatic habitats that can intercept contaminated ground water as it discharges to surface water (U.S. EPA, 2008). For sites underlain by fractured bedrock systems, transport of HOCs associated with the NAPL through the fracture network may provide a focused pathway for transport to surface water or to shallow unconsolidated sediments underlying the surface water body (e.g., Cho et al., 2008; Banks et al., 2009).

The potential phase distribution of the NAPL-HOC mixture in both the unsaturated and saturated zones of the subsurface is illustrated in detail in Figure 2. Due to the hydrophobic nature of the NAPL-HOC mixture, the contaminant may exist as a separate liquid phase within the sediment interstitial (pore) space or a fraction of the mass may partition into air, water or solid surfaces. Fundamental parameters that are often used to make initial assessments of partitioning behavior into the water, air or solid surfaces are the HOC solubility, Henry's law constant, and the octanol-water partitioning coefficient, respectively. Sorption to solid surfaces will involve a distribution of particle sizes, including colloidal-sized particles that may be susceptible to mobilization at the velocities of ground-water flow. Due to the viscosity and density of typical NAPLs with which HOCs are associated, horizontal transport over large distances is generally not anticipated to be a primary mechanism for HOC transport. Once in the ground water, the primary mechanisms for HOC transport are advection and mechanical dispersion, the former resulting from the bulk ground-water motion, and the latter resulting from heterogeneities in the flow field on various scales. In addition, in some circumstances, HOC dissolved-phased transport in media with low hydraulic conductivity may be dominated by diffusion (e.g., Vulava et al., 2007; Chapman and Parker, 2005). Many HOCs exhibit strong partitioning behavior to solids because of their hydrophobic nature, and, in the case of an immobile solid matrix, this can result in significant retardation of the HOC relative to the flowing ground water. However, the extent of retardation may be reduced by two primary mechanisms that enhance partitioning into flowing ground water: increased aqueous solubility of the HOCs due to the presence of organic cosolvents with greater aqueous solubility, and/or the mobilization of colloidal solids to which the HOC is attached.

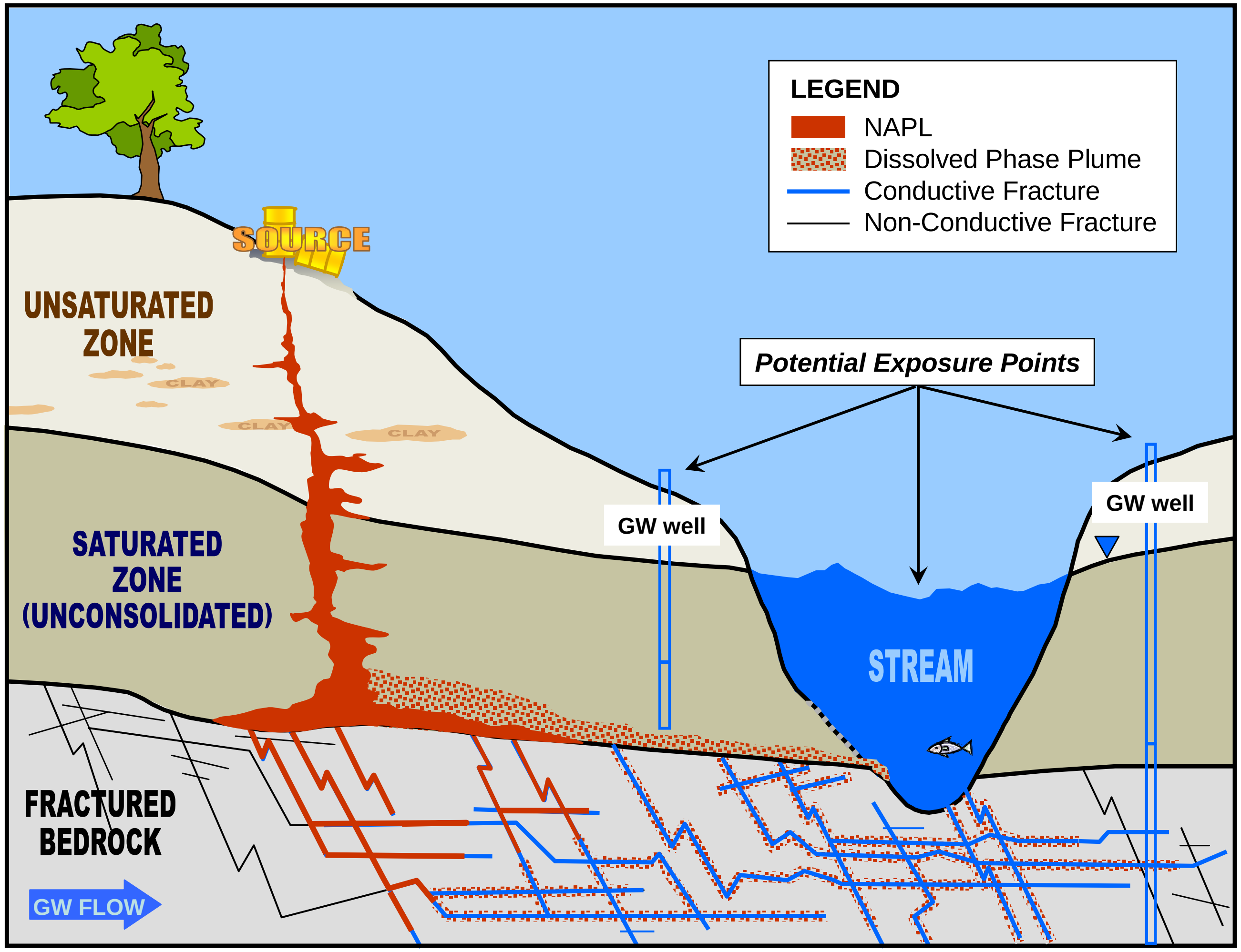

Figure 1. Generalized Conceptual Site Model (CSM) with Nonaqueous Phase Liquid (NAPL) Release into the Subsurface. For this depiction, the contaminant plume is distributed across the unsaturated zone, the saturated unconsolidated aquifer and an underlying fractured bedrock aquifer. The contaminant(s) is present as both NAPL and dissolved fractions within groundwater. The unconsolidated (alluvial) and bedrock aquifers are partially incised by a river, which receives a portion of its flow from ground-water discharge.

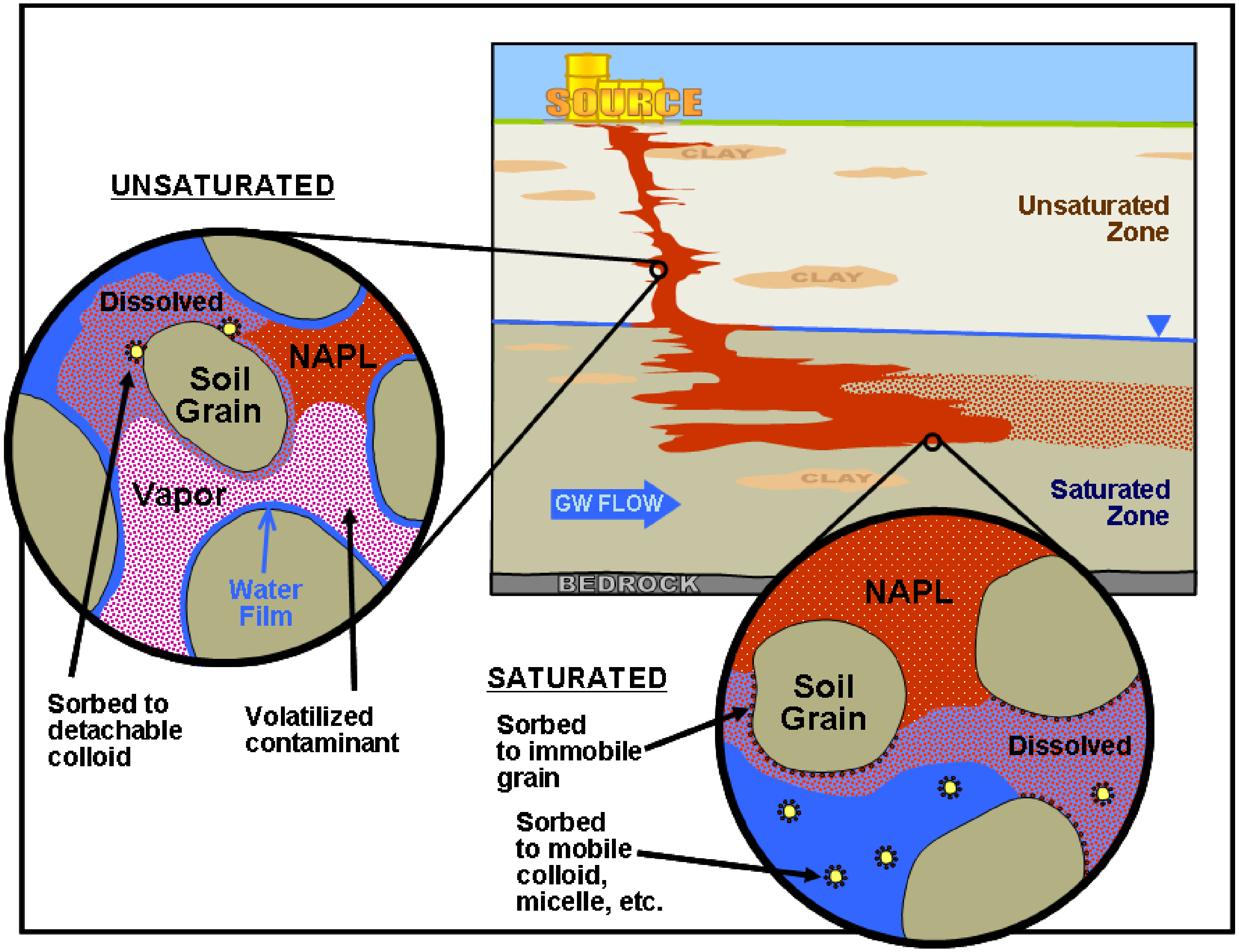

Figure 2. Depiction of the Distribution of Contaminant(s) within the Pore Space of the Unsaturated and Saturated Zones of an Unconsolidated Aquifer. For the two zones, contaminant partitions between nonaqueous phase liquid **(**NAPL**)**, aquifer/soil solid surfaces (including attached or mobile colloidal material), water and vapor (unsaturated zone). Contaminant movement will be influenced by gravity flow of NAPL, in addition to episodic and/or continuous water flux. Colloid transport will be governed by physical shear stresses from water movement and perturbations to ground-water chemistry that influence partitioning to immobile subsurface solids.

3. FACILITATED TRANSPORT OF HOCS

The occurrence of substantial concentrations of HOCs such as PCBs or dioxin in ground water presents a conundrum in that HOCs are thought to be relatively immobile due to partitioning onto soil or aquifer solids. Two predominant factors that contribute to enhanced HOC mobility include (1) increased partitioning of the HOC into the mobile aqueous phase or (2) mobilization of fine-grained particles from the aquifer matrix and/or natural organic molecules to which the HOC is partitioned. For the latter mechanism, the mobile solids are commonly referred to as "colloids." The following discussion provides the technical basis for these processes in contaminant plumes, provides context for conditions under which these mechanisms might be active, and outlines site characterization strategies that may be employed to determine the impact of these processes at a given site.

3.1. CONTAMINANT SOLUBILITY—SINGLE COMPONENT SYSTEMS

Aqueous solubility is a fundamentally important characteristic for assessing the fate and transport of contaminants in ground water or surface water. The aqueous solubility limit (S) refers to the equilibrium partitioning relationship of a compound between water and the pure compound, either in liquid or solid phase, or between water and a gaseous phase in which the compound resides at its equilibrium vapor pressure. In most cases, contaminants, when present in the aqueous environment, are at concentrations less than S, and consequently, S may be viewed as the maximum expected concentration of the contaminant in the environment. However, there are cases where contaminant concentrations may reach S, as for example, when single-component NAPL contaminants are released into the environment. If water is in close contact with the NAPL for sufficient durations, the aqueous concentration of the contaminant may reach values of S. Moreover, there are circumstances whereby aqueous concentrations may exceed S, in particular, due to the presence of a cosolvent in the aqueous phase as will be discussed further in the following sections. In general, facilitated transport includes those circumstances whereby contaminant concentrations exceed S.

Before proceeding, it is useful to note that S is a function of other environmental factors, namely temperature and dissolved inorganic salt concentrations (Schwarzenbach et al., 2003). Solubility increases nonlinearly with temperature for some compounds, while for others it is a convex function of temperature (i.e., *S* decreases to a minimum and then increases). However, given that ground-water temperatures vary little on an annual basis, changes in *S* due to changes in ground-water temperature are typically insignificant. Changes in surface-water temperature, however, may be more significant. If significant changes in temperature occur as ground water discharges to surface water, changes in *S* as a function of temperature may need to be considered depending on the contaminants in question and the extent of temperature variation. Inorganic salts may nonlinearly decrease values of *S* (i.e., salting-out effect). This effect, however, would most likely not be of concern except in coastal regions.

Values of *S* for contaminants of interest are typically obtained from published literature, and examples of references that have compiled *S* data include Verschueren (2001), Mackay et al. (1992), and Schwarzenbach et al. (2003). Online resources that may be helpful for obtaining solubility data include the Estimation Programs Interface (EPI) Suite™, which is a software package for screening-level evaluations of chemical properties and environmental fate developed by the EPA's Office of Pollution Prevention and Toxics and Syracuse Research Corporation (http://www.epa.gov/opptintr/exposure/pubs/episuite.htm); the International Union for Pure and Applied Chemistry (IUPAC)-National Institute of Standards and Technology (NIST) Solubility Database, which is an online database containing solubility data originally published in the IUPAC-NIST Solubility Data Series (http://srdata.nist.gov/solubility/intro.aspx); and Sparc Performs Automated Reasoning in Chemistry (SPARC), which calculates physical and chemical properties of contaminants based on their molecular structure and basic information about the environment, developed jointly by the EPA and the University of Georgia (http://archemcalc.com/). Additional databases and online calculators for chemical properties are available via a website maintained by the EPA (http://www.epa.gov/athens/learn2model/part-two/onsite/). As an illustration of the large range over which *S* may extend, Figure 3 summarizes *S* values for a variety of HOCs that may be found in ground water.

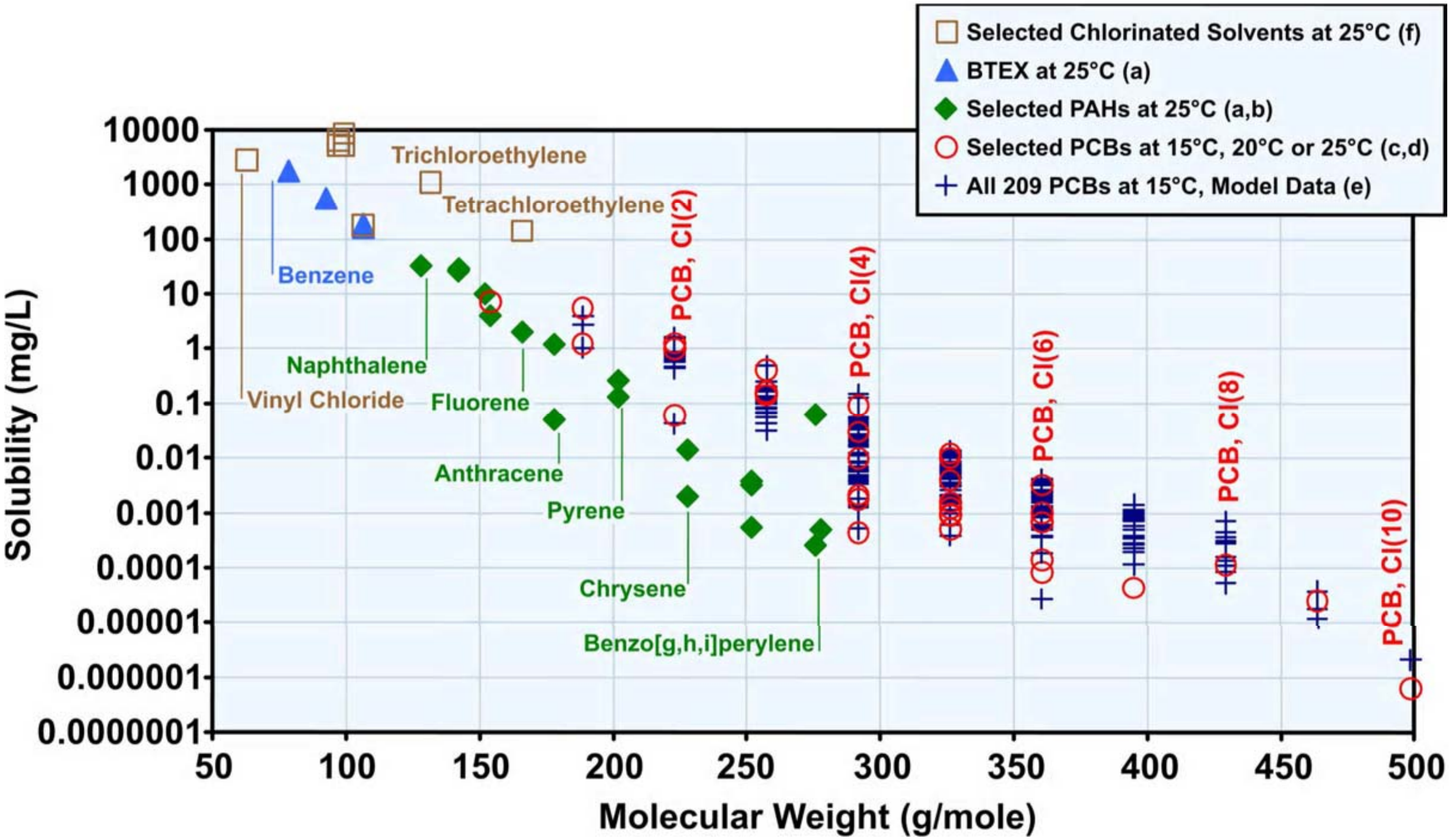

Figure 3. Aqueous Solubility Plotted as a Function of Molecular Weight for Selected Contaminants. Shown are selected chlorinated solvents at 25°C (open squares); benzene, toluene, and xylene (BTEX) isomers at 25°C (solid blue triangles); selected PAHs at 25°C (solid green diamonds); selected PCBs at 15, 20 or 25°C (open red circles) and all 209 PCB congeners at 15°C based on thermodynamic considerations (blue crosses).

Sources: (a) Peters et al., 1999; (b) D'Affonseca et al., 2008; (c) Dickhut et al., 1986; (d) Huang and Hong, 2002; (e) Paasivirta and Sinkkonen, 2009; (f) Schwarzenbach et al., 2003.

3.2. CONTAMINANT SOLUBILITY—MULTICOMPONENT SYSTEMS

In contrast to aqueous dissolution from single-component NAPLs, aqueous dissolution of compounds from multicomponent NAPLs, such as fuels, coal tar or Aroclor mixtures, is a more complex process (Brusseau, 1993). At equilibrium, the chemical potential of each solute is uniform among all phases. However, since the NAPL consists of multiple components, the equilibrium aqueous concentration of any given compound will be less than *S*. Being able to estimate the equilibrium solubility of the i^{th} solute dissolving from a NAPL mixture is important in the evaluation of facilitated transport mechanisms, and estimation methods can, in general, be divided into theoretical and empirical approaches. Described below is the most common theoretical approach (i.e., Raoult's law), a common empirical approach, and a relatively new and improved theoretical approach.

One of the most commonly used expressions to describe equilibrium dissolution from multicomponent NAPLs is Raoult's law (Banerjee, 1984). Using Raoult's law convention, the aqueous concentration of the i^{th} solute (C_i, molL^{-3}) in equilibrium with the NAPL mixture can be expressed as

$$C_i = x_i S_i \qquad \text{(eq 1)}$$

where x_i is the mole fraction [−] of the i^{th} solute in the organic phase, and S_i [molL^{-3}] is the aqueous solubility limit of the i^{th} solute (in the absence of other solutes). Raoult's law is derived from the equilibrium relationship that states the thermodynamic activity of each solute in both solvents is equal (Cline et al., 1991). Three assumptions are then made: the mole fraction of water in the organic phase can be neglected, the activity coefficient of the i^{th} solute in water with all solutes is the same as that if the i^{th} solute was the only one present (i.e., ideal aqueous mixture), and the activity coefficient of the solute in the organic phase is equal to unity (i.e., ideal organic mixture). The last assumption is most often investigated when considering nonideal behavior. If the components of the NAPL have a similar chemical structure, the activity coefficient is close to unity (Banerjee, 1984; Lesage and Brown, 1994; Broholm and Feenstra, 1995), and, consequently, the organic mixture can be considered ideal. Cline et al. (1991) found the activity coefficient for a variety of fuels to range between 1.3 and 1.5. They also described Raoult's law in terms of a NAPL:water partition coefficient (K_i) for the i^{th} solute as

$$K_i = \frac{C_i^N}{C_i} = \frac{C_i^N}{x_i S_i} = \frac{\rho}{S_i MW} \qquad \text{(eq 2)}$$

where C_i^N [molL^{-1}] is the concentration of the i^{th} solute in the NAPL, ρ is the NAPL density [ML^{-3}], and *MW* is the average NAPL molecular weight [Mmol^{-1}]. This equation can be used to estimate the partitioning of the i^{th} solute between water and the NAPL mixture using parameters (ρ, *MW*, and S_i) obtained from manufacturer's information (e.g., of a particular fuel), by measurement, or through the literature.

Raoult's law has been used in a number of cases to describe partitioning behavior between NAPL mixtures and water. For example, it has been used to describe partitioning between PCB NAPLs (i.e., Aroclors) and water (Luthy et al., 1997; Ghosh et al., 1998), gasoline and water (Cline et al., 1991; Reckhorn et al., 2001), diesel fuel and water (Lee et al., 1992a), coal tar and water (Lee et al., 1992b; King and Barker, 1999; D'Affonseca et al., 2008; Fraser et al., 2008), and chlorinated solvents and water (Broholm and Feenstra, 1995; Broholm et al., 2005). In the case of coal tars, reasonable agreement between measurements and estimates based on Raoult's law has been reported, with the difference between the two ranging from factors of 2 to 4 (Lee et al., 1992a,b; King and Barker, 1999). Others, however, have noted order-of magnitude-differences (Lane and Loehr, 1995). Mahjoub et al. (2000) reported that Raoult's law was not appropriate to describe dissolution from coal tars in the experiments they conducted and noted that the equilibrium relationship was not applicable because of kinetic limitations in mass transfer resulting from diffusional transport of the solute in the NAPL. In addition, a film was noted to form at the water/coal tar interface, and they suggested that the film resulted from the loss of the more soluble components at the interface leaving a localized area of less soluble, more viscous compounds. This, in turn, then created additional kinetic limitations in mass transfer by limiting the rate of solute diffusion across the interface.

Several alternative methods have been used to estimate equilibrium partitioning between multicomponent NAPLs and water. Recently, polyparameter linear free energy relationships have been introduced as an improved means to estimate equilibrium partitioning between complex NAPLs and water (Goss and Schwarzenbach, 2001; Endo and Schmidt, 2006). Polyparameter linear free energy relationships are an extension of single-parameter linear free energy relationships wherein partitioning of a solute in one two-phase system is related to the partitioning of the solute in another two-phase system. For example, partitioning of a solute between a given fuel and water may be related to the partitioning of the solute between octanol and water using the relationship $\log K_{f/w} = \beta \log K_{ow} + \alpha$, where α and β are empirical constants, and K_{ow} is the octanol-water partitioning coefficient. The underlying theory for this approach is that the free energy associated with solute partitioning in one system (e.g., octanol-water) is linearly related to the free energy in the other system (e.g., fuel-water). A limitation of this approach is that the empirical constants are only applicable to solutes of similar structure, and different empirical constants are needed for structurally different classes of solutes. In contrast, polyparameter linear free energy relationships are based on a more mechanistic description of the intermolecular interactions that result in partitioning, and are therefore more broadly applicable to a range of solutes, solvents, and sorbents. As an illustration, Endo and Schmidt (2006) noted the general form of a polyparameter linear free energy relationship describing the partitioning of a solute between a solvent j and water:

$$\log K_{j/w} = c + eE + sS + aA + bB + vV \qquad \text{(eq 3)}$$

where E, S, A, B and V are Abraham's solute descriptors and denote different intermolecular interaction mechanisms associated with the solute, and c, e, s, a, b and v denote the solvent's role in the corresponding interaction mechanisms. A detailed discussion of the intermolecular interaction mechanisms is provided by Goss and Schwarzenbach (2001) and Endo and Schmidt (2006). Arey and Gschwend (2005) used this approach to describe partitioning between fuels and water, and Endo and Schmidt (2006) used this approach to describe partitioning between complex NAPLs (fuels, coal tar, and creosote) and water. In general, this approach provides an improved means to estimate partitioning coefficients; however, it requires information to define both the solute and solvent/sorbent parameters.

3.3. COSOLVENT TRANSPORT

At sites where a mixture of contaminants has been released, either concurrently or sequentially, the transport of contaminants may be significantly different from the fate and transport processes of a single contaminant in the environment. In particular, if one or more of the components in the contaminant source act as a cosolvent, then the concentration of the HOC contaminant in the solvent mixture may exceed its aqueous solubility for a situation in which water was the only solvent phase. For example, Zemanek et al. (1997) investigated PAH partitioning behavior in soils collected from petroleum and creosote contaminated sites. Concentrations for several PAH compounds exceeded pure aqueous solubility limits by factors ranging up to ~50 for the more hydrophobic compounds. It was suggested that soluble phenolic and heterocyclic compounds that make up ~15% weight per weight of the creosote may have acted as cosolvents, and that this, along with colloidal interactions, may have resulted in the enhanced concentrations. In general, a cosolvent can be thought of as an agent that reduces the polar nature of water, thereby enhancing the dissolution of nonpolar compounds into the mixture. Cosolvents can be either completely miscible in water (such as methanol), or they can be partially miscible in water (such as *n*-octanol). To help differentiate these cases, adopted herein is the convention used in EPA (1991b) in which mixtures of water and completely miscible solvents are called mixed solvents, and mixtures of water and partially miscible cosolvents are multiphasic solvents.

While the main topic herein addresses mixed solvents, a few comments regarding multiphasic solvents are important to note. First, it may be difficult to distinguish between dissolved contaminant concentrations and total sample concentrations (i.e., dissolved plus the concentration associated with the NAPL). While the latter may represent a form of facilitated transport (e.g., emulsified NAPL), it may also be the result of sampling artifacts (e.g., Zemo, 2006). Second, it is important to note that a multiphase system may not necessarily result in HOC solubility enhancement. Coyle et al. (1997) reported a reduction in HOC (biphenyl, 2,2',4,4'-tetrachlorobiphenyl, and 2,2',4,4',5,5'-hexachlorobiphenyl) solubility in the presence of multiphase solvents (methylene chloride and chloroform). The solubility reduction was noted to increase for increasing multiphase solvent concentration and for increasing HOC hydrophobicity. It was suggested that the HOC solubility reduction was due to a salting-out effect, whereby water molecules were prevented from associating with HOCs because of association with the multiphase solvent. Finally, it is important to recognize that NAPLs may represent a separate solvent phase (hence multiphasic) into which contaminants may partition (e.g., Luthy et al., 1997; Russold et al., 2006). This is a somewhat different perspective from how NAPLs are typically viewed, wherein NAPLs are considered as the contaminant themselves. However, NAPLs are hydrophobic in nature and, therefore, may act as a solvent to other hydrophobic contaminants. If the NAPL is mobile, then it may facilitate the transport of the hydrophobic contaminants for which it is a solvent (e.g., Han et al., 2008; Serralde et al., 2008; Weber et al., 2008). Moreover, if the NAPL is more soluble or degrades more quickly than the hydrophobic contaminant, then the latter's mole fraction in the NAPL will increase with time, which could result in increases in its aqueous concentration as well (e.g., McNamara et al., 2005).

3.3.1. Mathematical Descriptions of Cosolvency

The solubility of an organic contaminant in a solvent mixture (S_m, ML^{-3}) consisting of water and another solvent (cosolvent) has been described by Morris et al. (1988) using a log-linear function:

$$\log S_m = \log S + f\sigma \tag{eq 4a}$$

or, for solvent mixtures with N cosolvents ($N > 1$):

$$\log S_m = \log S + \sum_{i=1}^{N} f_i \sigma_i \tag{eq 4b}$$

where f_i is the i^{th} cosolvent volumetric fraction [−] and σ_i is a dimensionless constant for the i^{th} cosolvent, equal to the ratio of the solute solubility in the pure i^{th} solvent (S_i^c) and water:

$$\sigma_i = \log\left(\frac{S_i^c}{S}\right) \tag{eq 5}$$

The term σ has been called the cosolvency power (Pinal et al., 1990), and can be calculated using equation 5 and published compilations of solubility data (e.g., Verschueren, 2001). When solubility data for the compound of interest is not available, it is sometimes possible to estimate the cosolvency power based on K_{ow} of the solute (Morris et al., 1988) using

$$\sigma = a \log K_{ow} + b \qquad \text{(eq 6)}$$

where a and b are empirical constants. Figure 4 illustrates the solubility enhancement, defined as the ratio of solubility with cosolvent to aqueous solubility, resulting from a cosolvent using equation 4a. Cosolvency powers were selected to range from 3 to 7 based on published data (Morris et al., 1988; Pinal et al., 1990; Chen and Delfino, 1997).

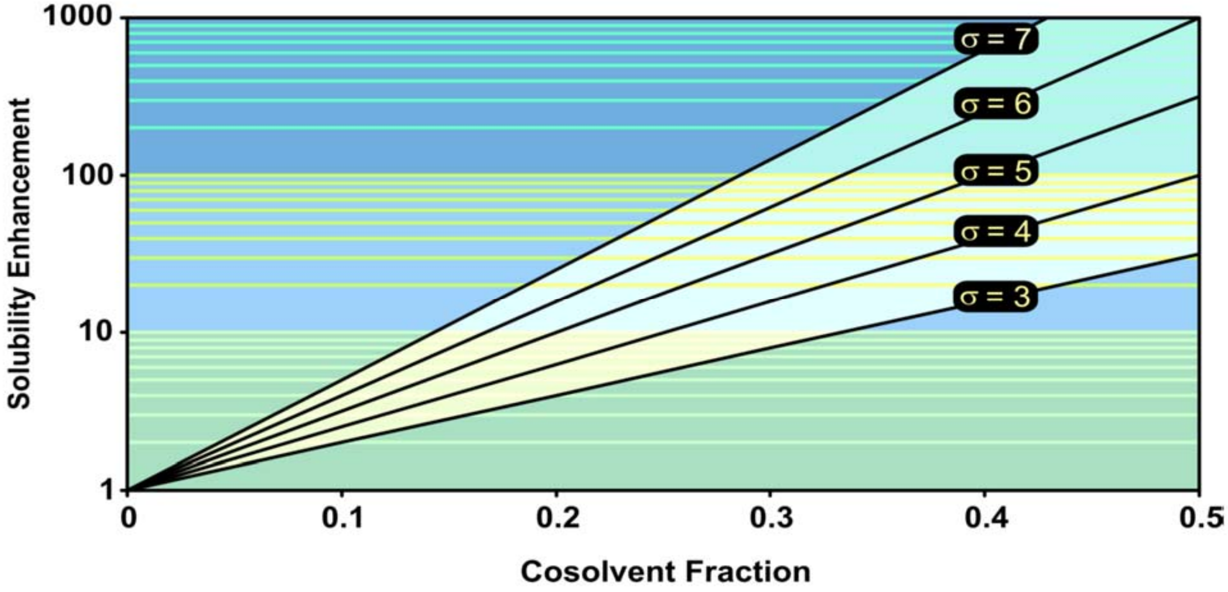

Figure 4. Solubility Enhancement, Defined as the Ratio of Solubility with Cosolvent to Aqueous Solubility, Plotted as a Function of the Cosolvent Fraction Using the Log-Linear Cosolvency Model (equation 4a). Cosolvency powers were selected to range from 3 to 7 based on published data.

Sources: Morris et al. (1988), Pinal et al. (1990), Chen and Delfino (1997).

In general, the projections shown in Figure 4 illustrate that, for cosolvents commonly encountered in contaminant plumes, significant solubility enhancement (e.g., greater than a factor of 2) would require a cosolvent volume fraction of 0.05 or greater. The utility of this mathematical calculation for site evaluation is currently limited by the lack of data on either cosolvent fraction(s) or cosolvency power for mixtures commonly encountered in HOC contaminant plumes. In response to this data gap, discussion is provided below for alternative approaches to evaluate the potential influence of cosolvent interactions on HOC transport employing measurements of total organic carbon (TOC) in ground water and/or measurement of the surface tension of ground-water samples collected along relevant transport pathways.

3.3.2. Cosolvency and Reduced Sorption

Because cosolvents reduce the polar nature of water, a cosolvent would likewise reduce the hydrophobic-induced attraction between contaminants and sorption sites associated with the porous media. Reductions in the extent of sorption produce more mobile contaminants, which, therefore, represents another facilitated transport mechanism. Similar to the log-linear model for the relationship between cosolvency and solubility, a log-linear model has been used to describe the relationship between sorption and cosolvency, although in this case, there is an inverse relationship between sorption and the cosolvent fraction (Rao et al., 1985; Rao et al., 1990; Wood et al., 1990; Brusseau et al., 1991; U.S. EPA, 1991b; Bouchard, 1998; Krauss and Wilcke, 2001; Chen et al., 2008). Given the linear relationship between contaminant retardation R and the equilibrium sorption coefficient K [L^3M^{-1}] (i.e., $R = 1 + \rho K/\theta$, where ρ and θ are the soil bulk density [ML^{-3}] and liquid phase content, respectively), a log-linear relationship between the equilibrium sorption coefficient and the cosolvent fraction results in a log-linear relationship between retardation and the cosolvent fraction. In general, a log-linear relationship between sorption and cosolvent fraction ignores interactions between the cosolvent and the porous media (Rao et al., 1990). Given the experimental evidence for the log-linear relationship, however, the significance of this interaction is considered minimal.

3.3.3. Oxygenated and Alternative Fuels

One scenario, in particular, that has been investigated for its potential to induce facilitated transport by cosolvency is the release of oxygenated fuels or alternative fuels (Cline et al., 1991;

Chen and Delfino, 1997; Powers et al., 2001; Reckhorn et al., 2001; Corseuil et al., 2004; Chen et al., 2005). Over the last 30 years, oxygenates consisting either of alcohols (e.g., methanol, ethanol, tert-butyl alcohol) or ethers (e.g., methyl tert-butyl ether [MTBE], tert-amyl methyl ether, ethyl tert-butyl ether) have been added to fuel to increase the octane rating and/or reduce air pollution. More recently, ethanol, and to a lesser extent methanol, have been considered as alternative fuel sources to help alleviate demand for petroleum-based fuels. By far, the three compounds most studied for their potential to act as fuel-related cosolvents are methanol, ethanol, and MTBE. Methanol and ethanol are completely miscible in water, and MTBE has a very high aqueous solubility (>40,000 mg/L); moreover, they each may have significant cosolvent effects if present in sufficient quantities. Chen and Delfino (1997) investigated the cosolvency effect of fuel-related methanol, ethanol and MTBE on 18 PAH compounds ranging from naphthalene (molecular weight of 128 g/mole and log K_{ow} of ~3.4) to benzo[ghi]perylene (molecular weight of 276 g/mole and log K_{ow} of ~7.1). Methanol cosolvency powers ranged from 3.72 for naphthalene to 6.90 for benzo[ghi]perylene; ethanol cosolvency powers ranged from 3.99 for naphthalene to 7.08 for benzo[ghi]perylene; and MTBE cosolvency powers ranged from 4.06 for naphthalene to 7.09 for benzo[ghi]perylene. These results highlighted the greater impact that a cosolvent has on solutes with greater hydrophobicity.

However, even though a cosolvent may have the ability to significantly enhance the dissolution of a given HOC (i.e., large cosolvency power), its presence in the NAPL plume may not necessarily result in enhanced dissolution if its concentration is not sufficiently high (Brusseau, 1993). As a point of reference, typical remediation efforts that are based on enhanced dissolution due to ethanol cosolvency employ flushing solutions with ethanol concentrations on the order of ~70% by volume or more (Jawitz et al., 2000; Brooks et al., 2004). Research has demonstrated the limited influence of MTBE (Cline et al., 1991; Chen and Delfino, 1997) or ethanol (Corseuil et al., 2000; Powers et al., 2001; Reckhorn et al., 2001; Corseuil et al., 2004) to induce significant cosolvent effects on organic cocontaminants because if insufficient quantities in the fuel mixtures (i.e., MTBE <15% and methanol <20% by volume). For contaminant plumes with a finite mass/volume, the influence of the water-soluble cosolvent would diminish in time and spatial extent with dilution in ground water.

3.3.4. Screening Evaluation of Cosolvent Facilitated Transport

Mackay and Gschwend (2001) and Rawson et al. (2002) describe the use of TOC and air-ground-water interfacial tension (IFT) measurements to assess facilitated transport mechanisms. These measurements are relatively easy to complete and should be useful in screening evaluations of facilitated transport mechanisms. As discussed above, cosolvents such as methanol, ethanol, or MTBE have to be present in sufficient quantities to significantly enhance solute solubility. Typically, this is in the percentage concentration range, which would result in TOC concentrations much greater than 10,000 mg/L. Consequently, a screening-level assessment for facilitated transport by cosolvents could be conducted by an evaluation of TOC samples. Figure 5 provides an illustration of solubility enhancements as reported in the literature plotted as a function of TOC associated with various cosolvents (i.e., methanol, ethanol, and MTBE). Also shown for comparison are solubility enhancements resulting from cyclodextrin and humic acid. Cyclodextrin has been investigated as a remedial agent to enhance HOC solubility in water through a 1:1 inclusion complex (Brusseau et al., 1994) rather than influencing the polarity of water as a cosolvent. Likewise, humic acid does not enhance solubility through a cosolvent action but through the formation of an HOC-humic acid complex. As indicated in the figure, the amount of agent needed to enhance solubility as measured by TOC concentrations, decreases as the hydrophobicity of the HOC increases. Hydrophobicity of a particular HOC may be assessed through its octanol-water partitioning coefficient, and the insert graphic in Figure 5 shows HOC octanol-water partitioning coefficients as a function of molecular weight. Consequently, it is important to note that while elevated TOC concentrations may suggest facilitated transport conditions, highly hydrophobic HOCs may become mobile at TOC concentrations that are not elevated.

Surface tension measurements may also provide a screening level assessment about the likelihood of facilitated transport. Corey (1990) reported that water in natural porous media often has a $\sigma \cos \alpha$ (where σ is surface tension and α is the contact angle) value of ~60 dynes/cm. Assuming a contact angle of zero, a typical range for the surface tension of unimpacted ground water may be 60 dynes/cm or larger. For example, air-ground-water surface tension measurements at a coal tar impacted site were reported as 70.6 ± 3 dynes/cm by Mackay and Gschwend (2001) and were reported to be similar to pure water (~72 dynes/cm) at a PCB-impacted site by Rawson et al. (2002). However, cosolvents present in large concentrations in the subsurface environment would not only result in large TOC concentrations, but they would also reduce surface tension to values significantly less than 60 dynes/cm. Surface tension measurements for various concentrations of methanol and ethanol are shown in Figure 6, and indicate that the surface tension drops below 60 dynes/cm once the alcohol concentration exceeds 100,000 mg/L (equivalent to 20,000−40,000 mg/L TOC). ***Consequently, high TOC concentrations (>10,000 mg/L) and reduced surface tension values would be strong indications of the potential for facilitated transport due to the presence of a cosolvent.***

Reduced surface tension may also result from the presence of surfactants, and, therefore, suggest another facilitated transport mechanism. At sufficient concentrations, surfactants form micelles, which have hydrophobic interiors, and, therefore, provide a structure for the facilitated transport of HOCs. Moreover, surfactants may influence HOC sorption characteristics; however, unlike cosolvents, surfactants may enhance HOC sorption by sorbing themselves and effectively increasing the organic carbon (OC) content of the solid matrix (e.g., Edwards et al., 1994). While use of surfactants in subsurface remediation applications has been investigated, the presence of surfactants as a codisposed waste and subsequent agent in facilitated transport is not commonly reported (Grant et al., 2011). Nonetheless, given their potential to impact HOC transport, initial formulations of the CSM should assess the presence of surfactants and their potential to facilitate transport.

Surfactants at sufficient concentrations to produce micelles may also result in reduced surface tension and/or the formation of an emulsion. For example, Kanga et al. (1997) investigated the ability of a glycolipid biosurfactant to enhance the solubility of selected PAH compounds and compared results to the synthetic surfactant Tween-80. For both the biosurfactant and synthetic surfactant, at sufficient concentrations to form micelles, the IFT was reduced to ~30 dynes/cm. Unlike cosolvents, however, TOC concentrations may not necessarily suggest the presence of surfactants because surfactant concentrations sufficient to form micelles are typically in the mg/L range. ***Consequently, reduced surface tension in combination with moderate TOC concentrations in the range of 100−10,000 mg/L, may suggest facilitated transport by surfactants.*** Likewise, normal surface tension and elevated TOC concentrations may also suggest a facilitated transport mechanism. As an example, Figures 5 and 6 show the resulting TOC concentration and surface tension values associated with a sugar-complexing agent (hydroxypropyl-β-cyclodextrin [HPCD]). While HPCD does not appear to significantly affect the surface tension, concentrations sufficient to significantly enhance solubility should result in elevated TOC concentrations.

As previously discussed, the types of cosolvents that are commonly encountered in NAPL contaminant sources possess cosolvency powers typically <10 (see Figure 4). Thus, as reflected by data presented in Figure 5, relatively high cosolvent concentrations (i.e., >100,000 mg/L expressed as TOC) may be necessary to observe significant enhancement in HOC solubility. In contrast, data presented in Figure 5 for the influence of a soil-derived humic acid (data labeled "SSHA") suggests that this compound has a significantly higher cosolvency power compared to the other organic compounds referenced in this figure. While one may view naturally derived humic/fulvic substances as a "cosolvent" or "surfactant," for the purpose of this document, these compounds are treated as colloids. In general, humic acid compounds exist as large, macromolecular constituents in natural waters, with molecular dimensions that fall within the size range in which colloidal material is classified. In the following text, further discussion is provided on the potential importance of colloid-facilitated transport for HOCs and the significant role that humic/fulvic compounds may play for this class of organic contaminants.

Cosolvent and Surfactant Facilitated Transport—Key Points

- High TOC concentrations (>10,000 mg/L) and reduced surface tension values in ground-water samples are indicators for potential facilitated transport by cosolvents.
- Moderate TOC concentrations (100−10,000 mg/L) and reduced surface tension values in ground-water samples are indicators for potential facilitated transport by surfactants.

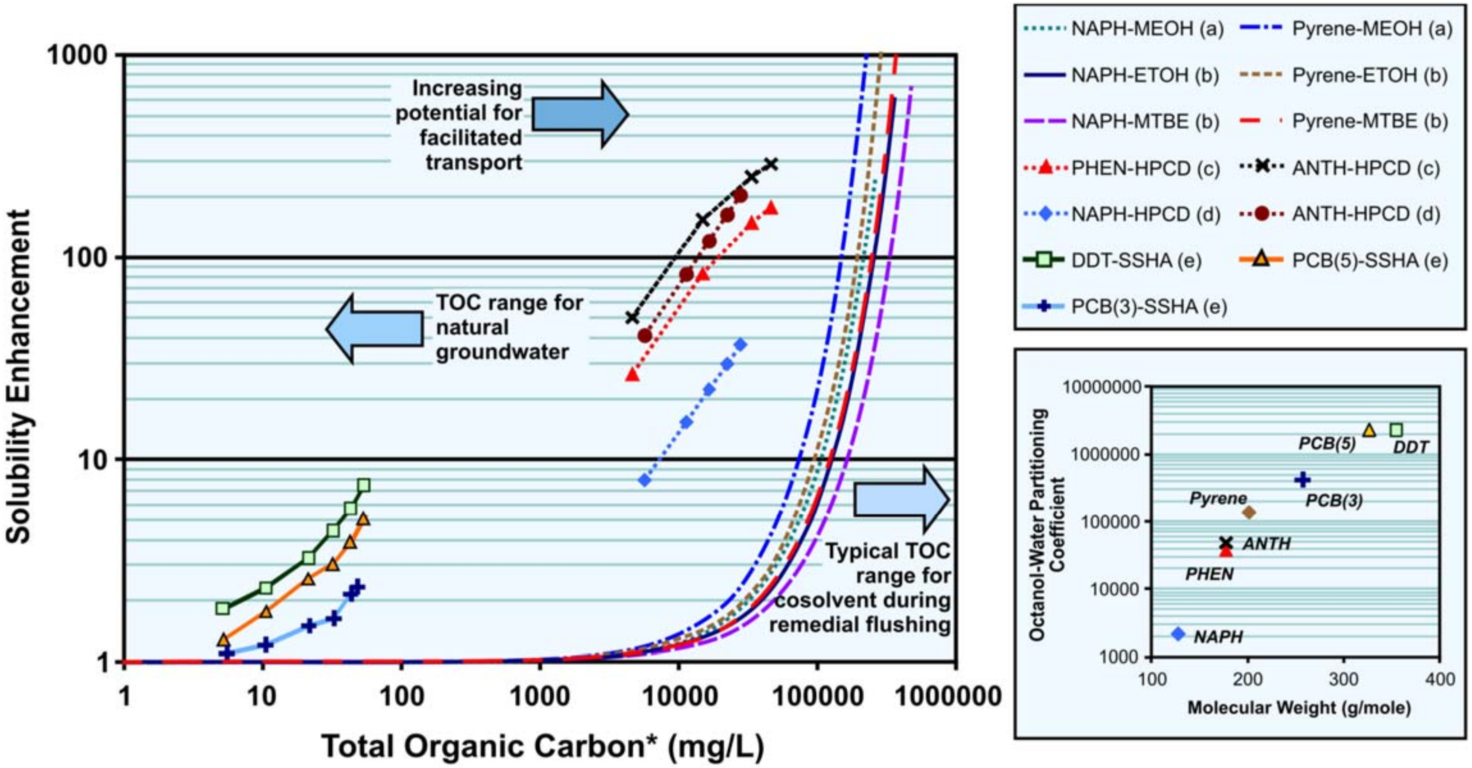

Figure 5. Solubility Enhancement (Ratio of Enhanced Hydrophobic Organic Contaminant [HOC] Solubility with Cosolvent, HPCD, or Humic Acid to Aqueous Solubility) Plotted as a Function of Total Organic Carbon (TOC, mg/L). For the purposes of this graphic, TOC is based solely on the cosolvent, HPCD, or humic acid concentration.

Sources: (a) Pinal et al., 1990; (b) Chen and Delfino, 1997; (c) Viglianti et al., 2006; (d) Wang and Brusseau, 1993; and (e) Chiou et al., 1986.

NAPH = naphthalene; MEOH = methanol; ETOH = ethanol; MTBE = methyl tert-butyl ether; PHEN = phenanthrene; HPCD = hydroxypropyl-β-cyclodextrin; ANTH = anthracene; DDT = *p,p'*-dichlorodiphenyltrichloroethane; SSHA = Sanhedron soil humic acid; PCB(3) = 2,4,4'-polychlorinated biphenyl; PCB(5) = 2,4,5,2',5'-polychlorinated biphenyl.

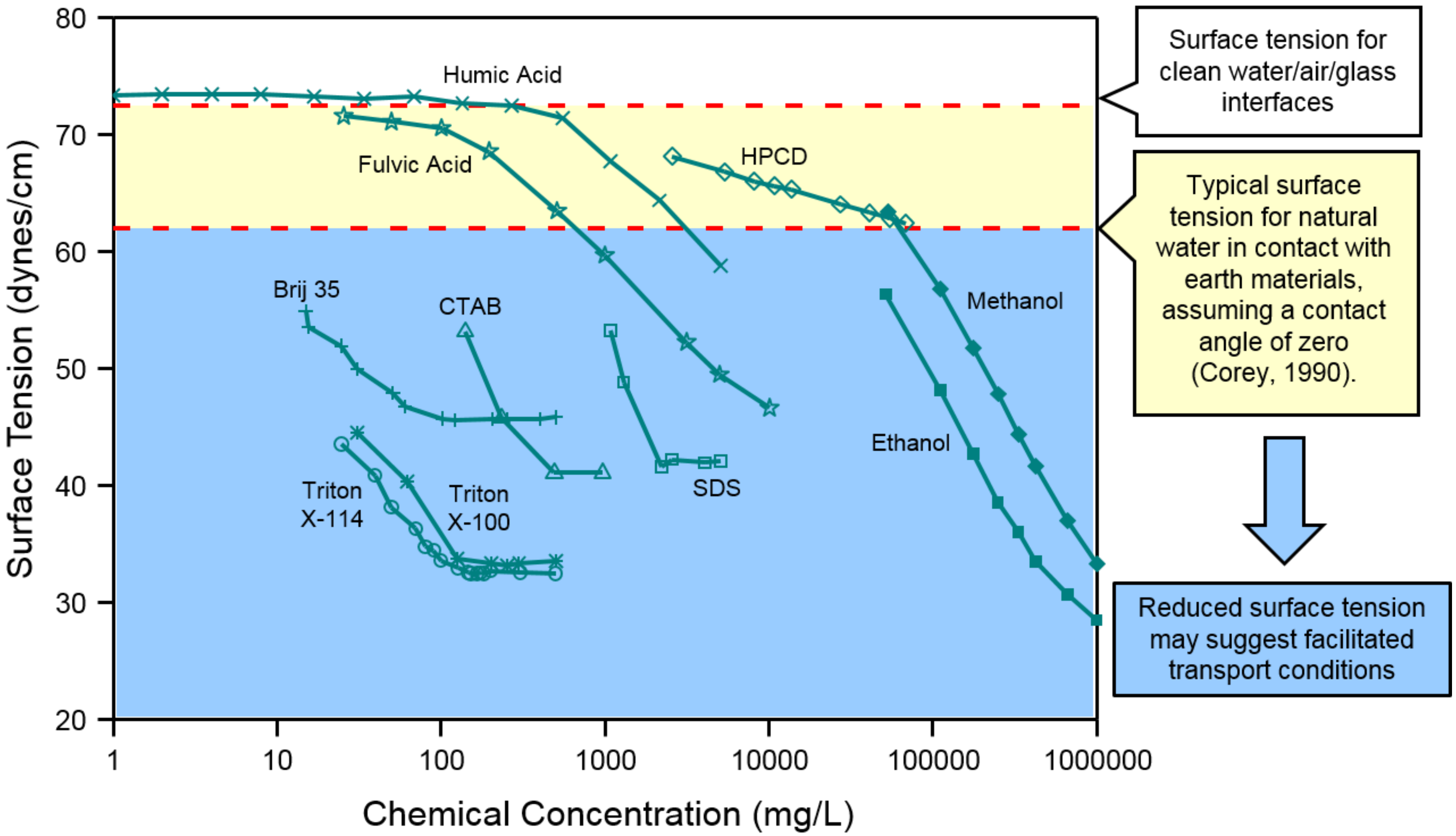

Figure 6. Surface Tension for Selected Chemicals that may Facilitate Hydrophobic Organic Contaminant (HOC) Transport. Shown are surface tension measurements as a function of the concentration of methanol and ethanol (Vázquez et al., 1995), hydroxypropyl-β-cyclodextrin (HPCD) (Wang and Brusseau, 1993), humic acid (Tuckermann and Cammenga, 2004), Suwannee River fulvic acid (Aumann et al., 2010) and selected surfactants (Kile and Chiou, 1989): Triton X-100, Triton X-114, Brij-35, sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB).

3.4. COLLOIDAL TRANSPORT

The association of contaminants with suspended colloidal material in ground water is a possible transport mechanism and a complicating factor for designing subsurface monitoring systems to assess transport of HOCs (U.S. EPA, 1989a; McCarthy and Zachara, 1989). The mobile colloidal phase must be highly reactive for HOC partitioning, of sufficient quantity, and stable (i.e., remain in suspension due to physical or chemical perturbations to the aquifer) to enable the transport of a significant mass of contaminant. Field and laboratory investigations provide evidence that colloidal transport of contaminants may be significant for some species under some hydrogeologic conditions (e.g., Villholth, 1999; Mackay and Gschwend, 2001). Thus, it is important that sampling methods, contaminant transport models, and site assessments be designed to provide direct measures of colloidal transport and simulation of this transport mechanism in projecting plume evolution.

Colloids are generally defined as particles with diameters less than 10 microns (µm) (Stumm and Morgan, 1981). Based on theoretical considerations, Yao et al. (1971) and O'Melia (1980) have estimated that the most mobile colloidal particles in filtration studies in porous media may range from 0.1 to 1.0 µm. These include both organic and inorganic materials such as natural organic matter and minerals derived from the aquifer (e.g., Baumann et al., 2006). Recent estimates of colloidal concentrations in ground water range as high as 63 mg/L (Buddemeier and Hunt, 1988), 60 mg/L (Ryan and Gschwend, 1990), and 20 mg/L (Puls and Eychaner, 1990). Colloidal solids such as organic carbon particles, clay minerals and iron/aluminum oxides have a high surface area per unit mass, which may result in substantial reactive surface area for HOC partitioning. If mobile in subsurface systems, these colloids can affect the migration of contaminants for much larger distances than many transport models would predict because sorbing contaminants may spend a significant fraction of time associated with mobile rather than immobile solids.

The relative importance of colloids on the total concentration of HOCs in contact with solid porous media is illustrated in Figure 7. The data presented in this figure were derived from Hawthorne et al. (2005) based on their measurements of "total" and "dissolved" concentrations of PAH compounds isolated from pore water from a range of sediments. In this work, the colloidal (or particulate) concentration of PAH compounds was operationally defined as the difference between the total pore water concentration less the measured concentration following flocculation of the “particulate” fraction (Hawthorne et al., 2005; Hawthorne et al., 2009a). While there is not yet a uniform technical consensus on the most appropriate methods for distinguishing the colloidal fraction suspended in natural water, this published data set provides useful perspective on the importance of both colloid concentration and the chemical properties of the HOC contaminant. Data presented in the top panel in Figure 7 illustrate the relationship between the calculated particulate/colloidal PAH fraction and the total PAH concentration measured in the isolated pore water from three different sediment samples. These data point to the analytical difficulty of assessing the colloidal fraction of HOCs for low colloid and total contaminant concentrations (i.e., note the number of calculated observations showing negative values for particulate/colloidal fraction for the sediment pore water with 3 mg/L colloid OC concentration). However, based on this data set, one might anticipate that this analytical issue will be less problematic for higher total colloid concentrations. The calculated particulate/colloidal fractions (for samples with positive values) are plotted in the bottom panel of Figure 7 as a function of log K_{oc} for a range of PAH compounds for the same set of pore water samples. As one would anticipate, there is a positive correlation between the calculated particulate/colloidal fraction and PAH log K_{oc}. The correlation appears more robust for samples with higher particulate/colloidal concentrations. These data set the stage for further consideration of the potential importance of colloid-facilitated transport of HOCs, with specific emphasis on the relative importance of naturally-derived humic/fulvic compounds in subsurface systems.

Colloidal material may be released from the soil or geologic matrix and transported large distances given favorable hydrological and geochemical conditions. Changes in solution chemistry resulting from subsurface contaminant releases or changes in ground-water recharge chemistry can bring about changes in the aqueous saturation state in the subsurface leading to precipitation of new colloid-sized inorganic solids that become entrained within flowing ground water, or can cause the dissolution of matrix-cementing agents, promoting the release of colloid-sized particles. In addition, changes in the concentrations of solutes that affect colloid surface charge, such as pH or organic anions, can change the stability of colloids.

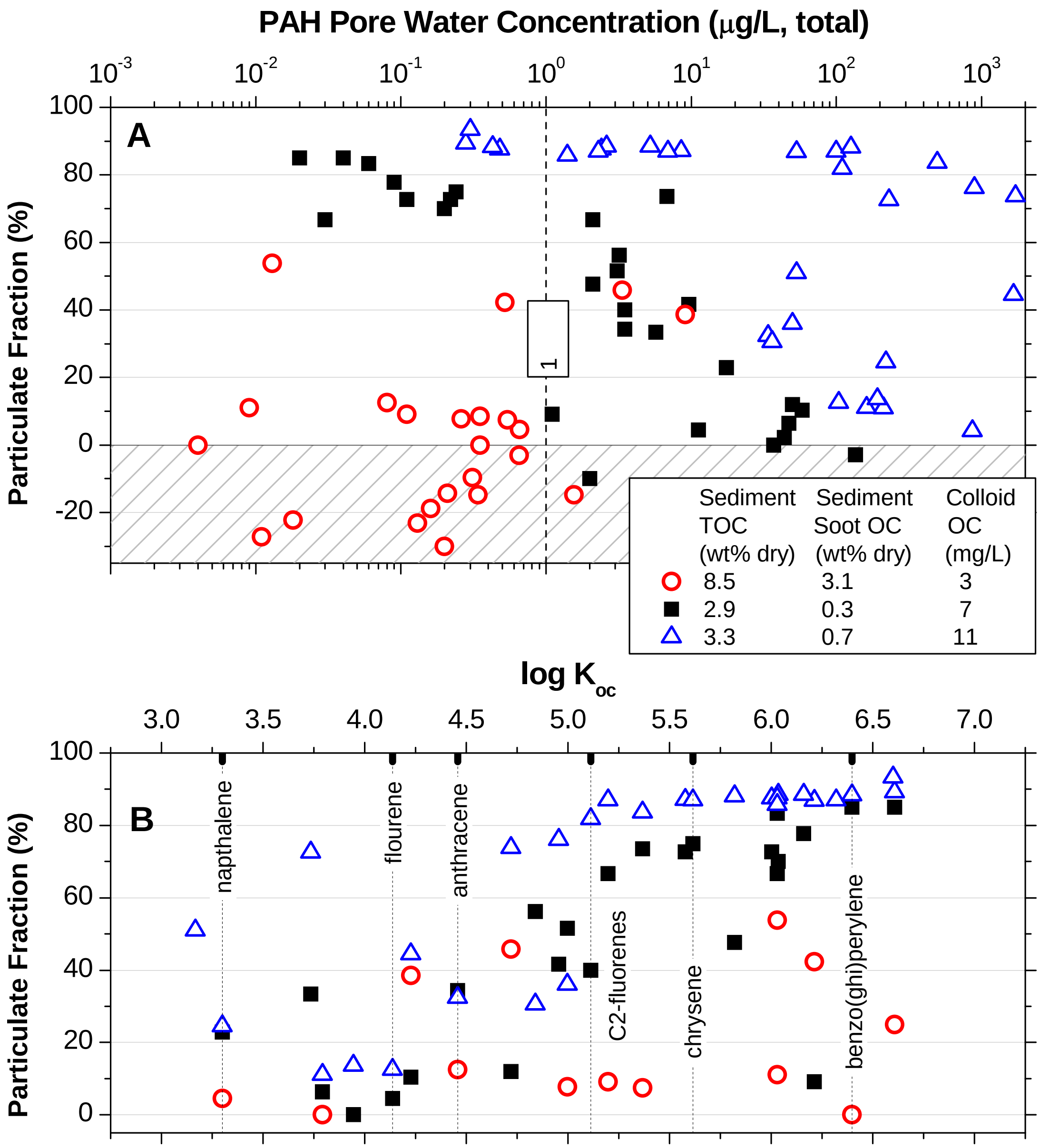

Figure 7. Data from Hawthorne et al. (2005) Illustrating the Distribution of PAH Contaminants Between the Dissolved and Particulate/Colloidal Fraction in Sediment Pore Water Isolated from Sediments Collected from a Freshwater Harbor Near a Former Manufactured Gas Plant Site; Particulate/Colloidal Fraction is Attributed to Natural Humic/Fulvic Compounds. The top panel illustrates the relative fraction of PAH contaminants associated with the colloidal (particulate) fraction as a function of total PAH concentration in pore water recovered from three sediments. The bottom panel illustrates the relationship between the colloidal (particulate) PAH fraction as a function of the log K_{oc} of each PAH for sediment pore water with three different colloid concentrations; values for log K_{oc} were taken from U.S. EPA (2003).

An excellent review of the mechanisms of colloidal release, transport and stability was published by McCarthy and Zachara (1989). Reference to field and laboratory studies provide examples of situations representative of sites with subsurface contamination where periods of colloid mobilization may exist. For example, Gschwend and Reynolds (1987) demonstrated that submicron ferrous phosphate colloids were suspended and presumably mobile in a sand and gravel aquifer. The colloids were formed from sewage-derived phosphate and iron released from aquifer solids due to reduction and dissolution of ferric iron from the soil. Thompson et al. (2006) have also demonstrated that microbially driven redox cycling of iron bound to soils may also lead to release of colloidal solids via indirect impacts on water chemistry. In this instance, the mobilized colloidal fraction was dominated by solid organic carbon.

One special type of colloid suspension that may form within the subsurface fluid matrix is a Pickering emulsion (Harrold et al., 2005; Roy-Perreault et al., 2005; Yaron-Marcovich et al., 2007). Pickering emulsions are water/oil emulsions stabilized by the presence of solid particles that are much smaller than the dispersed immiscible liquid drops in the continuous liquid phase (Binks, 2002). In this case, the NAPL phase with which the HOC is associated can form a Pickering emulsion during interaction with colloidal-sized aquifer fines. Review of the technical literature under real and/or simulated ground-water conditions suggests that Pickering emulsions can form, but their significance is relatively minor in the absence of surfactants introduced at elevated concentrations to remediate NAPL residuals (Torres et al., 2008) and/or physical perturbations to the aquifer such as drilling (Kueper et al., 2004). The formation of a Pickering emulsion due to well drilling activities may result in short-term contaminant concentration spikes in monitoring wells near the drilling location. From this perspective, the formation of Pickering emulsions is not likely to be a primary factor for HOC transport over extended distances in the absence of physical manipulations to the subsurface environment. However, the potential for unintended subsurface translocation of HOCs due to site characterization activities should be considered during design of the investigation.

Results from field observations indicate that colloid mobilization in the subsurface may be transient (e.g., Nightingale and Bianchi, 1977; Miekeley et al., 1992; Baumann et al., 2006). Nightingale and Bianchi (1977) observed that ground-water turbidity may increase for periods of time due to mobilization of colloidal solids coincident with time-varying recharge events. These observed turbidity increases were abated with time as the aquifer returned to steady-state conditions. In addition, Baumann et al. (2006) observed high colloid concentrations in leachate from landfills, but colloid concentrations decreased rapidly in ground-water down gradient from the landfill. These observations suggested that the change of hydrochemical conditions at the interface, from a reducing, high ionic strength environment inside of the disposal sites to an oxidizing, low ionic strength environment in the ground water (together with physical filtration effects for the larger particles) was an effective chemical barrier for colloid migration. Thus, it appears that while colloid mobilization (along with associated contaminants) probably does occur, there are several physicochemical mechanisms that might limit colloid migration significant distances beyond the point of generation. A conceptual framework for understanding colloid stability and transport in ground water has been developed (Degueldre et al., 2000), and it is recommended that this be consulted as a point of reference for assessing the potential importance of this process at a given site.

3.4.1. Forms of Colloidal Material Relevant to HOC Transport

Most accounts of HOC association with mobile colloids indicates that natural dissolved organic carbon (DOC), either as a single phase or associated with colloidal-sized aquifer minerals, is the most likely carrier phase (e.g., Villhoth, 1999; Mackay and Gschwend, 2001; Persson et al., 2003; Kim et al., 2008; Persson et al., 2008). The source of DOC in aquifers is typically the release of organic matter, e.g., humic/fulvic compounds, from surface soils that infiltrates deeper into the subsurface as meteoric water percolates through the unsaturated zone into saturated portions of the aquifer (e.g., Kaplan et al., 1997). [For more detailed discussion of the properties and measurement of humic compounds, refer to literature sources such as Haitzer et al. (1999) or Ehlers and Loibner (2006).] Research conducted by Kim et al. (2008) indicates that release of organic matter from soils may be enhanced under anaerobic conditions. The mechanisms responsible for this process may include weathering transformations in the organic matter assemblage during microbial reactions (Kim et al., 2008) or the dispersal of organic matter-iron oxide aggregates due to reductive dissolution of iron oxide-cementing agents. Regardless of the mechanism, this observation indicates that reducing conditions that frequently develop in association with HOC plumes may be a source for enhanced mobilization of colloidal DOC. As suggested by Persson et al. (2003), the importance of DOC-facilitated transport for nonionic PAHs was greatest for PAHs with log $K_{ow} > 5$ and DOC concentrations greater than

250 mg C/L. Thus, the total mass of colloidal DOC within the subsurface system factors into the potential for colloidal transport.

3.4.2. Conditions Conducive to Colloid Mobilization in Ground Water

Two general conditions to consider relative to the potential for colloid transport through the subsurface include (1) the hydrogeologic setting and (2) chemical perturbations to the aquifer due either to the dynamics of ground-water recharge for the system or the influence of plume chemistry. While colloid transport is known to occur in unconsolidated, porous aquifer solids (McCarthy and Zachara, 1989), it has also been observed that highly fractured consolidated aquifers or karst systems may be susceptible to higher colloidal mass fluxes (e.g., Atteia and Kozel, 1997; Shevenell and McCarthy, 2002; Vesper and White, 2003). Thus, it will be important during development of the site conceptual model and design of the ground-water monitoring system that consideration be given to the types of subsurface hydrogeologic features that may lie along ground-water flow paths (e.g., see Figure 1). As an example, Massei et al. (2002) have characterized a hydrogeologic system in which ground-water transport to wells within an unconsolidated, alluvial aquifer consisted of episodic infiltration through the overlying unsaturated zone and via hydraulic connection to a highly transmissive karst aquifer. For this complex system, colloid characteristics differed as a function of the predominant source of recharge to the alluvial aquifer. Given differences in flow characteristics for karst and highly fractured bedrock systems versus granular, unconsolidated aquifers, flow dynamics will play a larger role for colloid mobilization for the former subsurface systems.

For unconsolidated, porous media, field investigations of colloid mobilization in subsurface systems generally demonstrate that colloid transport is greatest when the system is perturbed from its steady-state condition. Examples of the types of perturbations that may occur include changes in the ionic strength (or specific conductivity) of infiltrating water (Seaman et al., 2007), changes in redox conditions driven by microbial processes (Kim et al., 2008) and the physical stress of large infiltration events or freeze-thaw cycles (Totsche et al., 2007; Wehrer and Totsche, 2008). Thus, the extent of colloid mobilization may be tied to seasonal weather patterns as well as the influence of plume chemistry. The dynamics of seasonal weather patterns will likely be of greatest importance for shallow unconsolidated aquifers and highly fractured consolidated aquifer systems with connection to surface recharge events. Biogeochemical influences on colloid mobilization will likely be important where high fluxes of dissolved salts originate from contaminant source areas or where the subsurface microbiology is stimulated by the influx of degradable organic compounds (e.g., cosolvents or volatile organic compounds) and/or dissolved constituents such as terminal electron acceptors (e.g., nitrate or sulfate). Knowledge of the dynamics in water flux and/or the flux of dissolved constituents through the subsurface may prove critical for designing the monitoring strategy (frequency and locations) for assessing the importance of colloid-facilitated transport of HOCs.

3.4.3. Field Approaches to Characterize Subsurface Colloidal Transport

Determination of whether colloidal transport is a factor for HOC transport in ground water will be predicated on implementation of well installation, development and sampling protocols that avoid potential artifacts leading to colloidal loss or production of colloidal material not present within the plume. One approach to differentiate the relative influence of the freely dissolved-phase and colloidal transport of HOCs involves determination of contaminant concentrations for samples retrieved using low-flow purging techniques as well as in situ passive sampling of only the dissolved phase. The difference between these two measurements would be attributed to the fraction of the HOC transported by a colloidal phase. One advantage of this approach over the use of postsampling size fractionation is the avoidance of artifacts that can be problematic due to manipulation of ground water removed from the chemical and physical conditions within the aquifer. In addition, this approach avoids some of the analytical problems associated with pressure/vacuum membrane filtration procedures for fractionating the HOC between "colloidal" and "dissolved" phases. Bopp et al. (2005) have demonstrated use of a sampling device constructed of a cylindrical ceramic membrane that houses a sorbent to collect the HOC that passes through the membrane via diffusion. This device is designed in a manner such that temperature, which influences HOC diffusion coefficients, and aqueous contaminant concentration are the only variables that influence mass accumulation within the device. The performance of the device was validated under field conditions at a former gas works site for a range of PAHs. Although ground-water temperature may not vary significantly throughout the site or as a function of time for a given well location, one can further constrain the uncertainty in time-weighted average contaminant concentration derived from this device through continuous monitoring of ground-water temperature using in situ data logging devices.

The success of determining the colloidal fraction of the transported HOCs by difference using this methodology would depend on the ability to retrieve a ground-water sample free from particulates derived from sources other than truly mobile colloids. Potential limitations to the collection of artifact-free ground-water samples are discussed below, along with recommendations for steps that can be taken to minimize these potential artifacts.

3.4.4. Importance of Initial Well Development and Sampling Approach

Well installation procedures may be a source of suspended solids retrieved during well sampling. Two common types of solids include fine-grained materials used in drilling fluids (e.g., bentonite) and colloidal-sized aquifer solids either dislodged from the matrix or resulting from breakdown of larger-sized matrix particles due to physical forces from the drilling activity. Introduction of anthropogenic, fine-grained materials may be avoided through the use of drilling methods that do not require lubricants such as clay suspensions or through the use of water as the drilling fluid. Aggressive development of the well (e.g., surging and/or high pumping rates) can be used to remove these types of solids from within the well screen and the portion of the aquifer in contact with the screened interval. As suggested by Backhus et al. (1993), one approach to discern if residual solids contamination persists for a given well screen is to examine trends in initial turbidity from the initiation of well purging for multiple sampling events spaced through time. In general, it is anticipated that the initial turbidity would decrease with each sampling event if residual solids are the primary source of suspended solids.

Another potential source of artifactual solids retrieved during sampling may be due to precipitated solids that accumulate on well-screen materials and are physically dislodged by the sampling activity (e.g., Houben, 2006). An example of this type of solid is the accumulation of iron oxides that result from the oxidation and precipitation of ferrous iron during natural or anthropogenic intrusions of dissolved oxygen within the screened interval of the aquifer. While use of dedicated down-hole sampling devices may help minimize physical disturbance of these precipitates, changes in ground-water chemistry and/or low purging rates still provide potential routes to suspend these solids during sampling. From this perspective, it is recommended that the well screen be redeveloped (e.g., high purge rates and/or down-hole scrubbing with a pipe brush) prior to initiating low-flow purging to establish stabilization of field parameters. Because these types of mineral precipitates are typically dissolved by mild reductants or acids, it is recommended that their occurrence within a sampled well screen be assessed by measuring acid-digestable total metals concentrations from a subsample of the suspensions collected during the redevelopment process. [Note: For well screens susceptible to iron oxide precipitation, it is possible to conduct this analysis in the field using HACH Method 8008 for ferrous iron, which uses a mild reductant suitable for dissolving iron oxides such as ferrihydrite. Likewise, comparison of ferrous iron concentrations using HACH Method 8146 (dissolved Fe^{2+} by 1,10-phenanthroline) and HACH Method 8008 can be used to rule out possible precipitation of ferrous iron during sampling (Hassellöv et al., 2007).]

Zemo (2009) provides clear examples of potential analytical bias for samples collected from zones in which both free phase (NAPL) and dissolved forms of organic contaminants may be present. For several of the case study examples (Zemo, 2009), elevated turbidity above that in the ambient ground-water flow field was likely caused by either incomplete initial development of the well screen following installation or the use of procedures for retrieving water from the well casing that caused mobilization of aquifer fines that were otherwise immobile. Since HOCs may strongly partition to aquifer solids throughout the plume, it is critical to ensure that suspended solids that are present in sampled ground water are truly mobile within the formation. ***For this reason, it is recommended that ground-water sampling for the purpose of evaluating the presence of mobile colloids be conducted using permanent monitoring points that have a clear record of well construction (including description of granular solid materials employed during drilling and screen placement within the formation), procedures used for development, and the data used to evaluate the adequacy of well development.*** As an example, the removal of three well-casing volumes is often employed as a general reference point for establishing adequate well development. However, the degree that aquifer fines, physically dislodged during the well installation process, are removed during the well development process will likely vary as a function of the rate at which ground water can be flushed through the screen and the physicochemical characteristics of the particulates. (This may also apply to solid materials such as bentonite or screen sand packs used in well construction.) As noted by Kim (2003), the well drilling process can have long-lived impacts (days to months depending on formation flow rates) on the composition of sampled ground water from the well screen due to the physical abrasion or breakdown of aquifer solids. These observations all indicate that, in addition to establishing that ground-water purging and sampling procedures are optimized, it is also important to examine the record of stabilization results for a given well screen throughout its period of use to establish that it is a source of reliable data on mobile colloids in the screened interval of the formation.

The results from a limited number of studies have indicated that passive collection of ground-water colloids might be achieved (e.g., Ronen et al., 1992; Petruzzi and Silliman, 2006). Based on the hydrologic characteristics for these studies, it appears this would only be successful for highly transmissive systems where ground-water replacement within the well screen was rapid. As noted by Ronen et al. (1992), rigorous development of the screened interval needs to be conducted in order to avoid many of the artifacts associated with poor well development prior to low-flow sampling procedures. Due to the lack of studies comparing performance of passive and low-flow sampling of colloidal material, the reliability of passive sampling methods is unknown. However, this approach may have some merit for sampling colloids in karst or highly fractured bedrock systems, and further evaluations of this technique are recommended.

3.4.5. Stabilization Criteria to Ensure Representative Formation Water

The importance of observing the chemical and physical parameters of purged ground water to establish that representative formation water is being sampled has recently been reviewed by Barcelona et al. (2005). This review reinforces the findings and recommendations of the original EPA Ground-Water Issue Paper that established the basis for using low-flow, minimal drawdown sampling procedures (U.S. EPA, 1989b). The importance of establishing stabilization of the physicochemical ground-water parameters has been reinforced by field studies for a wide range of sites (e.g., Backhus et al., 1993; Jensen and Christensen, 1999; Gibs et al., 2000). It should also be noted that the detailed results published by Backhus et al. (1993) demonstrate that stabilization of turbidity is the most critical parameter for establishing that the solids retrieved are representative of mobile colloids moving with the flow of ground water. ***Thus, it is recommended that strict adherence to the criterion for establishing stabilization of turbidity be observed for sampling of mobile colloids.***

To illustrate this point, analysis of well-stabilization data from Jensen and Christensen (1999) is presented in Figure 8. The relative percent change between subsequent field parameter measurements is shown for turbidity, pH, specific conductance, and temperature. It should be noted that pH and specific conductance stabilized rapidly during purging, suggesting that ground-water chemistry had stabilized. However, stabilization of turbidity (±10% is a commonly accepted criterion) required longer purge times, with stability being established after approximately 4 hours of purging at <100 mL/min (Jensen and Christensen, 1999). Estimates of the cumulative purge volume indicate that 10−25 liters (2.64−6.60 gallons) of ground water needed to be purged in order to achieve this stabilized condition. The results from these field-sampling studies indicate that long periods of well purging (i.e., in excess of 3−4 hours) may be required to establish stable turbidity measurements. Thus, the time needed to ensure optimal conditions within the well screen and stabilization of pumped ground water indicates that sampling for mobile colloids will most likely be practically and successfully implemented for only a subset of monitoring wells for the site. This will likely require careful consideration by all stakeholders of what monitoring wells will provide the most useful observations relative to HOC transport at a given site.

While turbidity can provide a surrogate indicator for mobile colloids, it does not necessarily provide a direct measure of colloid concentration in ground water. Turbidity is measured using light scattering in most field instrument designs, i.e., that portion of source illumination that is scattered at an angle of 90° from the path of the light source. Therefore, the amount of scattered light will depend on the light scattering characteristics of the colloidal material. The degree of light scattering will depend on the total density of particles, but it will also depend on the distribution of particle sizes and the chemical composition of the colloidal material (Wehrer and Totsche, 2009). As shown by Baumann et al. (2006), there is a range of inorganic and organic compositions of colloids in subsurface systems, including dissolved organic carbon (e.g., humic molecules derived from overlying soils) and minerals such as carbonates, aluminosilicates and iron/aluminum oxides. Ultimately, it may be necessary to identify the specific colloidal phase that is responsible for HOC transport.

Colloid Facilitated Transport—Key Points
• Documentation of ground-water well construction, development and maintenance procedures are critical for evaluating the presence of mobile colloids. • Acquisition of ground-water samples to establish the presence of mobile colloids should strictly adhere to the criterion for demonstrating stabilization of turbidity during well pumping.

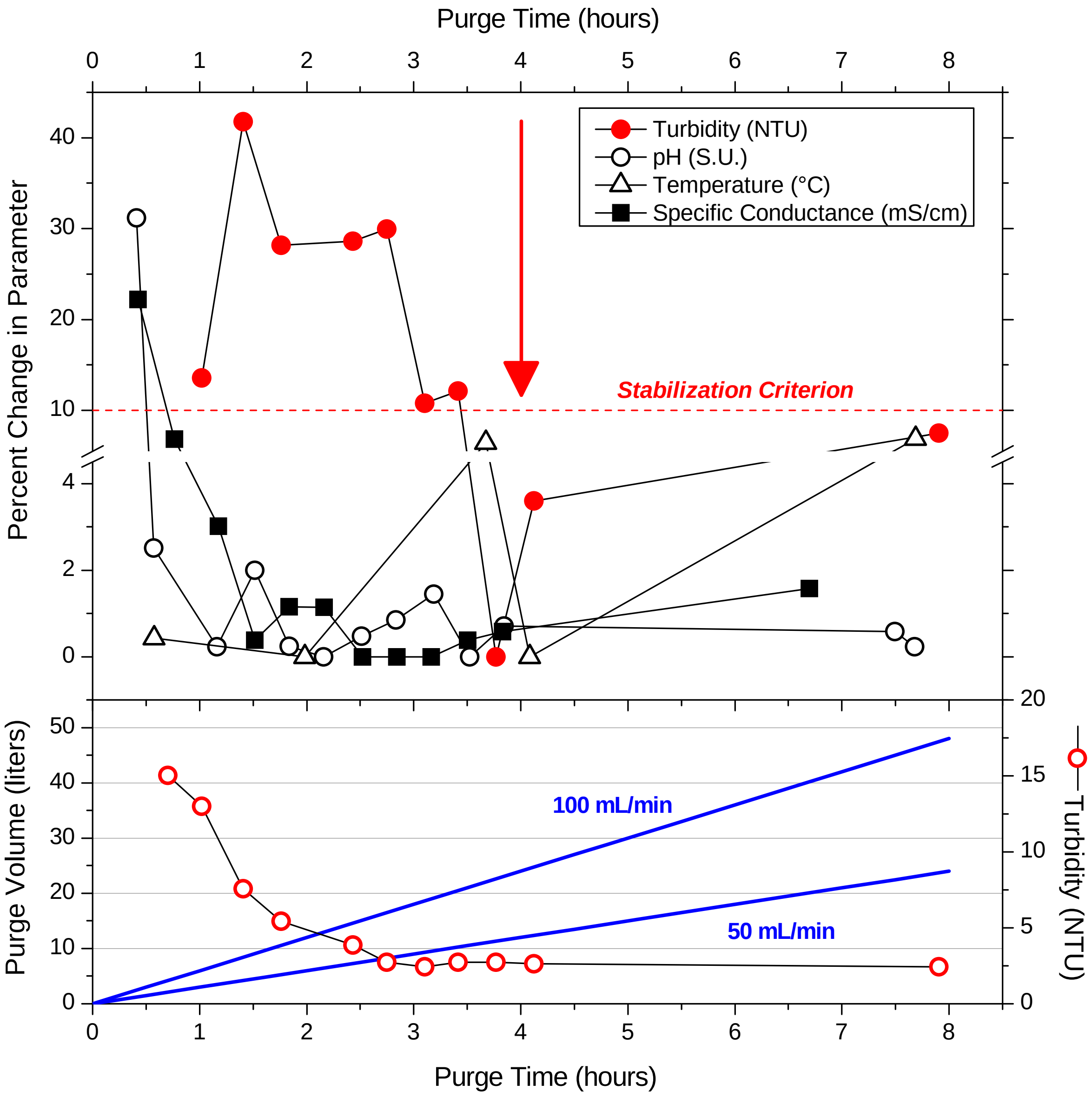

Figure 8. Analysis of Field-Measured Ground-Water Parameters for Establishing that Purged Groundwater is Representative of Conditions Within the Natural Ground-Water Flow Field. (Note break in y-axis scale in top panel.) The original data were digitized from Figure 1 published in Jensen and Christensen (1999); absolute values of percentage change were calculated as 100 * ((Value$_{i+1}$ − Value$_{i}$)/Value$_{i}$). The bottom panel shows the digitized turbidity values used to calculate percentage change and example estimates of cumulative purged water volume assuming either purge rates of 100 mL/min or 50 mL/min; Jensen and Christensen (1999) report purge rate of <100 mL/min.

S.U. = standard unit; NTU = nephelometric turbidity unit.

4. EVALUATING ECOSYSTEM EXPOSURE AND RISK

In the preceding discussion, the technical basis for enhanced subsurface transport of HOCs was presented along with approaches one can employ to assess the mechanism(s) controlling HOC mobility within ground water. For contaminated sites, assessment of the current extent or potential for HOC migration is needed to evaluate potential risks to downgradient receptors and/or evaluate potential remedial alternatives to control the flux of HOCs through the subsurface. The complexity in the subsurface distribution of HOCs between multiple phases, in conjunction with the complex hydrogeologic flow environments commonly encountered at contaminated sites, indicates sole reliance on model projections of HOC transport and exposure will not provide substantial predictive insight into the potential for downgradient exposure. The uncertainty of these model projections is further increased by the lack of technical consensus on appropriate approaches to incorporate and constrain mathematical descriptions of facilitated transport of HOCs in subsurface systems. ***Thus, development of a firm understanding of the hydrogeologic system in which the HOCs have been introduced, along with the acquisition of contaminant distribution data for transects of monitoring locations perpendicular and parallel to the subsurface flow gradient, currently provides the most straightforward approach to assess the extent of downgradient exposures.*** This is consistent both with published recommendations for characterizing sites contaminated with NAPLs (ITRC, 2003; U.S. EPA, 2009) and guidance for conducting an ecological risk assessment at sites where contaminant transport across the ground-water/surface-water (GW/SW) transition zone constitutes an exposure pathway (U.S. EPA, 2008).

4.1. ASSESSING EXPOSURE PATHWAY

Supplemental guidance published recently by the EPA illustrates approaches to characterize sites with suspected exposures in surface water bodies due to contaminated ground-water discharge (U.S. EPA, 2008). This document provides recommendations on approaches to site characterization to evaluate whether contaminant discharge from ground water is occurring and determine whether a complete exposure pathway exists. In Figure 9, potential physical scenarios for ecological exposures across the GW/SW transition zone are illustrated. As discussed earlier in this document, characteristics of subsurface fluid transport and proximity of surface or shallow subsurface contaminant source areas may influence the physicochemical process leading to ecological receptor exposure to HOCs. For situations in which the contaminant source area(s) is close to the receiving surface water body, overland or subsurface transport of the NAPL may serve as the primary process by which HOC contaminant mass is conveyed to sediments or overlying surface water. This may result in exposures to both benthic organisms and aquatic life within the water column due to physical contact with the NAPL or soluble HOC concentrations supported by dissolution of the NAPL (i.e., Scenarios 1 and 2 in Figure 9). For systems in which subsurface transport follows a path through the aquatic sediment layer, ecosystem exposure may occur within the sediments or in the overlying water column (Scenarios 3 and 4 in Figure 9). For systems in which HOCs are associated with residual NAPL trapped within sediments or the underlying shallow ground-water aquifer, transport of contaminants into the overlying surface water may occur via ebullition. This process leads to potential exposures in surface water depicted as Scenario 5 in Figure 9.

Duncan et al. (2007) provide a case study discussion that illustrates the application of site reconnaissance methods for delineating organic plume discharge into a tidally influenced waterway. This study also illustrates the usefulness of visual observations in assessing the potential that plume discharge is already occurring. Examples of visual indicators may include (1) evidence of hydrocarbon seeps along shorelines during low-tide or base flow conditions, (2) observations of free-phase pools of NAPLs in near-shore areas, and/or (3) the presence of organic sheens on the surface of near-shore waters that may be indicative of lighter hydrocarbon cocontaminants within the discharging plume (see Figure 10). ***These visual indicators provide a useful screening approach to support decisions regarding sample collection and characterization for acquisition of contaminant data used in estimating ecological exposures.*** For example, examination of the literature indicates that collection of this type of information can help inform approaches to site characterization and risk assessment (e.g., Michel et al., 2009).

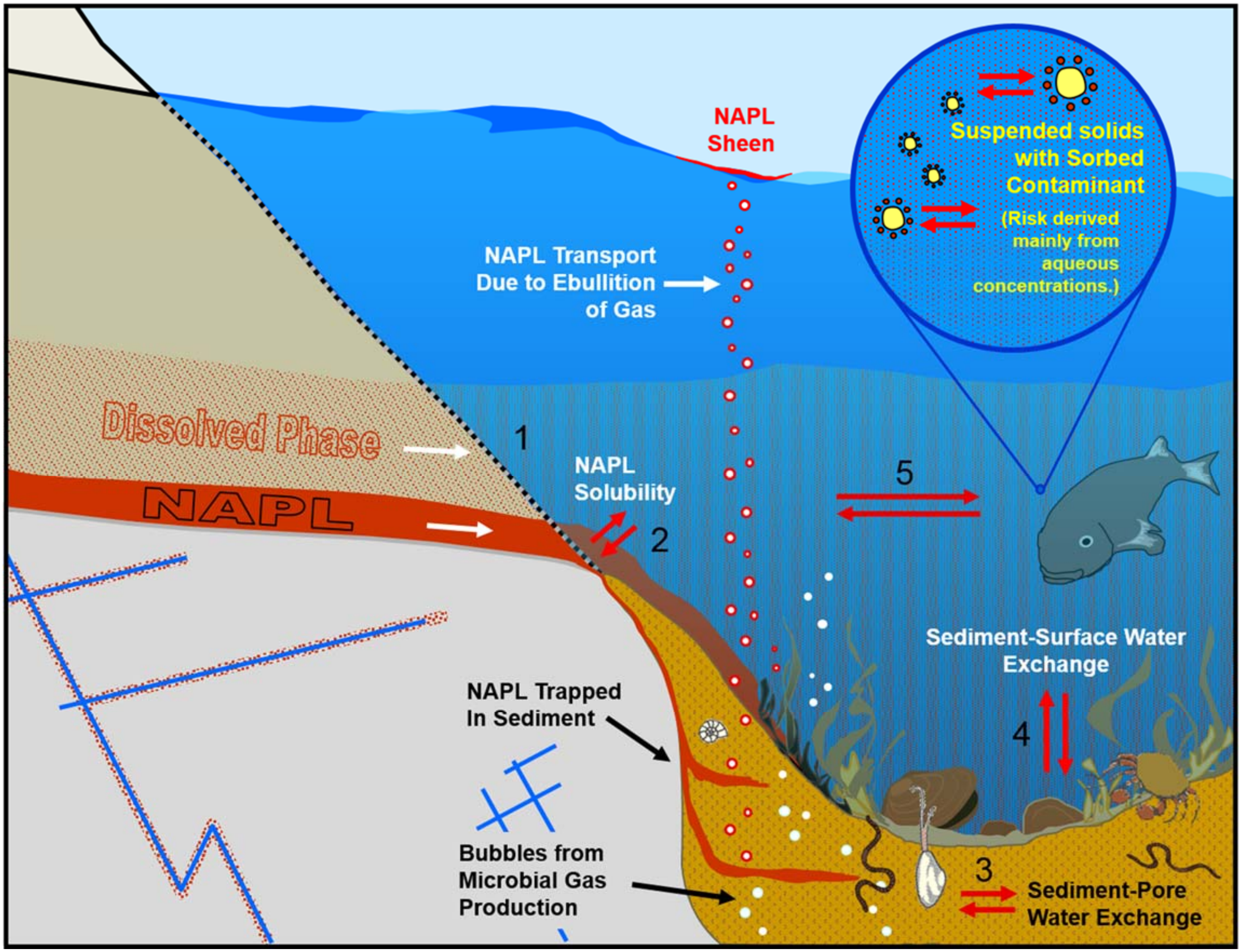

Figure 9. Illustration of Potential Scenarios for Ecological Exposures to Hydrophobic Organic Contaminants (HOCs) in Surface Water. (1) Exposure to dissolved or colloid-associated HOCs from direct plume discharge into surface water, (2) contact with NAPL or dissolved HOC in equilibrium with NAPL phase, (3) exposure to dissolved HOC in sediment pore water (benthic), (4) aquatic life exposure in overlying surface water due to desorption from contaminated sediments and (5) aquatic life exposure in overlying surface water due to ebullition.

Figure 10. Illustrations of NAPL Pools or Sheens at Sites with Subsurface Discharge/Release of NAPL with Associated Hydrophobic Organic Contaminant (HOC). (Left Panel) Transport due to groundwater discharge (Oregon DEQ, 2006) and (Right Panel) transport due to gas ebullition (photo courtesy of Steve Mangion, U.S. EPA).

Recent studies have pointed to greater reliability of in situ measurements of dissolved HOC concentrations to successfully predict actual contaminant uptake levels at contaminated sediment sites (e.g., Xu et al., 2007; Arp et al., 2009; Friedman et al., 2009; Hawthorne et al., 2009b; van der Heijden and Jonker, 2009; McDonough et al., 2010; Ruus et al., 2010; Werner et al., 2010). ***Because dissolved HOC concentrations can vary as a function of time and space at a ground-water discharge zone, design of the monitoring or detection systems need to capture this variability to the extent practicable.*** In designing the approach to characterize the extent and impact of HOC exposure, it is important to consider the following factors: (1) the spatial distribution of contaminated ground-water flux across the areal extent of the aquatic system (e.g., Conant et al., 2004; Hamonts et al., 2009; Landmeyer et al., 2010), (2) the temporal variation in the magnitude and direction of contaminated ground-water flux across the GW/SW transition zone (e.g., Kennedy et al., 2009) and (3) the spatial distribution in sediment properties that influence the capacity for and rate of HOC sequestration across the zone of plume discharge (e.g., Jonker and Barendregt, 2006; Smith and Lerner, 2008).

While exposure to the dissolved form of the HOC is generally assumed as the primary process controlling biological uptake (e.g., Brack et al., 2009; McDonough et al., 2010), transport of the NAPL into sediments or surface water may also contribute to ecological impairment. In Figure 9, scenarios 2 and 5 represent special situations in which NAPL transport into the surface water body may occur due to the proximity of contaminant sources to the impacted aquatic ecosystem. For these situations, components of the NAPL, in addition to specific HOCs, may contribute to the overall impact to ecological receptors (e.g., Driscoll et al., 2009; Muijs and Jonker, 2010). Site photographs shown in Figure 10 illustrate conditions where ground-water advection and/or ebullition contribute to the bulk movement of NAPL into surface water. The left panel in Figure 10 illustrates direct discharge of NAPL at a creosote site in Portland, Oregon (Oregon DEQ, 2006; Sower and Anderson, 2008). The right panel in Figure 10 illustrates transport of NAPL from sediments into surface water due to ebullition of biogenic gas from contaminated sediments at a site in Burlington, Vermont (ARCADIS BBL and Hart Crowser, 2008). The ebullition of biogenic gas during decay of newly deposited natural organic matter is a common phenomenon (e.g., Casper et al., 2000; Huttunen et al., 2001; Delongchamp et al., 2010; Varadharajan et al., 2010). For sites where trapped NAPL overlies sediment layers where methane is produced during anaerobic degradation of organic matter, ebullition-induced transport of NAPL and/or associated HOCs into the overlying surface water may occur (e.g., Viana et al., 2007; McLinn and Stolzenburg, 2009; Yin et al., 2010; Viana et al., 2012). For Scenarios 2 and 5, assessment of impairment to biological receptors may warrant delineating the presence of NAPL in addition to specific HOCs.

Knowledge of the location and dimensions of the upgradient plume along with information on the potentiometric ground-water surface can also be used to guide sampling of shallow ground water and/or sediments within the surface water body for the purpose of determining the presence of HOCs (e.g., Roy and Bickerton, 2010). Once contaminant discharge has been confirmed, then a more detailed monitoring network can be established within the GW/SW transition zone in order to map out the dimensions of the contaminated zone and determine contaminant discharge, and subsequently, estimate exposure point concentrations and ecological risk.

Evaluating Downgradient Exposures—Key Points

- A monitoring network developed from knowledge of the upland hydrogeologic system and contaminant distribution is an important component for design of the ecological exposure assessment.
- Visual observation of hydrocarbon seeps, NAPL pools and organic sheens at ground-water discharge zones can support design of the contaminant monitoring or detection systems.
- Design contaminant monitoring or detection systems to evaluate the temporal and spatial variability in HOC concentrations transported across the GW/SW transition zone.

4.2. ESTIMATING RISKS TO ECOLOGICAL RECEPTORS

A general assumption for assessing the extent of biological uptake for the exposure scenarios illustrated in Figure 9 is that the dissolved form of the HOC is the primary source of bio-uptake for the biological receptor. Evaluation of the distribution of HOCs between the dissolved, NAPL, and/or colloidal/particulate phases, and the influence of this phase distribution on exposure/toxicity to ecological receptors, is particularly important where facilitated transport occurs. Where a complete exposure pathway exists from ground water to surface water, several methodologies may be used to estimate risks to ecological receptors:

- Compare chemical concentrations in ground water, interstitial water (Greenberg et al., 2014) or overlying water to water-only toxicity values (i.e., effect concentrations) such as final chronic values (FCVs) or secondary chronic values (SCVs).

- Compare organic carbon normalized sediment concentrations to equilibrium partitioning sediment benchmarks (ESBs) derived from water-only effects concentrations and respective organic carbon-water partition coefficients (U.S. EPA, 2012). An ESB is the organic carbon normalized solid phase concentration for a particular HOC below which adverse effects are unlikely to occur and above which effects may occur.

- Compare concentrations derived through use of chemical uptake models or bioaccumulation studies to risk-based concentrations (e.g., references in Section 23.2.7 of Suter, 2007).
    - Chemical uptake models utilizing HOC distributions in sediments, pore water and overlying surface water may employ (1) laboratory-derived bioconcentration factors (BCFs) (U.S. EPA, 2000a), (2) field-derived

bioaccumulation factors (BAFs) (Ingersoll and MacDonald, 2002), or (3) biota sediment accumulation factors (BSAFs) (Burkhard, 2009).

- Compare results from toxicity and bioaccumulation tests (in situ preferred) to those from a reference site (Burton et al., 2005; Greenberg et al., 2002; U.S. EPA, 1994, 2000b).

The first two methodologies for estimating risk derive from a mechanistic approach to determine if a specific HOC (or mixture) is sufficiently bioavailable to cause a toxic effect. Burgess et al. (2013) provide context for the use of ESBs derived from the analysis of HOC and organic carbon concentrations in sediments versus direct measurements of dissolved HOC concentrations in interstitial water. For risk estimates that rely heavily on sediment-associated HOC concentration measurements, it may be important to evaluate sediment solid phase composition (e.g., presence and quantity of carbonaceous particles or NAPLs) and the potential influence this may have on estimates of HOC bioavailability (e.g., Ghosh et al., 2003; Jonker and Barendregt, 2006; Ghosh and Hawthorne, 2010; Witt et al., 2010). There can be uncertainty associated with the prediction of the bioavailability of sediment-associated HOCs (Mayer et al., 2014), which can lead to inaccuracy in estimated risk for a given site. With improvements in the accuracy and reductions in cost for direct analytical determinations of dissolved HOC concentrations, Burgess et al. (2013) project that the direct methods for assessing dissolved HOC concentrations will likely become more prevalent. For the third method for estimating risk, it is important to recognize and account for potential analytical artifacts observed for highly hydrophobic HOCs when determining laboratory-derived BCFs (Jonker and van der Heijden, 2007). For the fourth method, it is preferred that in situ tests of toxicity/bioaccumulation be employed using confined organisms. While laboratory-based tests provide a measure of relative differences in toxicity for sediments from a given site, they may be unable to replicate the physical and chemical dynamics of site conditions that factor into the cumulative toxicity to ecological receptors (Burton et al., 2005; Hose et al., 2006).

5. RECOMMENDATIONS SUMMARY

As illustrated in the preceding text, assessing the potential for HOC exposure in surface water via transport from upgradient source areas will depend on the accuracy of the conceptual site model. The types of information that underpin the conceptual site model include the chemical composition of the contaminant source(s), the characteristics of fluid (aqueous and NAPL) transport in the subsurface, and the hydraulic connectivity between the subsurface system and the downgradient surface water system. Due to the low water solubility of HOCs, the potential for ground water to transport these contaminants to the surface water system will most likely be due to the existence of fast pathways for fluid transport (e.g., fluid flow through a subsurface fracture network) and/or the existence of chemical conditions that facilitate transport through porous subsurface media. Facilitated transport through porous, unconsolidated aquifers is most likely due to the presence of other organic constituents in the contaminant source that increase the dissolved concentrations of HOCs over that predicted by aqueous solubility (i.e., cosolvents or surfactants) and/or the generation of mobile colloidal phases. Assessing the relative importance of these factors will depend on review or acquisition of organic constituent composition data for waste materials that have been released to the subsurface, and the installation and sampling of a ground-water monitoring well network that minimizes sampling artifacts for colloid identification.

The decision analysis process illustrated in Figure 11 provides a summarized view of the upland, contaminant source characteristics that need evaluation in order to establish if facilitated transport of HOCs may occur at a given site. The decision analysis process is divided into three tiers that attempt to address all potential mechanisms that can result in HOC transport to surface water. The tiers are divided to address situations in which NAPL, ground water and mobile colloids are the primary medium for HOC movement in the subsurface. The following list summarizes the potential transport pathways considered in the decision analysis process.

Tier 1—NAPL as Primary Transport Medium

- Synthetic or natural surfactant compounds create NAPL emulsions that are more readily transported
- Cosolvents present in the source zone interact with NAPL to promote its movement through porous media

- NAPL is sufficiently mobile, or becomes remobilized, to represent a direct risk to the surface water body

Tier 2—Ground Water as Primary Transport Medium

- Source zone cosolvents completely or partially soluble in water increase HOC aqueous solubility
- Source zone surfactants increase HOC aqueous solubility

Tier 3—Mobile Colloids as Primary Transport Medium

- Conditions conducive to generation of mobile colloids; sample quality issues critical

The decision analysis process shown in Figure 11 incorporates consideration of the screening tests and monitoring system design recommendations highlighted in Sections 3.3 and 3.4. Screening evaluations of the relationship between TOC concentrations, IFT measurements, and HOC concentrations in ground-water samples can guide assessing the potential influence of cosolvents or surfactants within the contaminant plume. Likewise, screening evaluations of the relationship between ground-water turbidity and HOC concentrations provide a basis for assessing the potential influence of colloid-facilitated transport, provided demonstration that well installation or sampling artifacts are absent. In conjunction with knowledge of subsurface hydrogeology, these ground-water quality characteristics provide a basis for identifying potential pathways for plume discharge to surface water.

Following determination of a complete pathway for HOC transport to downgradient ecological receptors, delineation of the spatial extent and magnitude of contaminant flux migrating across the GW/SW transition zone will ultimately help target approaches to estimate the extent of bioaccumulation and/or ecological risk that more accurately capture realistic exposure scenarios for biota in the surface water body. Evaluation of the distribution of HOCs between the dissolved, NAPL, and/or colloidal/particulate phases, and the influence of this phase distribution on exposure/toxicity to ecological receptors, is particularly important where facilitated transport occurs. Where a complete exposure pathway exists from ground water to surface water, risks to ecological receptors can be estimated using the following methodologies:

- Compare chemical concentrations in ground water, interstitial water or overlying water to water-only toxicity values (i.e., effect concentrations) such as final chronic values (FCVs) or secondary chronic values (SCVs).

- Compare organic carbon normalized sediment concentrations to equilibrium partitioning sediment benchmarks (ESBs) derived from water-only effects concentrations and respective organic carbon-water partition coefficients.
- Compare concentrations derived from chemical uptake models or bioaccumulation studies to risk-based concentrations. Chemical uptake models utilizing HOC distribution in sediments, pore water and overlying surface water may employ laboratory-derived bioconcentration factors (BCFs), field-derived bioaccumulation factors (BAFs), or biota sediment accumulation factors (BSAFs).
- Compare results from toxicity and bioaccumulation tests to those from a reference site.

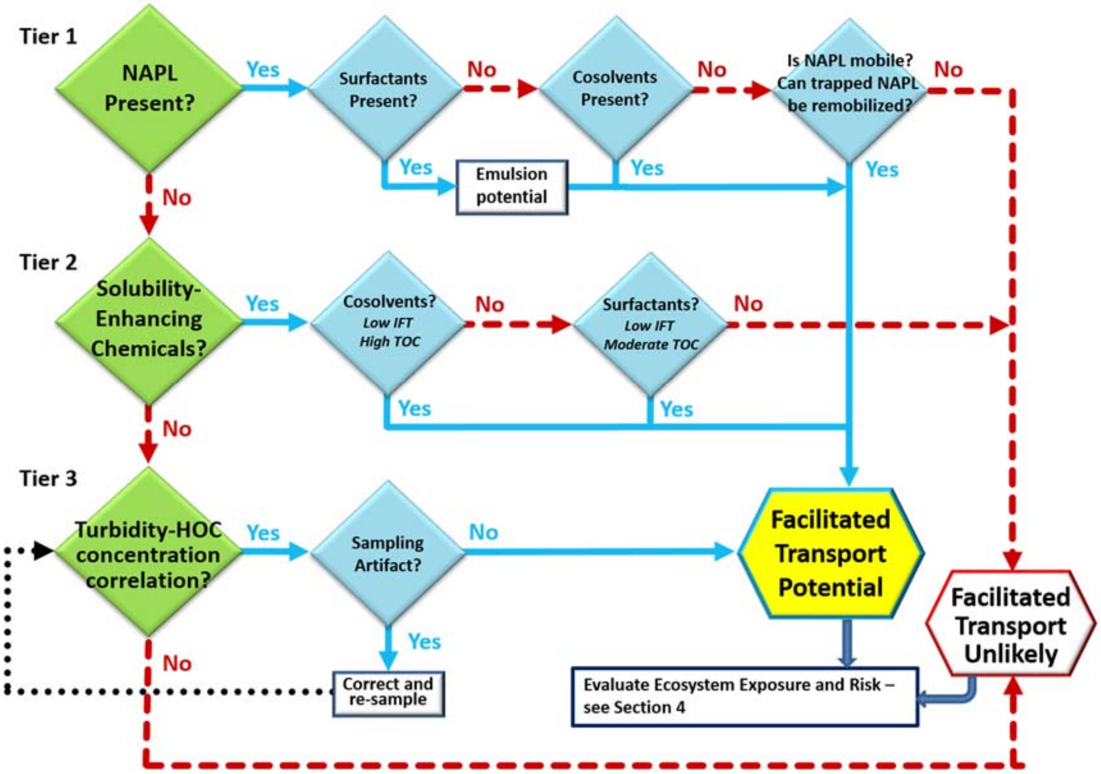

Figure 11. Decision Analysis Process for Assessing the Potential for Facilitated Subsurface Transport of Hydrophobic Organic Contaminants (HOCs). The analysis begins with the assessment of the presence of NAPLs, then proceeds forward based on evaluation of the organic constituent composition of the contaminant source and groundwater characterization data from screening measurements.

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