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Developing Sediment Remediation Goals at Superfund Sites Based on Pore Water for the Protection of Benthic Organisms from Direct Toxicity to Non-ionic Organic Contaminants

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Developing Sediment Remediation Goals at Superfund Sites Based on Pore Water for the Protection of Benthic Organisms from Direct Toxicity to Non-ionic Organic Contaminants

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Executive Summary

Evaluation of the risk posed to benthic organisms from contaminated sediments has been a long-standing technical challenge. This document contains a methodology for developing and applying pore water remediation goals (RGs) for nonionic organic pollutants (contaminants) in sediments for the protection of benthic organisms. The document provides the technical approach and basis for using the final chronic values (FCVs) from EPA's Ambient Water Quality Criteria (AWQC) for the protection of aquatic life or secondary chronic values (SCVs) derived using EPA's Great Lakes Water Quality Initiative (GLI) methodology to set the pore water RGs for contaminants in sediments, although other water column values may be appropriate at any specific site or situation. Concentrations of the contaminants in the sediment pore water are measured using passive sampling. The passive sampling measurements directly incorporate bioavailability of the chemicals at the site into the development of site-specific remediation goals for sediment. This document also discusses how to evaluate the consistency between passive sampling measurements and sediment toxicity testing results. When these data are consistent, one can be reasonably assured that the causes of toxicity to benthic organisms in the sediment have been correctly identified and that the developed pore water RGs for the contaminants will be protective of the benthic organisms at the site.

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Glossary

ACR	Acute to chronic toxicity ratio
AWQC	US-EPA Ambient Water Quality Criteria for the protection of aquatic life
$C_{Polymer}$	Concentration of chemical in polymer phase (µg/kg (dw))
C_S	Concentration of chemical in sediment on a bulk basis (µg/kg (dw))
$C_{S:PWRG}$	Pore water RG expressed as concentration in bulk sediment (µg/kg (dw))
$C_{SOC:PWRG}$	Pore water RG expressed as concentration in sediment on an organic carbon basis (µg/kg (organic-carbon))
C_{SOC}	Concentration of chemical in sediment on an organic carbon basis (µg/kg (OC))
C_{free}	Concentration of freely dissolved chemical in pore water (µg/L)
$C_{free:PWRG}$	Pore water RG expressed as freely dissolved concentration in water (µg/L)
COC	Contaminant of concern
CSM	Conceptual site model
DQO	Data Quality Objective
DOC	Dissolved Organic Carbon content of water (mg/L)
EC50	Effect concentration of the toxicant that gives half-maximal response
EqP	Equilibrium Partitioning
ERL	Effects Range-Low
ERM	Effects Range-Medium
ESB	Equilibrium partitioning sediment benchmark
f_{OC}	Fraction of carbon that is organic in a sediment (kg organic carbon/kg dry weight)
$f_{OC:SS}$	Site-specific f_{OC}
FAV	Final acute value
FCV	Final chronic value
GLI	Great Lakes Water Quality Initiative
K_{OW}	n-octanol/water partition coefficient for a chemical
K_{OC}	An organic carbon normalized sediment-water partition coefficient for a chemical (L/kg-organic carbon)
$K_{OC:SS}$	Site-specific K_{OC}
$K_{Polymer}$	Polymer/water partition coefficient for a chemical
LC50	Lethal effect concentration of the toxicant that gives half-maximal response
NAPL	Nonaqueous-phase liquid
PAH	Polycyclic aromatic hydrocarbon
PEC	Probable effects concentration
POC	Particulate organic carbon content of the water (mg/L)
PWTU	Pore water toxic unit
PRC	Performance reference compound
RG	Remediation goal
RI	Remedial investigation
RI/FS	Remedial investigation/feasibility study
SAP	Sampling and analysis plan
SCV	Secondary chronic values
SSD	Species sensitivity distribution

TEC	Threshold effects concentration
TU	Toxic unit
WOE	Weight of evidence

Section 1

Introduction

1.1 Background

Globally, numerous freshwater and marine ecosystems have contaminated sediments that pose risks to the environment and/or human health. The volumes of contaminated sediments in these ecosystems are large (e.g., in the United States quantities approaching billions of metric tons (Baker 1980; Long et al. 1996; US-EPA 2005a)), and the costs associated with managing contaminated sediments arising from navigational dredging activities and from site remediations (i.e., dredging, capping and post-remedy monitoring) are in the billions of dollars (US-EPA 2005a).

Because of the potential adverse ecological effects from contaminated sediments, regulatory agencies need thresholds for determining if unacceptable risks exist for sediments from specific sites (Mount et al. 2003; Wenning et al. 2005) and if these sites warrant cleanup. Developing contaminant concentrations in sediment that are associated with risk thresholds has been technically challenging. One of the first approaches developed was the sediment quality triad that combined sediment toxicity, sediment contaminant concentrations, and benthic community data to assess the amount of risk associated with the sediment of interest (Bay and Weisberg 2008; Chapman 1987; Chapman et al. 1987; Long and Chapman 1985). However, the costs, in time and dollars, associated with assessing contaminated sediment for ecological risk using approaches dependent on toxicity testing, bioaccumulation studies, benthic community, or other data-intensive tools are very high and has fueled the development of alternative approaches that use simpler and less expensive measures to predict adverse effects associated with contaminated sediments.

Several approaches for developing chemical-specific sediment quality benchmarks have been developed for classifying contaminated sediments as toxic or non-toxic. Many of the initial approaches were developed from collections of data on the chemical concentrations in sediment and results of laboratory sediment toxicity tests or other measures of biological effect. Examples include the Effects Range-Low (ERL) and Effects Range-Medium (ERM) values proposed by Long and Morgan (Long and Morgan 1991), and the Threshold Effects Concentration (TEC) and Probable Effects Concentration (PEC) developed by McDonald and others ((MacDonald et al. 1996; MacDonald et al. 2000); see Mount et al. (Mount et al. 2003) for more detail). Based on these approaches, guidelines were determined empirically from large datasets by using various algorithms for evaluating concentrations of chemicals in sediments that were or were not associated with adverse effects.

While these empirical guidelines were shown to have some ability to classify sediments into groups with higher probability of toxicity or non-toxicity, most were based on mass-based concentrations of sediment contaminants (e.g., μg/kg dry weight) and did not consider additional factors that were gaining recognition as influencing sediment toxicity. Many studies demonstrated that sediment characteristics such as organic carbon content and sulfide (generally associated with iron) affect contaminant bioavailability and cause widely varying toxicity among sediments with the same chemical concentration when expressed on a mass basis. These observations drove research to develop approaches to sediment guidelines that could account for differing contaminant bioavailability among sediments.

For nonionic organic contaminants, early work demonstrated that sediment organic carbon controlled the partitioning of those contaminants between sediment solids and pore water surrounding those solids. In the late 1970s and early 1980s, Karickhoff et al. (Karickhoff et al. 1979) demonstrated that sediment-water partitioning of hydrophobic organic contaminants was related to the hydrophobicity of the chemical and the organic carbon content of the sediment. Predictive relationships of the form log K_{OC} = a + b x log K_{OW} and K_{OC} = b x K_{OW} were developed where K_{OC} is the sediment-water partition coefficient on an organic carbon basis and K_{OW} is the n-octanol-water partition coefficient for the chemical of interest. Additionally, their research demonstrated that the K_{OC} was independent of chemical concentration and could be described as a chemical-specific equilibrium constant. This constant, i.e., partition coefficient, is found using the equation:

$$K_{OC} = (C_s/f_{OC})/C_{free} \quad (1\text{-}1)$$

where C_S is the concentration of chemical in the bulk sediment (µg/kg dry weight), f_{OC} is the organic carbon content of the sediment (kg-organic carbon/kg-dry weight), K_{OC} is the organic carbon normalized sediment-water partition coefficient (L/kg-dry weight), and C_{free} is the freely dissolved chemical concentration in the sediment pore water (µg/L).

Freely dissolved chemical in water is chemical held in solution by water molecules only, and is not associated with dissolved organic carbon (DOC), particulate organic carbon (POC), or colloids in the water phase. The freely dissolved concentrations in water can never exceed the aqueous solubility of the chemical. For chemicals with log K_{OW}s less than 5, the chemical's C_{free} value and total concentration of the chemical in water (determined by the extraction of bulk water phase) are nearly identical. For chemicals with log K_{OW}s greater than 5, the chemical's C_{free} value is less than the chemical's total concentration in the water because the chemical sorbs to DOC, colloids, and POC in the water. With increasing K_{OW}, the portion of the total chemical that is freely dissolved decrease significantly.

The link between partitioning of organic chemicals and sediment toxicity was demonstrated in experiments by Adams et al. (Adams et al. 1985). In this classic study, midge larva (*Chironomus dilutus*, then *C. tentans*) were exposed to three different sediments spiked with the pesticide Kepone. The concentrations of Kepone in these sediments causing toxicity to midge varied by two orders of magnitude when the pesticide concentrations in the sediment were compared on the conventional basis of chemical mass per mass of dry sediment (Figure 1-1a). However, when exposure was expressed on the basis of Kepone concentration in the sediment pore water (chemical mass per L), the exposure-response curves for the three sediments were very similar (Figure 1-1b). Not only were the curves similar, but the concentration at which effects occurred in pore water was comparable to the Kepone concentration associated with toxicity in water only exposure. This suggested that one could predict the toxicity of a sediment by measuring (or predicting) the chemical concentration in the sediment pore water. As discussed above, sediment organic carbon was thought to be the primary sediment phase controlling partitioning between sediment solids and the pore water; when Adams normalized sediment Kepone concentrations to the organic carbon content of each sediment (chemical mass per mass organic carbon), toxicity of the three sediments were very similar, as it had been when expressed based on pore water (Figure 1-1c).

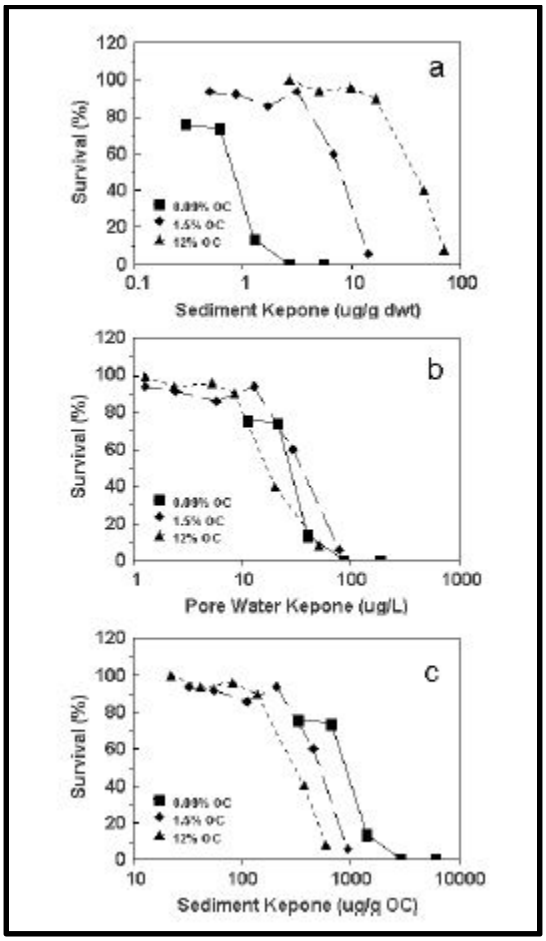

Figure 1-1. Toxicity of three Kepone-spiked sediments with different organic carbon content, expressed as Kepone in bulk sediment (a), Kepone in pore water (b), and organic carbon normalized Kepone in sediment (c). Redrawn from Adams et al. (1985).

Historically, measurement of concentrations of nonionic organic chemicals in sediment pore water was extremely challenging, and the method of choice for the isolation of pore water from the bulk solids was centrifugation. As stated in the ATSM sediment collection and handling standard E 1391-03 (ASTM 1994), the "principle aim is to use procedures that minimize changes to the *in-situ* condition of the water. It should be recognized that most sediment collection and processing methods have been shown to alter pore water chemistry, thereby potentially altering target contaminant bioavailability and toxicity" (see (Adams 1991; Adams et al. 2003; Ankley and Schubauer-Berigan 1994; ASTM 1994; Bufflap and Allen 1995; Carr and Nipper 2003; Sarda and Burton 1995; Schults et al. 1992)). As discussed in US-EPA (US-EPA 2012b) and ASTM (ASTM 1994), the potential for artifacts in the isolation process can be large depending upon the technique. Centrifugation was the preferred technique because of its ease of implementation in the laboratory and when performed with minimum of artifacts, can provide reliable quantifications. Sampling artifacts with centrifugation include the formation of dissolved and colloidal organic matter during pore water preparation and isolation that can result in an overestimation of the contaminant concentrations in the pore water (Burgess and McKinney 1997). Other potential artifacts can arise from absorption and adsorption, leading to the loss of the chemical to laboratory equipment

surfaces. Further, changes in redox potential can lead to the formation of new artificial particles caused by oxidation of reduced iron. A final challenge is that concentrations of highly hydrophobic contaminants in pore water can be very low, making analytical quantification difficult without exceptional laboratory technique (Adams et al. 2003; Ozretich and Schults 1998; Schults et al. 1992; US-EPA 2012a). However, as sediment assessment approaches were evolving during the 1990s, considerable uncertainty remained as to whether the challenges of accurate isolation and analysis would preclude reliance on pore water as a routine measurement for sediment assessment.

Rather than relying on direct analysis of pore water, focus shifted to basing guidelines on the more easily measured bulk sediment concentrations, and predicting chemical concentration in pore water using equilibrium partitioning relationships. EPA pursued the developing of sediment guidelines using the physical-chemical concept of Equilibrium Partitioning (EqP) proposed by Di Toro et al. (Di Toro et al. 1991). Simply put, EqP asserts that a contaminant's bioavailability is directly proportional to its chemical activity in sediment. EqP also asserts that a contaminant in bedded sediment is at equilibrium across all sediment phases, and as a result, the chemical activity of the contaminant is the same in all sediment phases. Since the freely dissolved concentration in pore water corresponds closely with chemical activity, this rationalizes the concept that bioavailability and toxicity are proportional to concentration in pore water as demonstrated by Adams and others. It's worth noting that despite its emphasis on chemical activity/concentration in pore water, EqP does not assume that pore water is the only route of exposure to organisms. Rather, the assumption is that the chemical activity (which is analogous to fugacity which be conceptualized as "chemical pressure") is the same among all sediment compartments (because they are in equilibrium) and therefore the intensity of organism exposure is the same regardless of the route, i.e., via sediment ingestion, pore water, dermal contact, or any combination of the three exposure routes.

Further analyses by Di Toro et al. (Di Toro et al. 1991) affirmed the findings of Adams (Adams et al. 1985), demonstrating that the freely dissolved concentration in pore water is not only proportional to toxicity, but directly comparable to the concentration causing effects in water only exposures to the same organism. Since most waters used for toxicity testing are generally low in dissolved organic carbon and other binding phases, nonionic organic chemicals that do not exhibit extreme hydrophobicity (Log Kow < 6) will be present in toxicity tests primarily in the freely dissolved form. Thus, it makes sense that similar toxicity occurs in a water only exposure of the chemical and a sediment exposure with a freely dissolved pore water concentration equaling that of the water only exposure. Thus, EqP can be used to estimate contaminant concentrations in sediments pore water that are in equilibrium with the bulk sediments concentrations corresponding to specific levels of toxicity (or non-toxicity) observed in water only toxicity tests.

For many chemicals, EPA has derived water quality criteria for the protection of aquatic life, which are chemical concentrations in water below which unacceptable effects on aquatic organisms are not expected. Using water quality criteria as threshold values for toxicity in water, the EqP approach translates these into bulk sediment concentrations using organic carbon normalized sediment-water partition coefficients (K_{OC}s) for the chemical of interest. Using this approach, EPA has developed mechanistic based sediment quality guidelines known as Equilibrium Partitioning Sediment Benchmarks (ESBs) for a number of common sediment contaminants, including 34 polycyclic aromatic hydrocarbons, 31 other nonionic organic chemicals, and metal mixtures (e.g., cadmium, chromium, copper, nickel, lead, silver, and zinc) (Burgess et al. 2013; US-EPA 2003a; US-EPA 2003b; US-EPA 2003c; US-EPA 2005b; US-EPA 2008). For the nonionic organic chemicals, the ESBs are expressed on an organic carbon normalized concentrations in the bulk sediment (i.e., ug/g-organic carbon). For metals, the ESBs are expressed on a

µmole/g-organic carbon basis in the bulk sediment after considering sequestration of metals by acid volatile sulfides (AVS) and organic carbon, or on a µg/L basis when metals are measured directly in the sediment pore water.

While the theoretical underpinnings of the ESBs approach are strong, their accuracy in application is dependent on the robustness of their underlying assumptions. In particular, the generic formulation of the ESBs uses a single K_{OC} value for each chemical. This single K_{OC} value is assumed to be appropriate for all sediments and does not change as a function of the quantity or quality of the organic carbon in the sediment (Burgess et al. 2000; Dewitt et al. 1992). Later research and practical experience has shown "organic carbon" in sediments includes a variety of diagenic, petrogenic, and pyrogenic forms, and these different forms can have different K_{OC} values, potentially resulting in different partitioning across various sediment types (Cornelissen et al. 2005; Hawthorne et al. 2006; Hawthorne et al. 2011; Jonker et al. 2003). Depending on the chemical and carbon type, these differences can range from negligible to substantial; in the particular case of PAHs, sediment-specific K_{OC} values for a single compound have been shown to vary as much as 100-fold. This can create substantial uncertainty in the assessment of ecological risks posed by such sediments.

In the past decade since EPA's development of the EqP approach and resulting ESBs, much work has been performed on developing the passive sampling technique for estimating the freely dissolved concentrations of contaminants in the column water and sediments (Hawthorne et al. 2009; Jahnke et al. 2012; Lydy et al. 2014; Maruya et al. 2009; Mayer et al. 2014; US-EPA 2012b). The passive sampling technique does not require isolation of the sediment pore water from the bulk sediment but rather is performed on the whole sediment (in the laboratory and field) or a sediment-water slurry. The technique is nondestructive, does not change the internal partitioning of the chemical among the sediment phases (i.e., solids, particulate, colloidal, dissolved carbon, and aqueous phases), and can be performed on small samples of wet sediment. In this approach, an organic polymer is placed into a sediment or sediment-water slurry, and allowed to equilibrate with the COCs. Polymers include low density polyethylene, polyoxymethylene and polydimethylsiloxane. During the deployment time, the contaminants diffuse from the pore water into the polymer and after their retrieval from the sediment, the chemicals in the polymer are quantified. With the resulting data, C_{free} for the chemicals of interest in sediment pore water can be estimated with minimal artifacts, and the technique is relatively simple to perform in the laboratory and field (Burgess et al. 2015; Fernandez et al. 2014; Gschwend et al. 2011).

The development of reliable techniques to measure chemical concentrations in pore water brings the EqP approach full circle; rather than basing the assessment on bulk sediment concentrations and predicting partitioning to pore water, a proxy for the chemical activity of sediment contaminants can be measured directly via passive sampling of pore water, and C_{free} concentrations can be used to predict residues and toxicity for benthic organisms (Kraaij et al. 2002).

1.2 Purpose and Scope

In light of the improved technologies and understanding described above, EPA's Office of Superfund Remediation and Technology Innovation requested that the Office of Research and Development develop guidance on applying these approaches to develop pore water Remediation Goals (RGs) for the protection of benthic organisms. Like the ESBs, pore water RGs are intended to protect organisms living in and on the sediments (e.g., oligochaetes, annelids, amphipods, bivalves, arthropods, and other invertebrates) from direct toxicity from sediment contaminants. This guidance is not designed to

explicitly protect higher trophic level benthic species from effects associated with food chain biomagnification (e.g., crab, lobster, catfish, and carp) or pelagic organisms. While the approach should be applicable to nonionic chemicals generally, specific values are provided for polycyclic aromatic hydrocarbons (PAHs), several pesticides, chlorobenzenes, several low molecular weight organic compounds, and some phthalates. Although ESBs have been developed for cationic metals (Cu, Cd, Zn, Pb, Ni, Ag), pore water RGs are not presented because passive sampling technology for these chemicals is in a different stage of development and standardization; however, a similar conceptual approach could be implemented using guidance contained in the ESB document for metals mixtures (US-EPA 2005b). Unless there is reason to believe that the toxicity or bioavailability would be fundamentally different in freshwater and marine ecosystems, the guidance provided is generally applicable to both. Applying the pore water RG approach requires two basic elements: a) a method for measuring or inferring the freely dissolved concentration of contaminant in pore water (C_{free}); and b) a toxicity threshold chemical concentration that delineates acceptable and unacceptable exposures. These elements are the focus of Sections 2 and 3 (respectively) of this document. Section 4 discusses how these two measures are brought together to evaluate sediments for compliance with pore water RGs.

Section 2

Estimating the Freely Dissolved Concentrations of Nonionic Organic Chemicals in Sediment Pore Water

As discussed in the Introduction, centrifugation has been a common technique for isolating pore water and measuring C_{free}. With the development of the passive sampling technique for estimating C_{free} in sediment and overlying water (Hawthorne et al. 2009; Lydy et al. 2014; Maruya et al. 2009; Mayer et al. 2014), the passive sampling technique is now the recommended approach for measuring the concentrations of chemicals in the sediment pore water. The passive sampling technique is relatively simple to perform in the laboratory and has lower potential for sample handling and processing artifacts in comparison to the centrifugation technique.

2.1 Measuring Freely Dissolved Chemical Concentrations (C_{free}) in Sediment Pore Water using Passive Sampling

With the passive sampling technique, a thin sheet or fiber of an organic polymer is equilibrated with the sediment (US-EPA 2012a; US-EPA 2012b). The target contaminant sorbs to the polymer, and after an appropriate equilibration time (typically 28-days), the chemical achieves equilibrium between the polymer; freely dissolved, colloidal, DOC and POC phases in the pore water; and the solids in the sediment. With knowledge of the partition coefficient between the freely dissolved chemical and the polymer, the freely dissolved concentration in the pore water can be determined after measurement of the concentration of the chemical in the polymer ($C_{Polymer}$). In equation form, C_{free} is computed:

$$C_{free} = C_{Polymer}/K_{Polymer} \quad (2\text{-}1)$$

where, $K_{Polymer}$ is the polymer-water partition coefficient for the chemical of interest. The $K_{Polymer}$ values are determined by equilibration studies in the laboratory, and in these studies, high purity water with dissolved chemical is equilibrated with the passive sampler. After equilibration, both phases are analyzed in order to compute the $K_{Polymer}$ value. Many of these values are available in the scientific literature for contaminants of concern like chlorinated pesticides and PAHs (US-EPA 2012a).

When a passive sampler is equilibrated with a sediment sample, equilibrium can be demonstrated by measuring a time series of $C_{Polymer}$ values and when these values don't change significantly over time, equilibrium conditions have been obtained (Mayer et al. 2014). Another approach for demonstrating equilibrium conditions is to use passive samplers with different surface to volume ratios, and when the $C_{Polymer}$ values are the same at a single time point in the equilibration process, equilibrium has been obtained (Mayer et al. 2014).

There will be cases where equilibrium conditions for more hydrophobic contaminants are not attained in the experimental time frame of 28-days. Causes of non-equilibrium conditions include slow diffusion kinetics for highly hydrophobic chemicals like dibenz[a,h]anthracene, slow desorption kinetics from soot (e.g., black carbon phases) to the pore water, presence of oils and greases, and potentially, biological growth on the passive sampler. To account for non-equilibrium conditions, passive sampling is often performed using performance reference compounds (PRCs) where the PRCs are loaded into the sampler prior to their equilibration with the sediment (Fernandez et al. 2009; Huckins et al. 2006; Reible and Lotufo 2012). If measurements demonstrate that all of the PRCs were lost from the sampler during

their equilibration, equilibrium conditions were obtained. If not, the loss of the PRCs enables one to determine the extent of the equilibration of the target contaminants. Assuming the loss kinetics of the PRCs from the polymer are similar to the uptake kinetics for the target chemicals of interest, for target chemicals not at equilibrium, the actual freely dissolved concentrations of the target chemicals at equilibrium can be calculated.

Passive sampling performed under actual equilibrium conditions or using PRCs to estimate equilibrium conditions provides accurate estimates of the bioavailable (freely dissolved) chemical in the sediment pore water. Two US-EPA documents provide details on the passive sampling approach (US-EPA 2012a; US-EPA 2012b), and field and laboratory procedures for using passive sampling are discussed in a US-EPA/SEDP/ESTCP (US-EPA/SERDP/ESTCP 2017) report. In addition, a series of papers from a recent SETAC workshop titled "Guidance on Passive Sampling Methods to Improve Management of Contaminated Sediments" published in *Integrated Environmental Assessment and Management* provided further information on the passive sampling technique (Ghosh et al. 2014; Greenberg et al. 2014; Lydy et al. 2014; Mayer et al. 2014; Parkerton and Maruya 2014; Peijnenburg et al. 2014).

2.1.1 Passive Sampler Fouling

Fouling occurs when the surface of the passive sampler is coated in a biological growth, nonaqueous-phase liquids (NAPL), or other organic material and is a well-known issue with this methodology. PRCs can be used to correct for the effects of biological growth or the presence of organic matter on chemical uptake by the sampler. For further information on PRCs and their use, consult the following references (Ghosh et al. 2014; Lydy et al. 2014; US-EPA 2012a; US-EPA 2012b; US-EPA/SERDP/ESTCP 2017).

At some sites, NAPL will be present, and samplers that come in contact with NAPL can become fouled. PRCs cannot be used to account for the effects of NAPL fouling. If the NAPL is not properly removed from the sampler prior to its analysis, passive sampler results will lead to overestimations of C_{free} (Heijden and Jonker 2009). Additionally, NAPL fouling may result in estimated concentrations in water above the chemical's solubility and potentially, increased variability. As suggested by Ghosh et al. (Ghosh et al. 2014), users should record incidents of NAPL presence and be aware of the potential for artifacts in the resulting data.

2.1.2 Passive Samplers: *In-situ* and *Ex-situ* Measurement

Passive samplers can be deployed in the field (*in-situ*) and in the laboratory (*ex-situ*). There are a number of reasons for performing *in-situ* passive sampling measurements. Primarily, the field measurements capture all processes and conditions existing at the site that would be difficult to replicate in the laboratory (Ghosh et al. 2014). Some of these processes and conditions include temperature, light, bioturbation, pH, salinity, sediment resuspension, groundwater flows, organism activity, and biodegradation of the contaminants, and all of these factors affect the target contaminants behavior in the sediment pore water. The major challenge with *in-situ* passive sampling is determining whether or not the target contaminants have achieved equilibrium with the passive sampler. As discussed earlier, there are at least four ways to address this issue including the use of performance reference compounds (PRCs) and temporal sampling (Lydy et al. 2014). Devices for passive sampling in sediments in the field are readily available (e.g.,(Lydy et al. 2014; Mayer et al. 2014; US-EPA 2012b; Witt et al. 2013)). *In-situ* sampling requires at least two field efforts, once to

deploy the devices and a second, to retrieve the devices. One critical issue with field sampling is that devices can be lost, damaged, or vandalized.

There are also a number of reasons for performing *ex-situ* measurements. *Ex-situ* measurements can be performed easily on numerous sediment samples, and *ex-situ* measurements requires only one sampling trip in terms of resources (i.e., collect sediments). A principle advantage of *ex-situ* sampling is that laboratory conditions can be manipulated to insure equilibrium is achieved between the target contaminants and passive sampler resulting in greater confidence in C_{free} estimates. For example, the sediments and passive samplers can be rolled to enhance contaminant transfer between environmental phases. One of the drawbacks of e*x-situ* deployments is that the measurements are only as good as the collected sediment samples. For example, collection of the top few centimeters of surficial sediment is difficult. Overall, the effects of sample collection, storage, and handling in the laboratory are incorporated into the *ex-situ* measurements. In addition, as discussed, unlike the *in-situ* deployments, *ex-situ* deployments do not incorporate realistic field conditions.

Studies comparing *in-situ* and *ex-situ* measurements of contaminant concentrations in sediment pore water are limited. Witt et al. (Witt et al. 2013) has demonstrated comparable measurements between *in-situ* and *ex-situ* measurements for PAHs and PCBs. In addition, Fernandez et al. (Fernandez et al. 2014) compared *in-situ* and *ex-situ* passive sampling for PCBs and DDTs at the Palos Verdes Shelf Superfund site located off the coast of Los Angeles (CA, USA). Good levels of agreement were observed in the calculation of DDT and PCB C_{free} values when comparing *ex-situ* passive samplers in rolled sediments to *in-situ* PRC-corrected passive samplers.

For applying the methodology in this document, *in-situ* and *ex-situ* measurements are acceptable.

2.2 Measuring Chemical Concentrations in Sediment Pore Water using Solid Phase Microextraction, ATSM Method D7363-13 and EPA Method 8272

Another approach to measuring freely dissolved nonionic organic chemical concentrations in sediment pore water is ASTM Method D7363-13 (ASTM 2013) or equivalently, EPA method 8272 (US-EPA 2007a). The method developed by Hawthorne et al. (Hawthorne et al. 2005) isolates and measures concentrations of pore water target contaminants by absorption to a solid-phase-microextraction (SPME) fiber. This method has been very effective for determining the concentration of several legacy nonionic organic contaminants in contaminated sediment pore waters (Arp et al. 2011; Hawthorne et al. 2007; Hawthorne et al. 2009; Hawthorne et al. 2008) and has been adopted as US-EPA method 8272 (US-EPA 2007a) and ASTM method D7363-13 (ASTM 2013). This method is not an equilibrium-based passive sampling method as described in 2.1 above and does not generate C_{free} values. In the Hawthorne et al. (Hawthorne et al. 2005) method, the pore water is isolated from the sediment or sediment slurry by centrifugation and treated with alum to precipitate and remove colloidal organic carbon. Deuterated internal standards are added to the isolated colloidal carbon-reduced pore water and subsequently, the SPME fiber is introduced into the sample. In this application, the SPME fiber is acting like an organic solvent in that the fiber is extracting any dissolved contaminants from the pore water sample into the PDMS polymer coating on the fiber. The fiber is then thermally desorbed and

analyzed for target contaminants. The dissolved concentrations are calculated based on the ratio of analytes to corresponding internal standards. This process creates an operationally defined form of C_{free} (i.e., pore water minus colloidal and dissolved organic matter precipitated by alum).

Section 3

Establishing Adverse Effects Concentrations in Sediment Pore Water for Benthic Organisms

3.1 Use of Aquatic Life Criteria as an Effect Benchmark

As outlined in the introduction, implementation of the pore water RG approach requires a threshold chemical concentration that delineates acceptable and unacceptable exposures. In the development of EPA's ESBs, the water only effect concentration chosen was the EPA Ambient Water Quality Criterion (AWQC) for the protection of aquatic life, and more specifically the "Final Chronic Value" (FCV). The FCV is a derived value that is intended to estimate a concentration that would protect 95% of tested species from chronic toxicity under long-term exposure. At contaminated sediment sites, a majority of benthic organisms are exposed to the sediment contaminants for their entire life cycle and resultantly, chronic exposure was selected as the appropriate time frame for exposure. In addition, the intended level of protection of the FCV, protecting the vast majority of organisms, was deemed an appropriate protection goal for ESBs. Pore water RGs as proposed here, are intended to provide this same level of protection, and therefore use the FCV (or an estimate thereof) as the effect threshold.

EPA's 1985 guidelines for deriving AWQC (Stephan et al. 1985) has stringent data requirements for developing AWQCs, and often sufficient data are not available to derive a FCV for a chemical. For some of the common sediment contaminants that don't have AWQCs, alternative methods are available for estimating the equivalent of a final chronic value, specifically the Great Lakes Water Quality Initiative (GLI) methodology (US-EPA 1995; US-EPA 2008). The GLI methodology was developed from a comprehensive distributional analysis of the relationship between the lowest available toxicity values and FCVs derived using the 1985 AWQC guidelines. Adjustment factors were developed to account for the uncertainties that exist when toxicity data are limited, and these factors can be applied to the available data to provide a reasonably conservative estimate of the FCV; these estimated FCV values are called "Secondary Chronic Values" or SCVs. FCVs and SCVs for many common sediment contaminants are provided in Table 3-1. For reference, Table 3-1 also contains EPA's ESBs for many common sediment contaminants.

Polycyclic aromatic hydrocarbons (PAHs) are common COCs at Superfund sediment sites, and have several characteristics that present challenges in the development of pore water RG. First, PAHs as a group represent a wide range of chemical structures that co-occur in the environment, and not all of these are commonly measured in routine sediment monitoring programs. Second, depending on the organism and the specific PAHs involved, PAHs can exert toxicity through multiple mechanisms, including narcosis, carcinogenicity, and mutagenicity, as well as photo-enhanced toxicity (US-EPA 2003c). For benthic invertebrates, it is believed that the narcosis mechanism determines the potency of sediment exposures to PAHs, and EPA has developed an ESB for PAH mixtures on that basis (Di Toro and McGrath 2000; Di Toro et al. 2000; Mount et al. 2003; US-EPA 2003c). An additional feature of the narcosis mechanism is that all PAHs contribute additively to the toxic effect, so effect concentrations in water are based not on the single PAHs, but on the aggregate potency of all measured PAHs. To assess the potency of individual PAHs, EPA used an approach similar to that described in the 1985 guidelines to

derive a FCV for each individual PAH; fractional contributions of each PAH are then calculated and summed to determine the additive potency of the mixture. Additional details on the derivation of water column potency estimates (used here as pore water RGs) are provided in the PAH ESB document (US-EPA 2003d). Section 4 of this document describes how pore water RG calculations for PAHs are performed.

Table 3-1 provides pore water RG values for a variety of chemicals based on their FCV or SCV values. Some of the chemicals in Table 3-1 that have SCV values are believed to affect benthic invertebrates through a narcosis mechanism. Because narcotic chemicals appear to have comparatively small inter-species differences in potency, as well as a comparatively small acute-chronic ratio, the GLI procedure for calculating an SCV tends to be fairly conservative when applied to narcotic chemicals, particularly those for which only limited data are available (therefore having relatively large uncertainty factors applied). For reference, Table 3-1 also contains pore water RGs calculated based on an assumed narcosis mechanism of action, based on the methods of DiToro et al. (Di Toro et al. 2000). These narcosis-based pore water RGs can be used instead of the GLI SCV for chemicals expected to act through the narcosis mechanism. However, if narcosis pore water RGs from Table 3-1 are used, it must be remembered that all narcotics present will contribute additively to the overall potency of the chemical mixture in the sediment, so compliance with an pore water RG must be assessed on an additive basis, combining the fractional contributions of all narcotic chemicals present. For the detailed derivation of the narcosis SCVs, the reader should consult EPA 2003 and 2008 (US-EPA 2003c; US-EPA 2008). Recently, Kipka and DiToro (Kipka and Di Toro 2009) extended the target lipid model of narcotic toxicity to polar narcotic chemicals using a polyparameter linear free-energy relationship (LFER). With the LFER model, narcosis SCVs for polar organics can now be derived when needed.

3.2 Sensitivities of Benthic and Pelagic Organisms

The calculation methodology for FCV and SCV values combined toxicity data for benthic and pelagic organisms, which provides a more robust and phylogenetically diverse sensitivity distribution. Applying FCV/SCV values as pore water RGs assumes that there is no inherent bias in applying these values in contexts where protection of benthic organisms is the explicit goal. The appropriateness of this assumption has been evaluated in a number of analyses, asking the question, “Are benthic organisms consistently more or less sensitive to chemical toxicants than are pelagic organisms?”

Figure 3-1 compares the acute toxicity values for the most sensitive benthic (infaunal and epibenthic) species to the most sensitive water column species (Di Toro et al. 1991). The data are from the 40 freshwater and 30 saltwater draft or published AWQC documents that meet minimum data base requirements for calculation of a final acute value (FAV). Plotted in Figure 3-1 are the lowest (i.e., most sensitive) LC50 values (lethal effect concentration of the toxicant that gives half-maximal response) for water column and benthic species, plotted separately for freshwater and marine organisms. As can be seen, the values are distributed closely around the unity, with no evidence of consistent bias above or below the line. This supports the assumption of equal sensitivity between benthic and water column organisms (Di Toro et al. 1991).

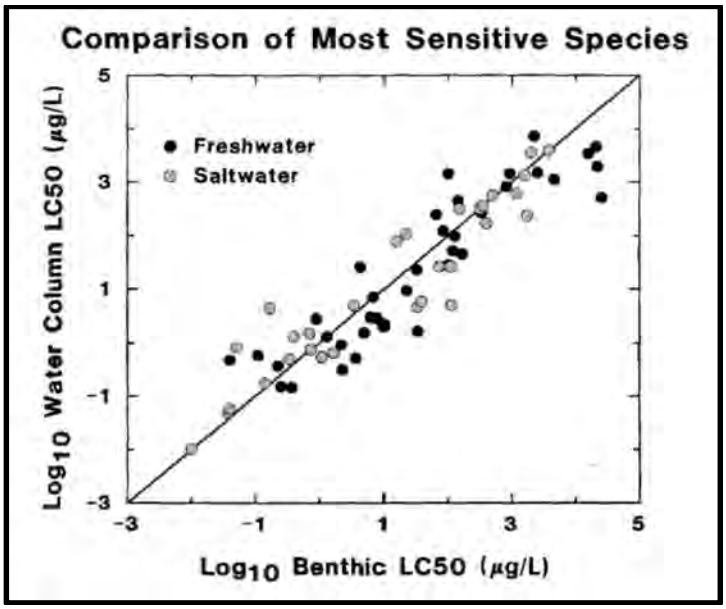

Figure 3-1. A comparison of the minimum LC50 for infaunal and epibenthic species (x-axis) and water column (y-axis) species. Each data point represents a particular chemical in either a freshwater and saltwater exposure. The diagonal line indicates a 1:1 relationship. The data are from AWQC or draft criteria documents (Di Toro et al. 1991). Reprinted with permission.

Figure 3-1 combines data across chemicals, but evaluates only the most sensitive organism for each chemical. Another way to address the benthic vs water column (pelagic) sensitivity question is to look at the distribution of values within the species sensitivity distribution (SSD) for a single chemical. Figures 3-2 to 3-4 show the SSDs of LC50 values for dieldrin (US-EPA 2003a), endrin (US-EPA 2003b), and PAH mixtures (US-EPA 2003c). The symbols represent broad phylogenetic groupings, and filled and open symbols show species that are benthic and pelagic, respectively. Examination of these figures shows that benthic and pelagic species are well distributed across the range in organism sensitivity, and all three plots have benthic species with sensitivities at or near the lower end of the distribution. Statistical analysis of these distributions can be found in the referenced source documents.

The above conclusion of similar sensitivities between benthic and pelagic organisms is further supported by a more recent analysis by Redman et al. (Redman et al. 2014). Redman et al. (2014) demonstrated that SSDs for terrestrial (soil) and benthic (sediment) species were similar to SSDs for aquatic species, i.e., differences less than 2 fold. Further, SSDs for acute-to-chronic toxicity ratios were similar for aquatic and soil/sediment species.

Based upon these analyses from Di Toro et al. (Di Toro et al. 1991), Redman et al. (Redman et al. 2014), and EPA's ESBs documents (US-EPA 2003a; US-EPA 2003b; US-EPA 2003c), the uniform conclusion is that there is no evidence that the toxicant sensitivity of benthic organisms is systematically biased relative to water column organisms. This in turn supports the use of FCV and SCV values calculated from toxicity data sets combining benthic and pelagic species, as is performed in the derivation of AWQC and GLI Tier II SCVs.

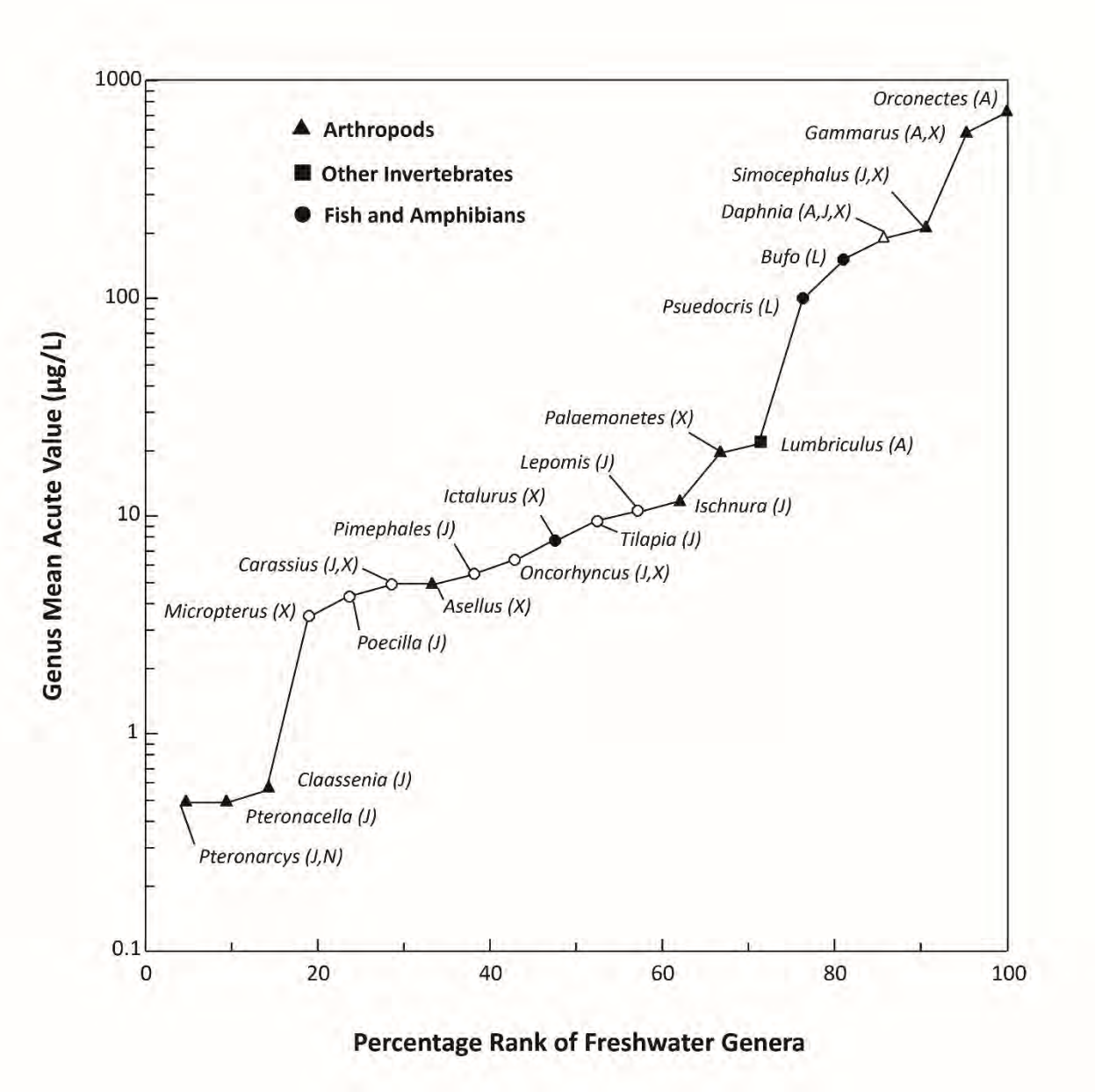

Figure 3-2. Species Sensitivity Distribution (SSD) for dieldrin of freshwater genera for acute toxicity (US-EPA 2003a). Genus mean acute values from water-only acute toxicity tests using freshwater species versus percentage rank of their sensitivity. Symbols representing benthic species are solid; those representing water column species are open. A=adult, J=juvenile, N=naiads, X=unspecified life-stage.

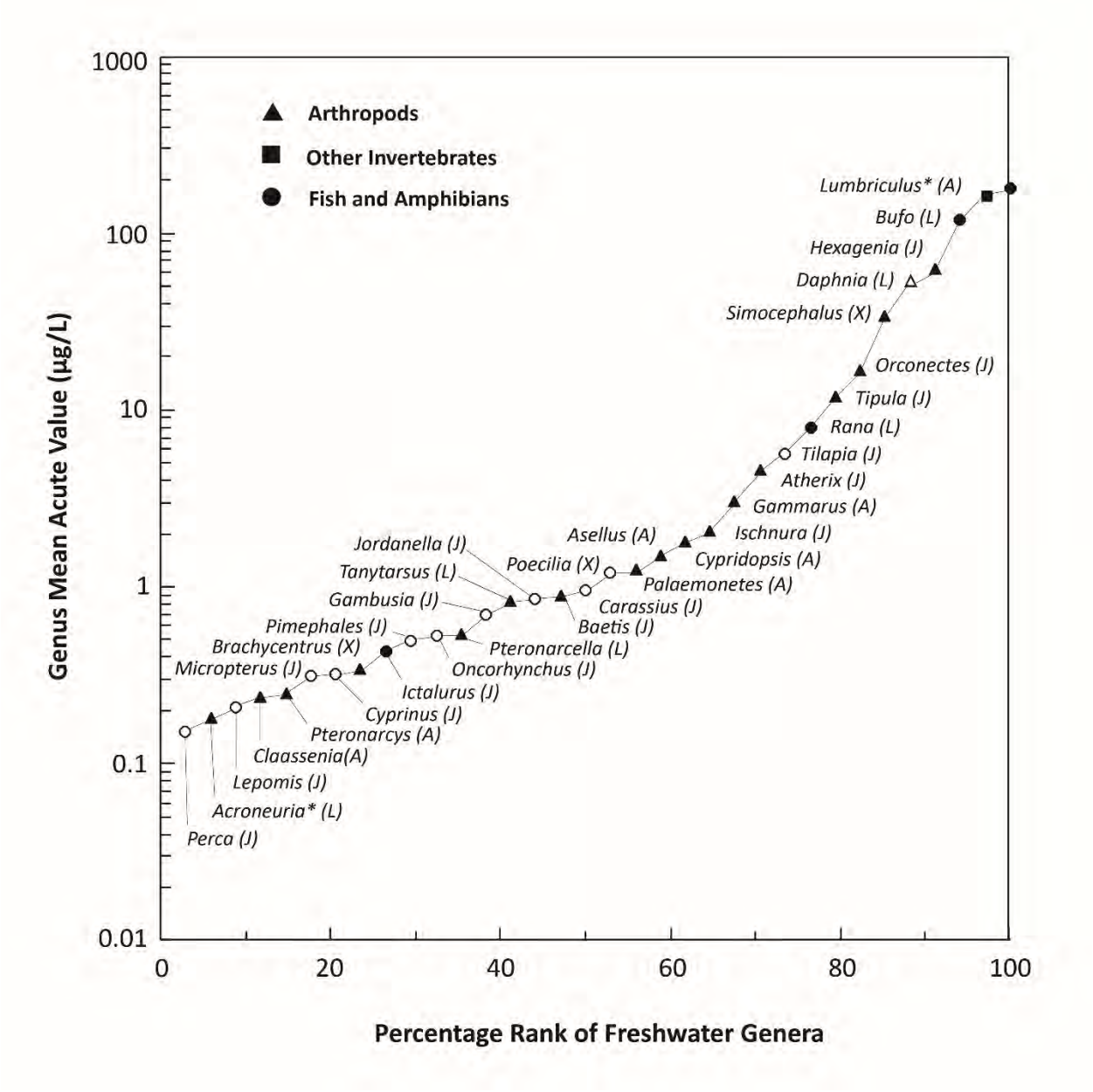

Figure 3-3. Species Sensitivity Distribution (SSD) for endrin of freshwater species for acute toxicity (US-EPA 2003b). Genus mean acute values from water-only acute toxicity tests using freshwater species versus percentage rank of their sensitivity. Symbols representing benthic species are solid; those representing water column species are open. Asterisks indicate greater than values. A = adult, J = juvenile, L = larvae, X = unspecified life-stage.

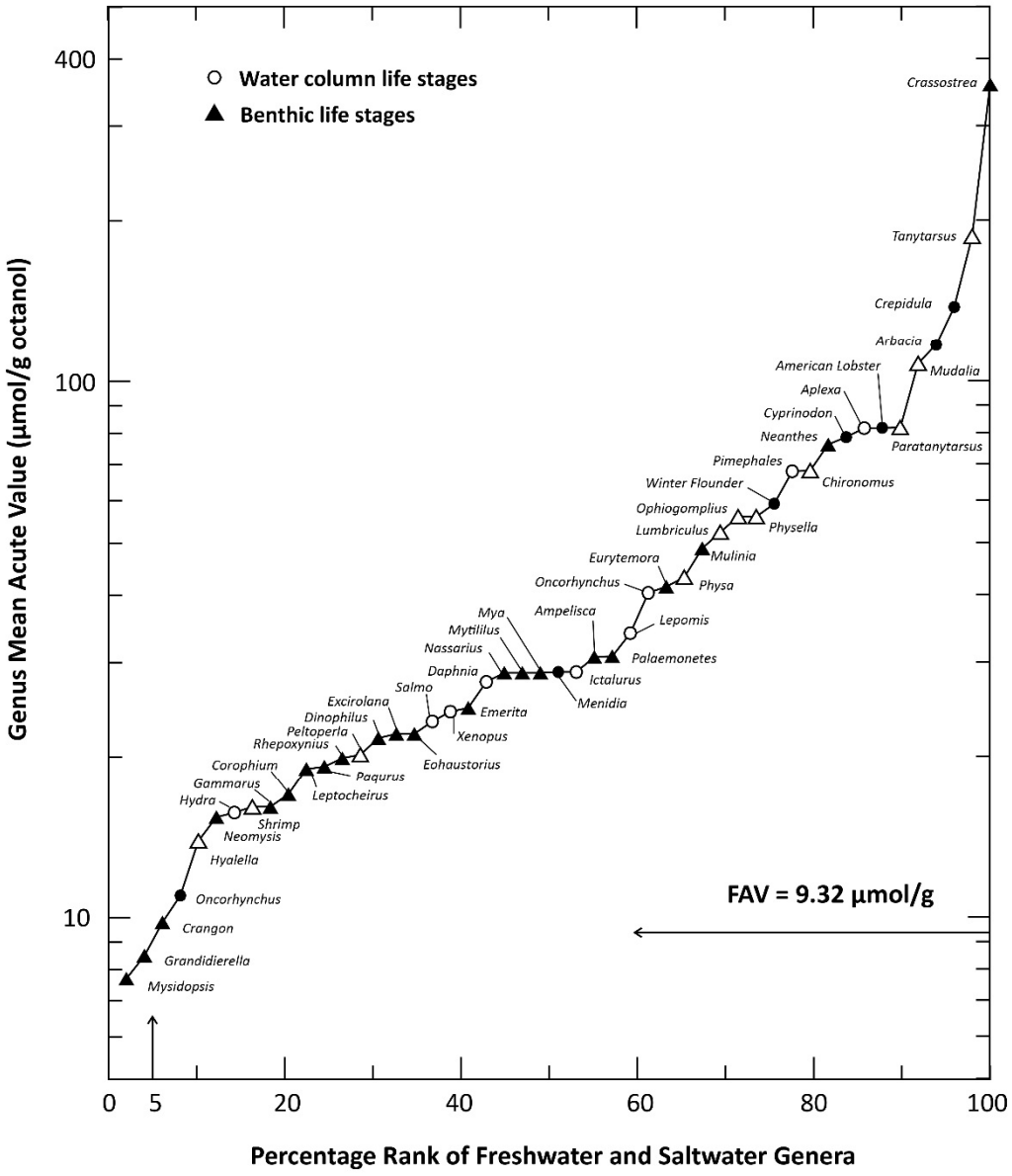

Figure 3-4. Species Sensitivity Distribution (SSD) for PAH mixtures for acute toxicity (US-EPA 2003c). Genus Mean Acute Values at a $\log_{10}K_{OW}$ of 1.0 from water-only acute toxicity tests using freshwater and saltwater genera versus percentage rank of their sensitivity.

Table 3-1. Conventional and narcosis water-only chronic toxicity values (µg/L) (FCVs and SCVs), Equilibrium Partitioning Benchmarks (ESBs), and narcosis equilibrium partitioning sediment benchmark (ESB) values (µg/g_{OC}) for a selection of nonionic organic chemicals (Burgess et al. 2013).

Chemical	Log K_{ow}	Conventional ESB (µg/g_{OC})		Narcosis ESB	Conventional FCV or SCV (µg/L)		Narcosis SCV
		Freshwater	Marine	(µg/g_{OC})	Freshwater	Marine	(µg/L)
Ethers							
4-Bromophenyl phenyl ether	5.00	120	120	1600	SCV = 1.5	SCV = 1.5	19
Low Molecular Weight Compounds							
Benzene	2.13	16	16	660	SCV = 130	SCV = 130	5300
Chlorobenzene	2.86	41	41	570	SCV = 64	SCV = 64	880
1,2-Dichlorobenzene	3.43	33	33	780	SCV = 14	SCV = 14	330
1,3-Dichlorobenzene	3.43	170	170	780	SCV = 71	SCV = 71	330
1,4-Dichlorobenzene	3.42	34	34	780	SCV = 15	SCV = 15	340
Ethylbenzene	3.14	8.9	8.9	970	SCV = 7.3	SCV = 7.3	790
1,1,2,2-Tetrachloroethane	2.39	140	140	830	SCV = 610	SCV = 610	3700
Tetrachloroethene	2.67	41	41	840	SCV = 98	SCV = 98	2000
Tetrachloromethane	2.73	120	120	770	SCV = 240	SCV = 240	1600
Toluene	2.75	5.0	5.0	810	SCV = 9.8	SCV = 9.8	1600
Tribromomethane (Bromoform)	2.35	65	65	1200	SCV = 320	SCV = 320	6000
1, 1, 1-Trichloroethane	2.48	3.0	3.0	660	SCV = 11	SCV = 11	2400
Trichloroethene	2.71	22	22	650	SCV = 47	SCV = 47	1400
m-Xylene	3.20	94	94	980	SCV = 67	SCV = 67	700
Pesticides							
Alpha-, Beta-, Delta-BHC	3.78	11	NA	[a]	SCV = 2.2	NA	[a]
Gamma-BHC, Lindane	3.73	0.37	NA	[a]	FCV = 0.08	NA	[a]
Biphenyl	3.96	110	110	1500	SCV = 14	SCV = 14	190
Diazinon	3.70	0.74	3.6	[a]	FCV = 0.1699	FCV = 0.8185	[a]
Dibenzofuran	4.07	37	37	1700	SCV = 3.7	SCV = 3.7	170
Dieldrin	5.37	12	28	[a]	FCV = 0.06589	FCV = 0.1469	[a]
Endosulfan mixed isomers	4.10	0.6	0.093	[a]	FCV = 0.056	FCV = 0.0087	[a]
Alpha-Endosulfan	3.83	0.33	0.051	[a]	FCV = 0.056	FCV = 0.0087	[a]

Beta-Endosulfan	4.52	1.6	0.24	[a]	FCV = 0.056	FCV = 0.0087	[a]
Endrin	5.06	5.4	0.99	[a]	FCV = 0.05805	FCV = 0.01057	[a]
Hexachloroethane	4.00	100	100	1400	SCV = 12	SCV = 12	160
Malathion	2.89	0.067	0.11	[a]	SCV = 0.097	FCV = 0.1603	[a]
Methoxychlor	5.08	1.9	NA	[a]	SCV = 0.019	NA	[a]
Pentachlorobenzene	5.26	70	70	1600	SCV = 0.47	SCV = 0.47	11
Toxaphene	5.50	10	54	[a]	FCV = 0.039	FCV = 0.2098	[a]
1, 2, 4-Trichlorobenzene	4.01	960	960	1100	SCV = 110	SCV = 110	120
Phthalates							
Butyl benzyl phthalate	4.84	1100	NA	[a]	SCV = 19	NA	[a]
Diethyl phthalate	2.50	77	NA	[a]	SCV = 210	NA	[a]
Di-n-butyl phthalate	4.61	1200	NA	[a]	SCV = 35	NA	[a]
Polycyclic Aromatic Hydrocarbons[b]							
Naphthalene	3.356	NA	NA	385	NA	NA	193.5
C1-naphthalenes	3.80	NA	NA	444	NA	NA	81.69
Acenaphthylene	3.223	NA	NA	452	NA	NA	306.9
Acenaphthene	4.012	NA	NA	491	NA	NA	55.85
C2-naphthalenes	4.30	NA	NA	510	NA	NA	30.24
Fluorene	4.208	NA	NA	538	NA	NA	39.3
C3-naphthalenes	4.80	NA	NA	581	NA	NA	11.1
Anthracene	4.534	NA	NA	594	NA	NA	20.73
Phenanthrene	4.571	NA	NA	596	NA	NA	19.13
C1-fluorenes	4.72	NA	NA	611	NA	NA	13.99
C4-naphthalenes	5.30	NA	NA	657	NA	NA	4.048
C1-phenanthrene/anthracenes	5.04	NA	NA	670	NA	NA	7.436
C2-fluorenes	5.20	NA	NA	686	NA	NA	5.305
Pyrene	4.922	NA	NA	697	NA	NA	10.11
Fluoranthene	5.084	NA	NA	707	NA	NA	7.109
C2-Phenanthrene/anthracenes	5.46	NA	NA	746	NA	NA	3.199
C3-fluorenes	5.70	NA	NA	769	NA	NA	1.916
C1-pyrene/fluoranthenes	5.287	NA	NA	770	NA	NA	4.887
C3-phenanthrene/anthracenes	5.92	NA	NA	829	NA	NA	1.256
Benz(a)anthracene	5.673	NA	NA	841	NA	NA	2.227

Chrysene	5.713	NA	NA	844	NA	NA	2.042
C4-Phenanthrenes/anthracenes	6.32	NA	NA	913	NA	NA	0.5594
C1-Benzanthracene/chrysenes	6.14	NA	NA	929	NA	NA	0.8557
Benzo(a)pyrene	6.107	NA	NA	965	NA	NA	0.9573
Perylene	6.135	NA	NA	967	NA	NA	0.9008
Benzo(e)pyrene	6.135	NA	NA	967	NA	NA	0.9008
Benzo(b)fluoranthene	6.266	NA	NA	979	NA	NA	0.6774
Benzo(k)fluoranthene	6.291	NA	NA	981	NA	NA	0.6415
C2-benzanthracene/chrysenes	6.429	NA	NA	1008	NA	NA	0.4827
Benzo(ghi)perylene	6.507	NA	NA	1095	NA	NA	0.4391
C3-benzanthracene/chrysenes	6.94	NA	NA	1112	NA	NA	0.1675
Indeno(1,2,3-cd)pyrene	6.722	NA	NA	1115	NA	NA	0.275
Dibenz(a,h)anthracene	6.713	NA	NA	1123	NA	NA	0.2825
C4-benzanthracene/chrysenes	7.36	NA	NA	1214	NA	NA	0.07062

NA = Not Available. [a] Conventional value should be used. [b] For C#-PAH groups, reported log K_{OW} values are the average log K_{OW} values of all structures (US-EPA 2003c). FCV = final chronic values. SCV = secondary chronic values.

3.3 Derivation of EPA's AWQC FCVs

As discussed in Section 3.2, FCVs from EPA's AWQC should be used as the appropriate adverse effects concentrations in the sediment pore water for the protection of benthic organisms. EPA's AWQC (Stephan et al. 1985) are derived by assembling species sensitivity distributions (SSDs) using the genus mean chronic toxicity values, and the FCV is the 5th percentile from the SSD for the chemical of interest. The preferred approach for developing the FCV is to use chronic toxicity data and directly compute the FCV from the chronic toxicity SSD. When insufficient chronic toxicity data are available, a SSD is developed using genus mean acute toxicity data and from this SSD, the 5th percentile Final Acute Value (FAV) is determined. Subsequently, the FAV is converted to a FCV using an appropriate acute to chronic toxicity ratio (ACR) for the chemical of interest.

3.4 Sensitivities of Toxicity Test Organisms in Relation to EPA's AQWC FCVs

Acute and chronic sediment toxicity tests with marine amphipods (*Ampelisca abdita, Eohaustorius estuarius, Leptocheirus plumulosus,* and *Rhepoxynius abronius*), and freshwater species (*Chironomus tentans* and *Hyalella azteca*) provide toxicity data for these, few, select species. The acute toxicity tests provide data on survival from a 10-day test (US-EPA 2000b, US-EPA and US-ACE 2001) while the chronic tests provides data on survival, growth, and reproduction from a 28-day (*Leptocheirus plumulosus*), 42-day (*Hyalella azteca*), and life-cycle (*Chironomus tentans*) tests (US-EPA 2000b, US-EPA and US-ACE 2001). Examination of the genus mean chronic value data for PAHs (Figure 3-5, Table 3-2) reveals that the freshwater and marine sediment toxicity test species reside at different points along the SSD. None of the common sediment toxicity test species have acute toxicity values at the FAV for PAHs of 9.32 µmole/g octanol (US-EPA 2003c). Because species used in sediment toxicity tests are not necessarily at the 5th percentile in the SSD, one should not expect them to be as sensitive as the FAV. Added to this is that the FCV is intended to protect sensitive organisms from effects on survival, growth, or reproduction when exposed over their entire life cycle. Because many sediment toxicity test methods do not include full life cycle exposure, further differences in sensitivity can be expected between the pore water RG (based on the FCV or comparable effect level) and the results of sediment toxicity tests. Finally, for chemicals whose pore water RG is based on a SCV calculated using the GLI Tier II procedures, additional conservatism may (and may not) be introduced by the adjustment factors applied for chemicals that have limited toxicity data availability.

To compare results of toxicity tests more directly to chemical concentrations measured in pore water, it is possible to calculate species/chemical-specific pore water effect concentrations based on the results of water column exposures using the same chemical, species, and endpoint. To do this, species/chemical-specific pore water toxic units (TUs) can be estimated by replacing the FCV with the applicable effect concentration from a water-only toxicity test and recalculating pore water TUs.

Table 3-2. PAH mixture species sensitivity distribution genus mean acute values for marine amphipods *Ampelisca abdita, Eohaustorius estuarius, Leptocheirus plumulosus,* and *Rhepoxynius abronius*, and for freshwater species *Chironomus tentans* and *Hyalella azteca.*		
Species	**Genus Mean Acute Value (µmole/ g octanol)**	**Percentage Rank of Genera**
5th Percentile distribution value	FAV = 9.32	5.0%
*Hyalella azteca***	13.9**	10.2%**
Leptocheirus plumulosus	19.0	22.4%
Rhepoxynius abronius	19.9	26.5%
Eohaustorius estuarius	22.1	32.6%
Ampelisca abdita	30.9	55.1%
Chironomus tentans	68.4	79.5%

**Later acute toxicity tests with *H. azteca* using 3 PAHs indicate sensitivity about 2.5-fold lower than indicated here (Lee et al. 2001); this may be related to low chloride concentration in the dilution water used in the test used for the sensitivity distribution. Recent research has suggested that low chloride concentrations are stressful to *H. azteca* and can lead to greater apparent sensitivity that may not be representative of aquatic organisms generally (Soucek et al. 2015).

3.5 Measuring Water Only Toxicity Value for Toxicant(s)

At some sites, effect concentrations for the species used by sediment toxicity tests might not be available for the toxicants of interest. Measurement of a water-only toxicity effects concentration(s) for the site's toxicant(s) can be conducted by performing aquatic toxicity tests with the chemical(s) of interest in water-only exposures. Standardized acute or chronic water toxicity test methods should be used (US-EPA 1996a; US-EPA 1996b; US-EPA 1996c; US-EPA 1996d). Proper implementation will require measured concentrations in the water over the duration of the toxicity test. Use of passive dosing techniques is suggested for more hydrophobic chemicals (Butler et al. 2013; Smith et al. 2010; Smith et al. 2009) and the use of solvent carriers, e.g., acetone or DMSO, to dissolve chemicals in the tests is not recommended. Results based upon nominal concentrations of the toxicants are unacceptable. The testing must involve a range of chemical concentration steps in order to create dose-response curve(s) for the toxicant(s) and enable the determination of an EC50(s) (effect concentration of the toxicant that gives half-maximal response) for the toxicant(s). With the newly measured toxicity value(s), a FCV or SCV can be derived for the chemical or mixture of chemicals of interest. Note, performing water-only toxicity tests will be costly and time consuming. As such, this approach is only recommended in those situations where the costs and time commitments warrant such efforts.

Section 4

Implementation of the Pore Water RG Approach within the Superfund Remedial Investigation/Feasibility Study (RI/FS) Process:

Following Superfund Guidance, the Remedial Investigation (RI) is a three part process (US-EPA 1997): 1) characterization of the nature and extent of contamination; 2) ecological risk assessment; and 3) human health risk assessment. The investigation of the nature and extent of contamination determines the chemicals present on site as well as their distribution and concentrations. The ecological and human health risk assessments determine the potential for adverse effects to the environment and human health, respectively. The focus of this document is the protection of benthic organisms living in and on the sediments, and resultantly, only characterization of the nature and extent of contamination and ecological risk assessment parts of RI will be discussed. For human health risk assessment, the reader should consult US-EPA (US-EPA 1989) for further information.

4.1 Characterization of the Nature and Extent of Contamination

Following Superfund guidance, the RI/FS process starts with Scoping Activities in which a conceptual site model (CSM) is assembled and initial data needs and Data Quality Objectives (DQOs) are identified for the site. In addition, a work plan for the site is developed along with a sampling and analysis plan (SAP) for field investigations. The RI should develop sufficient data to define (US-EPA 1988; US-EPA 1997):

- Site physical characteristics
- Physical and chemical characteristics of sources of contamination
- Volume of contamination and extent of migration
- Potential receptors and associated exposure pathways
- Baseline human health and ecological risks

In the RI, field investigations are conducted to characterize the nature and extent of contamination including the average contaminant concentrations. The field investigations are implemented in an iterative fashion such that the locations and concentrations of any migrating contaminants can be defined. The RI should collect adequate data of sufficient quality to support risk assessment and the analysis of remedial alternatives. As part of the baseline ecological risk assessment sediment toxicity tests on sediment samples from the site are often performed.

To lay groundwork for later development of pore water-based remedial goals, additional data should be collected during RI to define the following:

- Nature and variability of the organic carbon content (f_{OC}) of the sediments across the site
- Nature and variability of the site-specific sediment-organic carbon-water partition coefficients (K_{OC}s) across the site.

Rearranging Equation 1-1, illustrates why one needs to understand the nature and variability of f_{OC} and K_{OC} cross the site.

$$C_{free} = (C_S/f_{OC})/K_{OC} = C_{SOC}/K_{OC} \quad (4\text{-}1)$$

From the rearranged equation, the concentration of the freely dissolved chemical in the sediment pore water (C_{free}) is a function of both f_{OC} and K_{OC} parameters. The C_{free} values are used in the Risk Assessment part of the RI (see Ecological Risk Assessment section below) to determine if concentrations of the chemicals of concern in the sediments are at levels to cause unacceptable effects on benthic organisms. Understanding the nature and variability of the f_{OC} and K_{OC} parameters across the site allows the nature and extent of the contamination in the sediment pore water to be determined, i.e., C_{free} values in the sediments across the site. With the C_{free} values, assessments of risk can be performed for the chemicals of concern.

To provide some background on what one might see in terms of variability, f_{OC}, data from a few sites is provided below (Table 4-1), and the range in f_{OC}s for a site is potentially a factor of 10 or more.

Table 4-1. The f_{OC} in sediment samples from Superfund sites

Site	Average	Standard Deviation	Ratio of Maximum to Minimum Values	Minimum	Maximum	n	Reference
Fox River	0.0897	0.0655	17.5	0.0141	0.2462	10	a
Hudson River	0.0217	0.0146	8.8	0.0052	0.0456	10	a
Anniston	0.0152	0.0102	18.1	0.0022	0.0399	33	b
Portland Harbor	0.0220	0.0143	34.1	0.0020	0.0682	35	c
New Bedford	0.0192	0.0128	91.1	0.00057	0.0519	82	d

a (Burkhard et al. 2013) b (Ingersoll et al. 2014) c (Integral_Consulting_and_Windward_Environmental 2006) d (Nelson and Bergen 2012)

For K_{OC}, based upon the data from a limited number of sites (Table 4-2), the range in K_{OC}s for PCB congeners 118 and 153 at site can vary. For the Fox River and Anniston sites, the range in K_{OC}s is approximately an order of magnitude, and for the Hudson River site, range is smaller.

Table 4-2. The site-specific log K_{OC}s for PCB-118 and PCB-153 in sediment samples from Superfund sites

Site	PCB	Average	Standard Deviation	Range	Minimum	Maximum	n	Reference
Fox River	118	7.07	0.29	1.01	6.49	7.50	10	a
Fox River	153	7.38	0.27	0.69	6.97	7.66	10	a
Hudson River	118	7.35	0.21	0.57	7.11	7.69	10	a
Hudson River	153	7.40	0.10	0.31	7.28	7.59	10	a
Anniston	118	4.59	0.30	1.29	3.91	5.20	24	b
Anniston	153	5.02	0.26	1.00	4.56	5.56	25	b

a (Burkhard et al. 2013) b (Ingersoll et al. 2014)

Another evaluation of within and between site variations in K_{OC} values is presented by Hawthorne et al. (Hawthorne et al. 2006), who determined K_{OC} values for a range of PAHs found in 114 sediments collected in association with 8 different sites (six manufactured gas sites and 2 aluminum smelters). As shown in Figure 4-1, K_{OC}values varied by 100 to 1000-fold across the full range of samples, illustrating why assuming a single K_{OC} value for a site can introduce considerable uncertainty if applied blindly.

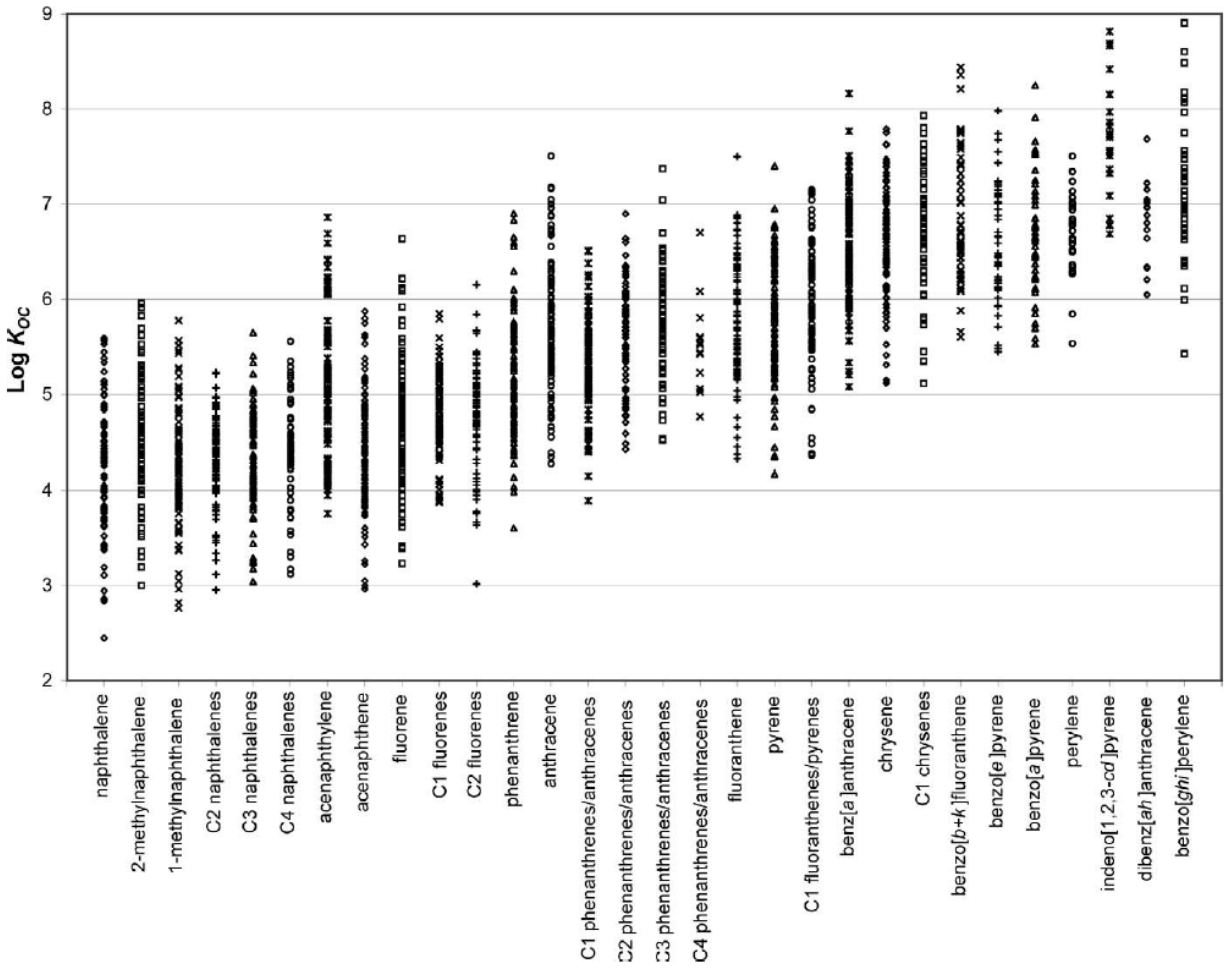

Figure 4-1. Measured K_{OC} values in sediments from manufactured gas and aluminum smelter sites as reported by Hawthorne et al. (2006). Reprinted with permission

The reasons why f_{OC} and K_{OC} parameters vary within and among sites are understood, even if they cannot be easily predicted. In ecosystems relatively untouched by human activities, organic carbon in the sediments arises, almost exclusively, from the diagenesis of plant materials. At Superfund sites, in addition to naturally derived organic carbon, anthropogenic carbon from industrial activities can be present, and could include coal, soot (black carbon), wood chips, sawdust, tars, NAPLs, oils/greases, and/or microplastic particulates. It is well documented that anthropogenic carbon types have sorption abilities that are different from the organic carbon resulting from the diagenesis of plant materials (Cornelissen et al. 2005), and in general, their sorption abilities are larger. This results in the K_{OC}s being larger than the K_{OC}s measured with organic carbon derived from the diagenesis of plant materials. With larger K_{OC}s for sediments containing anthropogenic carbon, the concentrations of chemicals in the sediment pore water are lower in comparison to sediments with little no anthropogenic carbon (when having the same concentrations of chemicals on a bulk dry weight basis with the same organic carbon content).

The f_{OC} parameter also varies at sites due differences in sedimentation rates, sediment type, and sediment movement at individual sites. For example, locations with sediments having high sand content generally have low organic carbon content (e.g., 0.2% or less), and depositional locations generally have higher organic carbon contents (often 10% or more). Even where K_{OC} is constant, this range in f_{OC} can lead to a 50-fold difference in the bulk sediment concentration expected to cause toxic effects. In characterizing the f_{OC} parameter for a site, measurement of TOC on all sediment samples is recommended. The analysis costs for f_{OC} is relatively inexpensive and with f_{OC} information, one can readily define the nature and variability of the f_{OC} parameter across the site.

For characterizing the nature and variability of the K_{OC} parameter for a site, the approach must balance cost and comprehensiveness. Passive sampling on every sample more than doubles analytical costs, because two sets of measurements are performed (i.e., measuring contaminant concentrations in the bulk sediment and measuring contaminant concentrations in the passive samplers) and additional effort is required to conduct the sample equilibration. However, the variability in K_{OC} shown in the examples above clearly shows that determining K_{OC} from just a single sample would fail to inform the assessment sufficiently.

At a minimum, a set of surface samples should be subjected to passive sampler measurements. The number and placement of these samples is dependent in part on the size and complexity of the site. Important characteristics to consider are how homogeneous the site sediments are (e.g., depositional versus higher flow areas), the complexity of past operations and/or sources, and the presence of key areas within the site that might influence remedial design (e.g., near boundaries between higher and lower levels of contamination. Overall, the samples taken should allow the nature and variability of the site-specific K_{OC}s across the site to be defined; this characterization is analogous to the efforts for defining the nature and variability of the chemical contamination at the site.

As discussed above, the RI process is an iterative process where field investigations and analytical techniques of increasing accuracy are employed to define the nature and extent of the contamination at the site. Similarly, passive sampling measurements can be employed in an iterative process. For example, one might not need to perform any passive sampling measurements on the initial sediment samples from the site, and use only total concentrations in sediment and f_{OC} to support a screening risk assessment (see Ecological Risk Assessment section below) to highlight areas of potential concern. These areas could then undergo targeted studies with passive sampling to refine risks posed by the contaminants. If the potential risks appear wide spread based upon the organic carbon normalized concentrations, a more extensive use of passive sampling might be warranted so that more reliable bioavailability corrections can be incorporated into the risk assessment. If at the site, large variations in total contaminant concentrations exist, defining how K_{OC}s (ultimately, the contaminant bioavailability) are a function of contaminant concentrations might be required. Successful and cost effective use of passive sampling requires a good CSM and well defined study objectives for the measurements.

4.2 Ecological Risk Assessment

Superfund's ecological risk assessment guidance is an eight-step process, and involves a screening level ecological risk assessment (Steps 1 and 2) ; followed by problem formulation (Step 3); then, study design and data quality objective development (Step 4); and results in a site's work plan (WP) and sampling and analysis plan (SAP). With the WP and SAP, site investigation (Steps 5 and 6) is performed followed by risk characterization (Step 7). The eight-step process is shown below in Figure 4-2, and Figure 4-2 is taken directly from Superfund's "Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments. Interim Final" guidance document (US-EPA 1997).

For COC identification, the methodology within this document does not require any additional steps or procedures beyond what is normally done in the RI process.

For exposure assessment, the methodology within this document requires the development of C_{free} values for the COCs in the sediment pore water across the site or appropriate locations and/or operational units for the site.

For toxicity assessment, the methodology within this document sets the unacceptable effects levels to the FCV for single contaminants, or for a mixture of contaminants of the same class (e.g., PAHs; see discussion below), the unacceptable effects level is found using the sum of the toxic units (TU; relative to the FCV) for the mixture and setting the sum to no more than 1.0. (See examples in Section 4.3.2.2 for calculation of TUs)

For risk characterization for organic chemicals in surface sediments, we recommend that concentrations be expressed on a total organic carbon basis, i.e., µg of chemical/kg of sediment organic carbon. Then, these values can be compared to EPA's ESBs (with units of µg of chemical/kg of sediment organic carbon) or similarly developed values for chemicals without published ESBs. If concentrations are less than the ESBs, then one would conclude that there is little potential for unacceptable risks to the benthic organisms from the COCs. This approach is based on the general experience that bioavailability of organic contaminants in sediments is generally no greater than would be predicted by assuming that $K_{OC} \approx K_{OW}$. Initially, evaluating contamination on an organic carbon normalized basis before performing passive sampling measurements focuses analytical resources and efforts for passive sampling on the locations of higher concern within the site, i.e., locations where the ESBs are exceeded.

When concentrations on an organic carbon normalized basis exceed the ESBs, unacceptable risks to benthic organisms might exist, but that risk is dependent on the degree of the chemical's bioavailability (partitioning). Passive sampling can address that uncertainty, by determining concentrations of COCs in

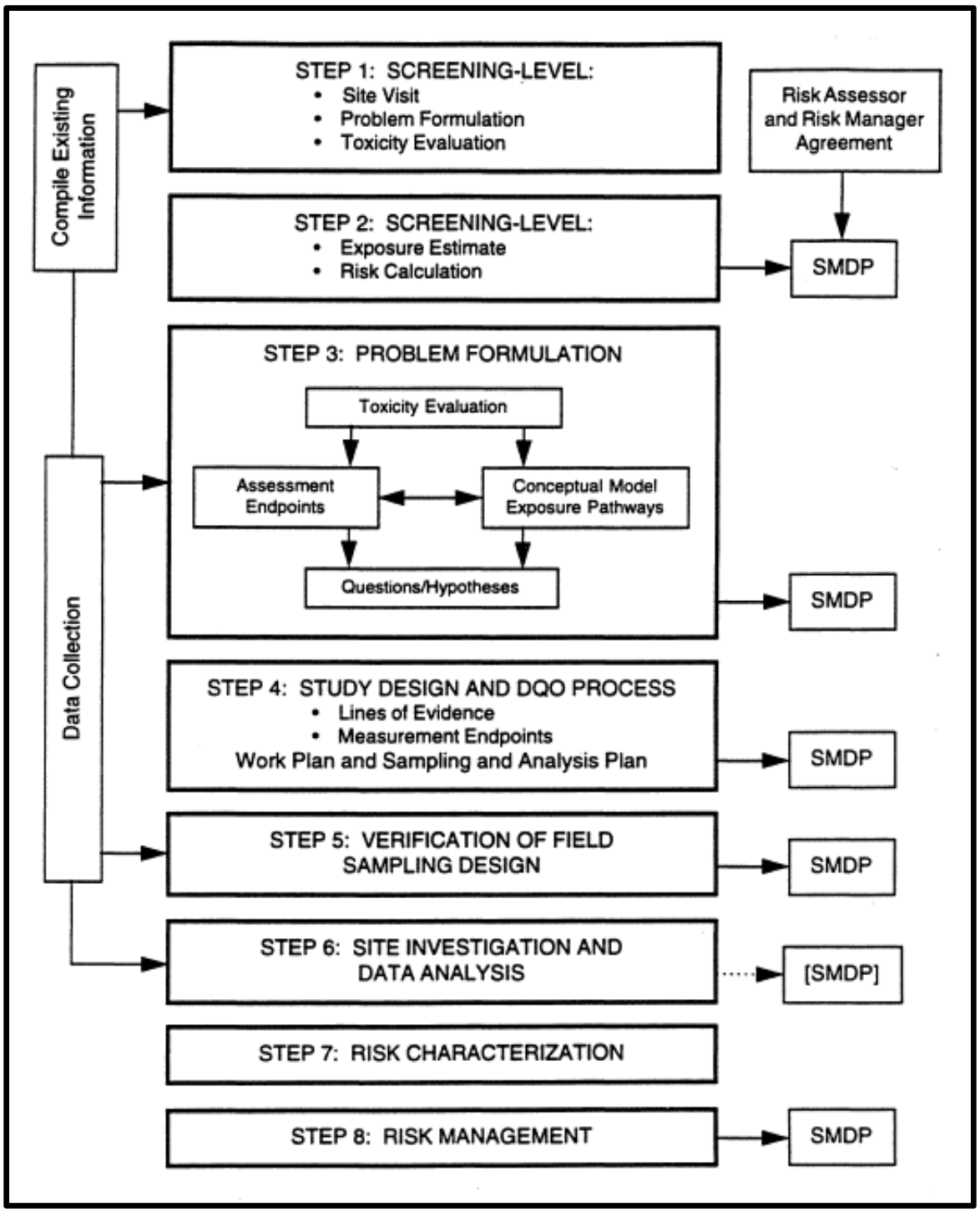

Figure 4-2a. Eight step ecological risk assessment process for Superfund (US-EPA 1997). SMDP = Scientific/Management Decision Point.

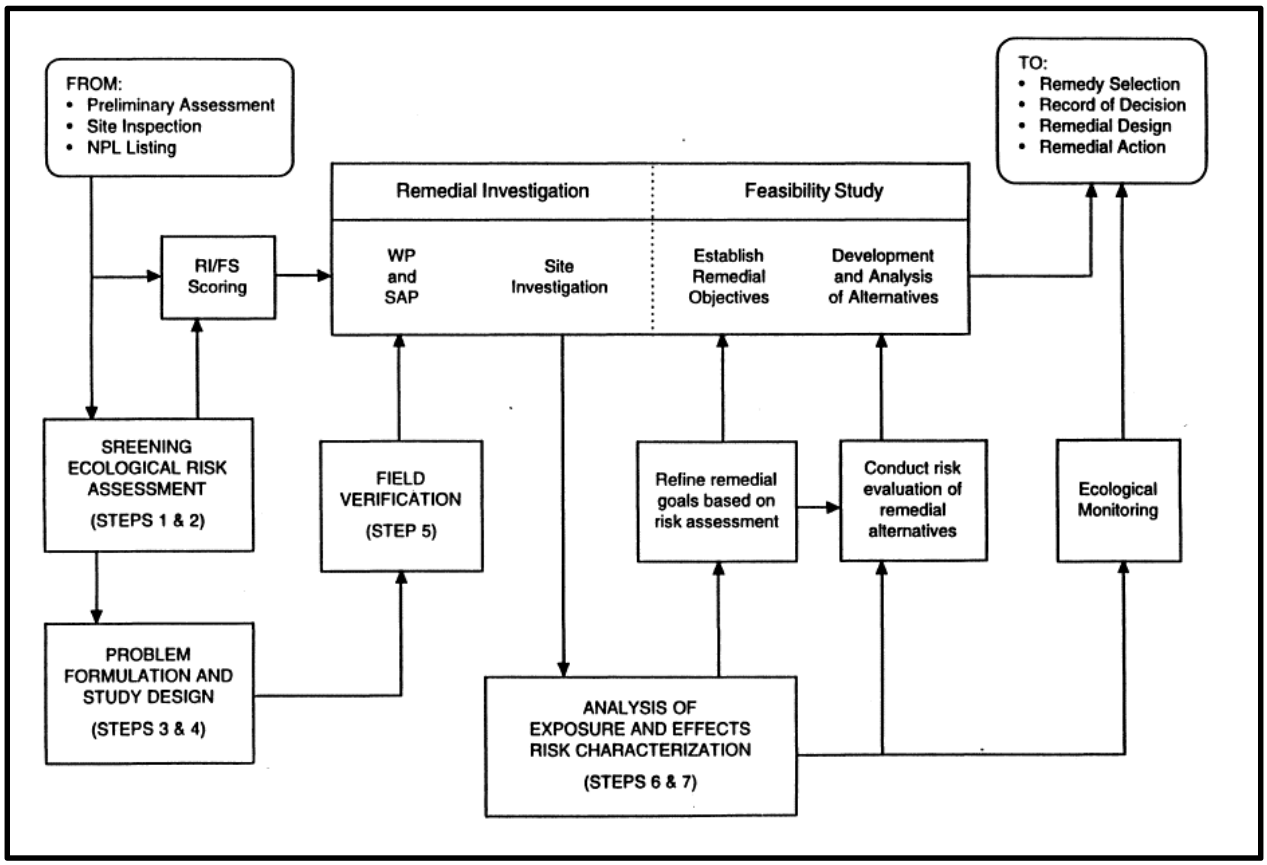

Figure 4-2b. Flowchart of eight-step ecological risk assessment process in the RI/FS process (US-EPA 1997).

pore water (and calculating associated K_{OC}s) for the areas with concentrations exceeding the ESBs. These C_{free} values are compared to the FCVs for the COCs or when a mixture of contaminants is present, the C_{free} values are used to determine the total TUs of the mixture. When values are higher than their FCVs or (for applicable mixtures) the total TUs exceed 1.0, unacceptable risks to benthic organisms are anticipated. When values are less than their FCVs or the total toxic units are less than 1.0, there is low potential risk to benthic organisms, despite the initial finding that C_{SOC} exceeded screening values. Depending upon data availability at your site, comparison of the COC concentrations to their ESBs might occur in the screening level ecological risk assessment (Steps 1 and 2). However, if field measurements are required, the comparisons would be performed later in the ecological risk assessment process, e.g., Steps 3, 4, or 6.

4.3 Pore Water Remedial Goal Development (PWRG)

In the ecological risk assessment, risks to benthic organisms are assessed based on C_{free} measurements and this information is used to develop PWRGs expected to be protective of benthic organisms. Although derived using the C_{free} in the pore water, remedial goals may be expressed on the bases of C_{free} itself or on conversion of C_{free} to C_{SOC} or C_S, depending on site characteristics and the needs

of the assessment. This section discusses remedial goal development based on different expressions of C_{free}.

4.3.1 Pore Water Remedial Goal Development using C_{free} Values

When developing PWRGs using C_{free} values, for situations where there is only one contaminant, the PWRG equals FCV for chemical. For situations where there is a mixture of contaminants present, PWRGs for each chemical are determined by using the composition of the mixture and setting the total amount of the mixture to a concentration where the total TUs for the mixture is equal to 1.0.

An example of where using C_{free} directly might be advantageous is in the addition of in-situ amendments such as activated carbon to the sediments (Beckingham and Ghosh 2011; Cho et al. 2009; Cho et al. 2012; Tomaszewski et al. 2007). The goal of these amendments is not to reduce C_S per se, but to use the sediment amendments to reduce the C_{free} values to meet the remedial goal.

4.3.2 Remedial Goal Development by Conversion of C_{free} Values to Concentrations in Sediment on an Organic Carbon Basis ($C_{SOC:PWRG}$) or to Concentrations in the Bulk Sediment ($C_{S:PWRG}$)

Some may wonder, "Why not simply express the PWRGs using C_{free} values at all sites when pore water measurements are made?" For some sites, developing PWRGs in terms of concentrations in the bulk sediment may lower analytical costs, simplify field collection efforts, and/or avoid issues with passive sampler devices being lost, damaged, and/or vandalized in the field. Additionally, these issues might apply in both RI/FS and post remedial monitoring phase for the site.

Conversion of pore water RGs expressed using C_{free} values to concentration in the sediment on an organic carbon basis ($C_{SOC:PWRG}$ (µg/kg organic carbon) requires rearranging Equation 1-1 and dropping of the $f_{OC:SS}$ term from the equation:

$$C_{SOC:PWRG} = K_{OC:SS} \times C_{free:PWRG} \quad (4\text{-}2)$$

Conversion of pore water RGs expressed using C_{free} values to concentration in the bulk sediment ($C_{S:PWRG}$ (µg/kg dry weight)) requires rearranging Equation 1-1:

$$C_{S:PWRG} = K_{OC:SS} \times f_{OC:SS} \times C_{free:PWRG} \quad (4\text{-}3)$$

where $K_{OC:SS}$ (L/kg-organic carbon) is the site-specific K_{OC}, $f_{OC:SS}$ is the site-specific f_{OC} (kg organic carbon/kg dry weight), and $C_{free:PWRG}$ is the pore water RG expressed as concentration in water (µg/L). When a single contaminant is present in the sediments, the $C_{free:PWRG}$ equals the FCV for the contaminant. When a mixture of contaminants is present in the sediments, the $C_{free:PWRG}$ values for each chemical are determined using the composition of the mixture in the sediment pore water and setting the total amount of the mixture to a concentration where the total TUs for the mixture is equal to 1.0. In the following discussion, these cases will be illustrated using RGs expressed using concentrations in the bulk sediment ($C_{S:PWRG}$). The RGs could, just as easily, be expressed using concentration in the sediment on an organic carbon basis ($C_{SOC:PWRG}$) using equation 4-2.

4.3.2.1 Derivation of $C_{S:PWRG}$ values for a Sediment with One Primary Contaminant – Dieldrin Example

The hypothetical example setting is a riverine Superfund site with sediments contaminated with dieldrin (Figure 4-3). In the RI process, concentrations of dieldrin and f_{OC}s were measured in the surface sediments in order to define their nature, variability and locations for the site. In this example, concentrations in the surface sediments were high at the source of the chemical and then, gradually decreased going downstream from the source (Figure 4-3: Graph B).

In the Risk Characterization phase of the Ecological Risk Assessment, concentrations of dieldrin in the surface sediments were converted to an organic carbon basis (Figure 4-3: Graph C), and subsequently, compared to dieldrin's ESB value of 12 ug/g-organic carbon (from Table 3-1). The surface sediments in river miles 148 to 159 have organic carbon normalized concentrations above the dieldrin's ESB. These data allowed the focusing of resources on the areas of the site where unacceptable effects to benthic organisms might potentially exist. In this example, the surface sediments in river miles 148 to 159 were sampled using passive samplers along with one additional surface sediment sample at river mile 138 for comparison purposes.

The C_{free} and resulting K_{OC}s from the passive sampling measurements for river miles 148 to 159 and 138 are shown in Graphs D and E of Figure 4-3. These data define the nature and variability across these locations within the site for K_{OC} and C_{free}. Overall, the measured K_{OC}s are similar across all measurement locations and there appears to be no substantial difference between the locations downstream and the highly contaminated areas of the river.

For this site contaminated with dieldrin, the pore water RG ($C_{free:PWRG}$) would be set equal to the FCV from EPA's AWQC for dieldrin, which is 0.06589 ug/L in the sediment pore water (Table 3-1)(US-EPA 2003a). As shown in Graph D of Figure 4-3, the C_{free} values in the sediment pore water are greater than dieldrin's FCV for river miles 151 to 159. The C_{free} value for river mile 138 is much lower than the FCV of dieldrin even though the measured K_{OC} at river mile 138 is similar to those in the river miles 148 to 159. Comparing Graphs C and D in Figure 4-3 reveals that the correction for chemical bioavailability (captured by measuring the C_{free} in the sediment pore water using passive sampling) lowers the number of locations in the river where unacceptable effects from dieldrin potentially exists for benthic invertebrates.

To convert the pore water RG ($C_{free:PWRG}$) expressed on a µg/L basis to a bulk sediment basis ($C_{S:PWRG}$), Equation 4-3 is used. In order to use the equation, values for $K_{OC:SS}$ (L/kg-organic carbon) and $f_{OC:SS}$ (kg organic carbon/kg dry weight) are needed. In Graph F of Figure 4-3, $C_{S:PWRG}$ values, calculated using Equation 4-3, are provided for river miles 151 through 159 using a variety of different calculation methods:

A) by individual sampling location, i.e., set $K_{OC:SS}$ and $f_{OC:SS}$ equal to the measured K_{OC} and f_{OC}, respectively, at each sampling location,

B) by setting the $K_{OC:SS}$ and $f_{OC:SS}$ equal to the average K_{OC} and average f_{OC} across the nine sampling locations,

C) by using the largest K_{OC} across the nine sampling locations with $f_{OC:SS}$ equal to the average f_{OC} across the nine sampling locations, and

D) by using the smallest K_{OC} across the nine sampling locations with $f_{OC:SS}$ equal to the average f_{OC} across the nine sampling locations.

As shown in this hypothetical example, depending upon how the $K_{OC:SS}$ and $f_{OC:SS}$ values are derived for the site, slightly different $C_{S:PWRG}$ values are determined: 900, 1900, and 300 ug/kg-dw for methods B, C, and D, respectively.

In this hypothetical example, all surface sediment samples with concentrations of dieldrin larger than the dieldrin's ESB value of 12 ug/g-organic carbon were passively sampled. Because of costs and sample availability, passively sampling all surface sediment samples with concentrations greater than the chemical's ESB might not always be feasible. The minimum number of surface sediments that should be passively sampled is tied to the variance of the K_{OC} values. Estimating the variance of the K_{OC} values for your site may be difficult initially because in the RI, concentrations of the COCs and f_{OC}s might be the only data available in the initial steps of the ecological risk assessment. In these cases, using variances for K_{OC} values from other sites is suggested as a starting point, recognizing that with data collection from your site, the variance of the K_{OC} values can be determined. With the variance for the site or sub-units (operational units or spatial locations within the site), the number of surface sediments for passive sampling can be defined using the level of uncertainties outlined in the CSM for the K_{OC} values and the appropriate statistical techniques.

The overall process in this hypothetical example is illustrated in Figure 4-4. In RI, the nature, extent, variability, and locations of the contamination and f_{OC} are determined for the site. In the Ecological Risk Assessment, areas where concentrations of the contaminant in the sediment, on an organic carbon basis, exceed the EPA's ESB for dieldrin, are subjected to passive sampling measurements. These measurements further refine the risks at the site and incorporate corrections for chemical bioavailability at the locations where EPA's ESB for dieldrin are exceeded. If passive sampling suggests unacceptable risks to benthic organisms, PWRGs should be developed. In Figure 4-4, the dashed box and arrows has been inserted in the pathway for development of the $C_{S:PWRG}$. In some cases, if both K_{OC} and f_{OC} values are reasonably consistent across the site, then dry weight normalization may be sufficient for developing the $C_{S:PWRG}$ values.

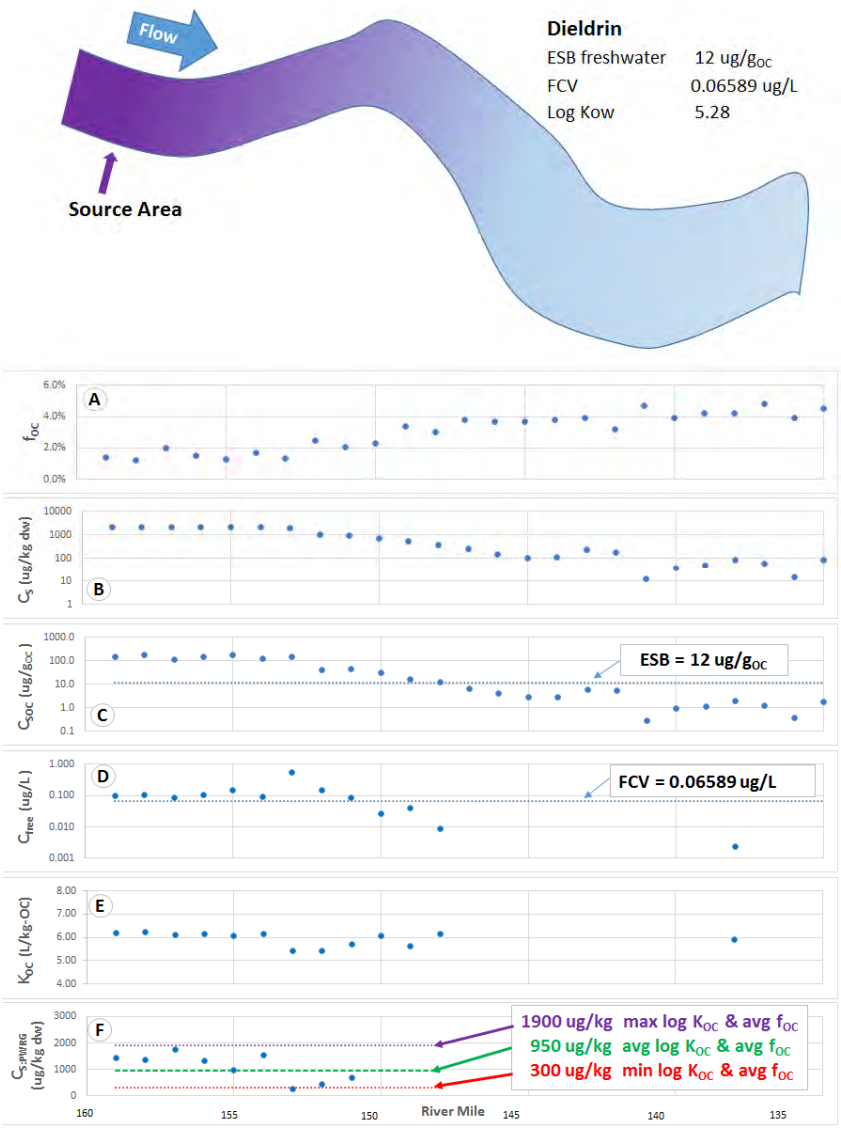

Figure 4-3. Hypothetical riverine Superfund site with sediments contaminated with dieldrin. Graph A – f_{OC} in sediments, Graph B – concentration of dieldrin in bulk sediment (µg/kg), Graph C – Concentration of dieldrin in sediment on organic carbon basis (µg/kg-organic carbon), Graph D – Concentration of freely dissolved dieldrin in sediment pore water (C_{free}, ug/L), Graph E – Sediment-water partition coefficient (K_{OC}). Graph F – sediment $C_{S:PWRG}$s (ug/kg dw) by individual sample, and by using average, minimum, and maximum K_{OC} values for river miles 151 through 159.

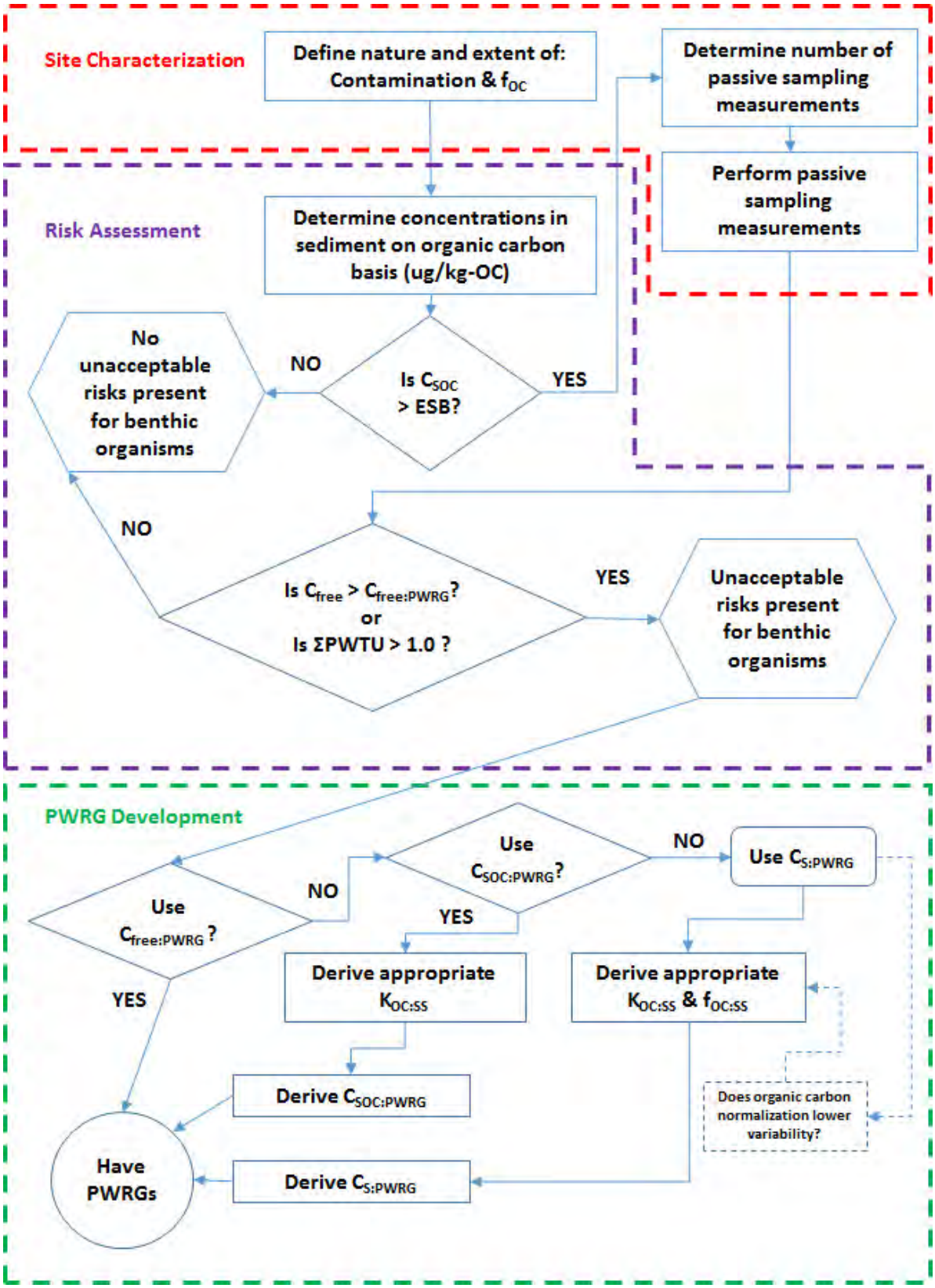

Figure 4-4. Components of developing PWRGs for sediment contaminants.

4.3.2.2 Derivation of $C_{S:PWRG}$ values for a Sediment with a PAH Mixture as the Primary COC

In this section, computation of the toxicity of a PAH mixture using toxic units is discussed. Unlike the dieldrin example above, for explanation purposes, the computations are limited, to a single sediment sample. The calculation would be conducted in the risk assessment portion of the RI, and for every sediment sample subjected to passive sampling analysis, this computation would be performed.

PAHs are one of the most common sediment contaminants because of their formation and release during the use of fossil fuels by developing and industrialized societies (Burgess et al. 2003b). Depending on the organism, the exposure setting, and the specific PAH compounds, PAHs can elicit toxicity via several toxic mechanisms, including narcosis, carcinogenicity/mutagenicity, and photo-enhanced toxicity (US-EPA 2003c). For benthic organisms, the primary mechanism of action for PAHs is narcosis; photo-enhanced toxicity is possible, but is unlikely to be a factor for benthic organisms except for sediments in very shallow water and where the water column has fairly high UV transmissivity. Accordingly, the ESB for PAHs is derived based on narcotic toxicity (US-EPA 2003c). Table 3-1 lists the narcosis FCVs/SCVs; readers can consult the ESB document (US-EPA 2003c) for more information on their derivation.

An important feature of narcotic toxicants like PAHs is that their toxicity is additive; in simple terms, if you have a pore water containing ½ the toxic concentration of PAH A, and ½ the toxic concentration of PAH B, the combination would be toxic. In practice, PAH mixtures in sediments consist of dozens of PAH structures, so the pore water RG calculation is more involved than the simple example above. Another important aspect of assessing sediments contaminated with PAHs using pore water RGs is that the common practice of measuring 13 to 16 of the common "priority pollutant" PAHs – all unsubstituted base ring or "parent" structures – does not capture all of the PAH structures that commonly contribute meaningfully to the toxicity of field mixtures. Measuring only the parent PAHs does not account for the effects of alkylated PAHs (e.g., methyl-, dimethyl-, ethyl-substituted PAHs like 1-methylnapthalene or 3,6-dimethylphenanthrene) that often represent from 50% to 90% of the overall toxicity potency of common PAH mixtures. For that reason, application of the pore water RG approach to PAH-contaminated sediments should be performed only when passive sampling includes the suite of 34 PAH structures described in the PAH ESB document (US-EPA 2003c) and listed in Table 4-3. Analytical methods are available for sediments and pore water measurements of the 18 parent PAHs and 16 alkylated groups (e.g., EPA 8270) when the alkylated PAHs are included as analytes in the analytical method, see (US-EPA 2007a; US-EPA 2014), NOAA Mussel Watch (NOAA 1998), Hawthorne et al. (Hawthorne et al. 2005), and ASTM D7363 (ASTM 2013).

Because many historical measurements of sediment PAH contamination involved only the 13-16 priority pollutant parent PAHs, the PAH ESB included correction factors/ratios for extrapolating total toxic units from the 16 priority parent PAHs (or some other subset of the PAHs) to the 34 PAHs (18 parent PAHs and 16 alkylated groups) required for the evaluation of toxicity via narcosis. However, these ratios are notably variable, and this variation can result in substantial under- or over-estimation of the total toxicity of sediment samples (US-EPA 2003c). While the costs of the more extensive PAH analysis is higher, these costs are generally small compared to potential remedial costs, so direct measurement of 18 parent PAHs and 16 alkylated groups in the pore water measurements is highly

recommended. This is not to say that site-specific correction factors couldn't be developed within site data in order to incorporate additional sediment PAH data into the overall site assessment, only that it is best to develop site-specific relationships rather than use generic factors.

While the components of the pore water RG process are the same for PAH mixtures as they are for a single compound, the calculations are more involved. Each of the 34 PAHs (or PAH groups) listed in Table 4-3 will have its own measured pore water concentration, FCV/SCV, and sample-specific K_{OC}, yet these must be combined into a single aggregate measure. This is done using a "toxic units" concept, wherein the fractional contribution of each specific PAH is determined, then these are summed across all PAHs to determine if the overall PAH pore water RG is exceeded. For each individual PAH, the measured concentration in pore water (column 3 in Table 4-3) is divided by its corresponding FCV/SCV from Table 3-1 (column 5 in Table 4-3); the result is the fractional contribution of that PAH to the overall sediment potency (Column 6), which is the pore water toxic units (PWTU):

$$PWTUi = C_{free,i}/FCV_i \tag{4-4}$$

where $C_{free,i}$ is the freely dissolved concentration measured in the pore water using a passive sampling technique for chemical "i", and FCV_i (or SCV_i) is from Table 3-1. The total toxicity of the mixture is estimated by summing the PWTU of each chemical:

$$PWTU_{Mixture} = \sum_{i=1}^{j} PWTU_i \tag{4-5}$$

where $PWTU_i$ is computed using equation 4-4 for each of the "j" chemicals in the mixture.

Using the example from Table 4-3, the measured concentration of naphthalene in this pore water was 2.89 µg/L, the PAH-specific FCV/SCV is 193 µg/L, and the resulting ratio is 0.0150, which is $PWTU_{naphthalene}$. These ratios are then calculated for each of the individual PAHs, and the ratios are added together to derive the overall toxic units (relative to the pore water RG) present. In the example in Table 4-3, this sum (ΣPWTU) is 58.68, indicating that the PAH exposure in this sediment greatly exceeds the PAH pore water RG, which is represented by a summed ratio of 1.00.

As discussed previously, site-specific K_{OC} and f_{OC} values are needed to convert pore water RG values back to bulk sediment RGs. In the case of a mixture like PAHs, this calculation is complicated by the need to base this calculation on the relative concentrations of each component of the mixture. For illustration purposes, Table 4-3 shows the calculation based on a single sample. For this example, ΣPWTU = 58.68, meaning that this mixture exceeds the pore water RG by 58.68-fold; put differently, pore water concentrations would have to be reduced to 1/56.68 or 1.704% of their measured concentration to meet the pore water RG. Column 7 of Table 4-3 shows the concentration in sediment pore water that are 1.704% of the measured concentrations. Column 9 shows the sample-specific K_{OC} values calculated from columns 2 and 3 along with the measured f_{OC} of 0.088 (8.8%). These values are combined using equation 4-3 to give a PAH-specific $C_{S:PWRG}$ values for each PAH in µg/kg dry weight (column 10). For this sample, remediation to non-toxic levels would require decreasing the total PAH concentration in the sediments from 191.27 to 3.26 µg/g (dw). Note, in this example, calculations were

performed using two significant digits for all values to provide clarity to the readers. At your site, appropriate significant digits should be used.

The detailed approach to handling a PAH mixture at a site would consist of:

1) Compute the total TUs (sum for all 34 PAH groups) for each sampling location and create a surface contour plot of total TUs for the site, operable unit, or appropriate sub-area of the site
2) Derive a surface contour map for total PAHs in bulk sediment or in sediment on an organic carbon basis that results in 1.00 TU contours for the site, operable unit, or appropriate sub-area of the site.

The map derived in 2 provides the concentrations of total PAHs in sediment protective of benthic species, and would be the RGs for the sediment at the site or appropriate sub-area of the site.

Simplification of the above detailed approach with 34 groups of PAHs will be highly site dependent because PAH contamination can arise from numerous sources with highly different PAH compositions (Burgess et al. 2003a). Additionally, fate and transport processes, and biological weathering can greatly affect the composition of the PAH mixtures in sediments. Depending on the characteristics of particular sites, simplification, possibly using a subset of the 34 groups of PAHs, in the above process might be possible.

Table 4-3. Example calculation of pore water toxicity and pore water RGs for a sediment with a PAH mixture as the known toxicants.

	Measured Concentration				*1.704% = 1/58.68*				
	Sediment	Pore Water (C_{free}) [a]	Aqueous Solubility [b]	Narcosis FCV/SCV	Pore Water Toxic Units [c]	$C_{free:PWRG}$	Pore water RG Toxic Units	Site-Specific Log K_{OC} [c]	Bulk Sediment $C_{S:PWWG}$
PAH	µg/g (dw)	µg/L	µg/L	µg/L		µg/L		L/kg (OC)	µg/g (dw)
Naphthalene	3.33	2.89	30,995	193.5	0.015	0.049	0.0003	4.154	0.057
C1-Naphthalenes	1.07	2.13		81.69	0.026	0.036	0.0004	3.794	0.018
C2-Naphthalenes	2.57	26.8 J		30.24	0.886	0.457	0.0151	3.074	0.044
C3-Naphthalenes	1.94	35.5 J		11.10	3.198	0.605	0.0545	2.830	0.033
C4-Naphthalenes	1.01	18.5 J		4.048	4.570	0.315	0.0779	2.830	0.017
Acenaphthylene	1.60	8.36	16,314	306.9	0.027	0.142	0.0005	3.375	0.027
Acenaphthene	6.69	75.1	3,800	55.85	1.345	1.280	0.0229	3.042	0.114
Fluorene	4.49	25.4	1,900	39.30	0.646	0.433	0.0110	3.340	0.077
C1-Fluorenes	1.69	17		13.99	1.215	0.290	0.0207	3.090	0.029
C2-Fluorenes	1.38	15 U		5.305	0.707	0.128	0.0241	3.357	0.024
C3-Fluorenes	0.673	0.343 U		1.916	0.045	0.003	0.0015	4.686	0.011
Phenanthrene	19.5	60.6	1,100	19.13	3.168	1.033	0.0540	3.600	0.332
Anthracene	8.33	15.2	45.0	20.73	0.733	0.259	0.0125	3.831	0.142
C1-Phenanthrenes/Anthracenes	7.13	37.8		7.436	5.083	0.644	0.0866	3.368	0.122
C2-Phenanthrenes/Anthracenes	3.94	33.8		3.199	10.566	0.576	0.1801	3.159	0.067
C3-Phenanthrenes/Anthracenes	1.76	15.7		1.256	12.500	0.268	0.2130	3.142	0.030
C4-Phenanthrenes/Anthracenes	0.912	1.0 U		0.5594	0.447	0.009	0.0152	4.354	0.016
Fluoranthene	20.2	19.8	239.9	7.109	2.785	0.337	0.0475	4.101	0.344
Pyrene	17.2	16.9	131.9	10.11	1.672	0.288	0.0285	4.100	0.293
C1-Fluoranthenes/Pyrenes	10.1	11.4		4.887	2.333	0.194	0.0398	4.040	0.172
Benz[a]anthracene	9.68	1.84	11.0	2.227	0.826	0.031	0.0141	4.814	0.165
Chrysene	8.35	1.45	2.0	2.042	0.710	0.025	0.0121	4.853	0.142
C1-Benzanthracenes/Chrysenes	4.37	1.27		0.8557	1.484	0.022	0.0253	4.629	0.074
C2-Benzanthracenes/Chrysenes	2.08	0.0138 U		0.4827	0.007	0.000	0.0002	6.572	0.035
C3-Benzanthracenes/Chrysenes	1.32	0.0174 U		0.1675	0.026	0.000	0.0009	6.274	0.022

C4-Benzanthracenes/Chrysenes	0.527	0.0235 U		0.0706	0.083	0.000	0.0028	5.744	0.009
Benzo[b]fluoranthene	6.95 J	0.448 J	1.501	0.6774	0.661	0.008	0.0113	5.283	0.118
Benzo[k]fluoranthene	8.35	0.53	0.7999	0.6415	0.826	0.009	0.0141	5.290	0.142
Benzo[a]pyrene	10.9	0.422 J	3.810	0.9573	0.441	0.007	0.0075	5.505	0.186
Perylene	2.93	0.175	0.4012	0.9008	0.194	0.003	0.0033	5.316	0.050
Benzo[e]pyrene	5.69	0.387	4.012	0.9008	0.430	0.007	0.0073	5.260	0.097
Indeno[1,2,3-cd]pyrene	6.39	0.12 J		0.2750	0.436	0.002	0.0074	5.819	0.109
Dibenz[a,h]anthracene	1.82	0.055 J	0.6012	0.2825	0.195	0.001	0.0033	5.612	0.031
Benzo[ghi]perylene	6.40	0.173 J	0.2600	0.4391	0.394	0.003	0.0067	5.661	0.109
Total Organic Carbon	8.08%								
Total	191.27	-	-	-	58.681	-	1.0	-	3.260

[a] U - undetected; value represents detection limit, J - estimated value. [b] (Mackay et al. 1992; US-EPA 2003c). [c] ½ detection limit used for non-detect values.

4.3.2.3 Derivation of $C_{S:PWRG}$ values for a Sediment with Other Contaminant Mixtures

With the exception of PAHs as discussed in Section 4.3.2.2, pore water RGs for other chemicals are given for individual chemicals. However, many Superfund sites have mixtures of chemicals which may warrant consideration of the toxicity of those mixtures as it may differ from that of the individual compounds. As a general rule, the expectation is that chemicals with dissimilar toxicological mechanisms will act independently, and can therefore be assessed using pore water RG values on a chemical by chemical basis. However, those that share a toxicological mechanism, are generally expected to show additive toxicity and are therefore likely to be more rigorously addressed using a mixture approach. PAHs are one such group, and the PAH ESB guidance uses an additive toxicity concept to address the potency of PAH mixtures (US-EPA 2003c). While explicit mixture guidance has not been developed for other mixtures likely to be encountered in sediments, there are additional chemical groups that share a common toxicological mechanism to benthic invertebrates and may co-occur; examples include chlorobenzenes, which contribute to narcotic effects; chlorinated cyclodiene pesticides (aldrin, dieldrin, endrin, heptachlor, chlordane, endosulfan) that act through the gamma-aminobutyric acid (GABA) receptor-chloride channel complex; the various isomers and metabolites of DDT (DDE, DDD); and acetylcholine esterase inhibiting organophosphate pesticides (e.g., chlorpyrifos, malathion, diazinon, and many others). The key in deciding to apply a mixture approach lies in 1) having reasonable scientific evidence that the group of chemicals share a toxicological mechanism; and 2) that there are enough chemicals in the group present at sufficient concentrations to warrant evaluating them together.

Speaking again in general terms, the degree of uncertainty introduced by failing to consider mixture effects is influenced largely by the number of chemicals involved, with the uncertainty generally increasing with larger numbers of similarly acting chemicals in the mixture. As a simple example, consider dieldrin and endrin, which have similar toxic action and whose toxicities would likely be additive. If these chemicals were only evaluated separately, then a worst-case scenario might be if both were at 0.9 PWTU, with an expected combined potency of 1.8 PWTU. While this would be an exposure higher than intended by a pore water RG of PWTU = 1, the magnitude of this difference is small compared to the same scenario for PAH mixtures (with 34 components) wherein the aggregate TU could be as high as 34 chemicals $\times$ 0.9 PWTU = 30.6 TU.

In real world mixtures, it is probable that the contributions of individual chemicals to overall mixture toxicity will vary, and would not all be right near the pore water RG. Using the dieldrin/endrin example, if the PWTU for dieldrin was generally 20% or less of the PWTU for endrin, then the magnitude of the resulting uncertainty would be small even if mixture effects were ignored. In the example in Table 4-3, the highest PWTU for a single PAH was 12.5 PWTU for C3-Phenanthrenes/Anthracenes, compared to the summed PWTU of 56.68, which would be about a 5-fold underprotection if mixture effects were ignored and all PAHs were compared to their pore water RG values individually.

The potential importance of considering mixtures can be evaluated from the passive sampler data by comparing the assessment conclusions if pore water RGs are applied individually or within a mixture approach. A simple sensitivity assessment can inform the assessor as to the degree to which ignoring mixture effects would influence the assessment. Again, the number of chemicals involved is likely to be

a key factor. So as an example, a site contaminated with a whole suite of chlorobenzene compounds might be a more likely candidate for a mixture approach than one contaminated with just a couple of chlorobenzenes.

If a mixture approach is chosen, the approach is parallel to that shown in section 4.3.2.2. PWTUs are calculated individually for each component of the mixture (Equation 4-3), then summed across the mixture (Equation 4-4). The pore water RGs for each chemical in the mixture are computed by dividing their C_{free} values by the $PWTU_{Mixture}$ value. Concentrations in the bulk sediment are found by dividing the bulk concentrations by $PWTU_{Mixture}$ value.

4.4 Suggested Methodology for Using Passive Sampler Measurements to Develop PWRGs

4.4.1 ESB Screening Approach

The suggested approach for implementing the use of passive sampling measurements at contaminated sediment sites to develop PWRGs is discussed in Sections 4.1 and 4.3.2.1, and is outlined below. The approach takes bulk concentrations of the COCs in the surficial sediments developed in the RI and compares them to EPA's ESBs. For surface sediments with concentrations less than EPA's ESBs, unacceptable risks to benthic organisms do not exist. For surface sediments with concentrations greater than the ESBs, passive sampling measurements are performed in order to refine risks at those locations. With the C_{free} measurements in the sediment pore water, the total TUs in the sediments are determined, and for samples/locations where the total TUs exceed 1.0, the potential for unacceptable risks to benthic organisms is noted. The approach below follows Superfund's eight-step ecological risk assessment guidance (US-EPA 1997). Depending upon data availability and when appropriate measurements are made, comparison of bulk concentrations of COCs to ESBs might occur in the Screening Level Ecological Risk Assessment or in the Site Investigation and Data Analysis steps of the eight-step ecological risk assessment procedure.

Screening Level Characterization of the Nature and Extent of Contamination

1) Measure f_{OC} and C_S for all COCs (µg/kg-dw) in surficial sediments across the site
2) Compute C_{SOC} (µg/kg-OC) for all COCs

Screening Level Ecological Risk Assessment

3) Compute Toxic Units (TUs) for COCs
    a. For single toxicant case, TU = C_{SOC} divided by ESB for the COC
    b. For mixture of toxicants, sum TUs for all COCs where $TU_i = C_{SOC,i}/ESB_i$ for each COC

Problem Formulation

Develop CSM, exposure pathways, and assessment endpoints

Study Design and DQO Process

Develop Work Plan (WP) and Sampling and Analysis Plan (SAP) in support of CSM and data needs

Site Investigation and Data Analysis

4) Passively sample surface sediments where total TUs > 1.0
5) Derive C_{free} and K_{OC} values for surface sediments with total TUs > 1.0

Risk Characterization

Baseline Ecological Risk Assessment

6) Compute Toxic Units (TUs) for COCs
    a. For single toxicant case, PWTU = C_{free}/FCV
    b. For mixture of toxicants, for each COC in the mixture:
        Compute pore water TU for each COC, $PWTU_i = C_{free,i}/FCV_i$
        Compute total mixture pore water TUs, $PWTU_{Mixture} = \Sigma PWTU_i$
7) For locations where:
    c. Total PWTUs ≤ 1.0, little potential for risk to benthic organisms.
    d. Total PWTUs > 1.0, unacceptable risks to benthic organisms indicated, proceed to Remedial Goal Development

Remedial Goal Development

8a) If pore water RGs are expressed on C_{free} basis ($C_{free:PWRG}$ µg/L):
    a. For single toxicant case, pore water RG is
        $C_{free:PWRG}$ = FCV
    b. For mixture of toxicants:
        Derive site-specific composition of the mixture
        Compute pore water RGs for each COCs,
            $C_{free:PWRG,i} = FCV_i \times PWTU_i / PWTU_{Mixture}$

8b) If pore water RGs are expressed on bulk sediment basis ($C_{S:PWRG}$ µg/kg dry weight):
    Derive site specific $f_{OC:SS}$ and $K_{OC:SS}$ values for each COC
    a. For single toxicant:
        Pore water RG for COC:
            $C_{S:PWRG} = K_{OC:SS} \times f_{OC:SS} \times C_{free:PWRG}$
                where $C_{free:PWRG}$ = FCV
    e. For mixture of toxicants:
        Derive site-specific composition of the mixture
        Pore water RG for each COC:
            $C_{S:PWRG,i} = K_{OC:SS,i} \times f_{OC:SS,i} \times C_{free:PWRG,i}$
                where $C_{free:PWRG,i} = FCV_i \times PWTU_i / PWTU_{Mixture}$
        Sum $C_{S:PWRG,i}$ for all mixture components to provide total bulk concentration of mixture
            $C_{S:PWRG,Mixture} = \Sigma C_{S:PWRG,i}$

8c) If pore water RGs are expressed on organic carbon basis ($C_{SOC:PWRG}$ µg/kg organic-carbon):
    Derive site specific $K_{OC:SS}$ values for each COC
    b. For single toxicant:
        Pore water RG for COC:
            $C_{SOC:PWRG} = K_{OC:SS} \times C_{free:PWRG}$
                where $C_{free:PWRG}$ = FCV
    f. For mixture of toxicants:
        Derive site-specific composition of the mixture
        Pore water RG for each COC:
            $C_{SOC:PWRG,i} = K_{OC:SS,i} \times C_{free:PWRG,i}$
                where $C_{free:PWRG,i} = FCV_i \times PWTU_i / PWTU_{Mixture}$

Sum $C_{SOC:PWRG,i}$ for all mixture components to provide total concentration of mixture on an organic carbon basis in the sediment

$C_{SOC:PWRG,Mixture} = \Sigma C_{SOC:PWRG,i}$

Section 5

Use of Passive Samplers, Toxicity Testing Results, and Pore Water RGs

To successfully use the methodology in Section 4 for deriving PWRGs for the protection of benthic organisms from direct toxicity within the RI/FS process, knowledge of passive sampling, sediment toxicity testing, and the interpretation of the results from both techniques is essential. We anticipate that many of the users of this document will be fairly knowledgeable on the passive sampling measurement technique and its resulting data, and less knowledgeable on the sediment toxicity testing and its resulting data. As part of the ecological risk assessment, sediment toxicity tests are often performed on sediment samples in order to characterize risks from the contaminants on benthic organisms at the site.

This section provides a basic primer on the toxicity data from sediment toxicity tests, followed by discussion of illustrative toxicity testing results that you might observe at your site. Successful development of PWRGs allows the responses from sediment toxicity testing to be explained in relation to (or are consistent with) the measured C_{free} values of the COCs in the sediment pore water. In this comparison, C_{free} values could be expressed on toxic units or concentration basis depending your site's COCs. Consistency means that samples non-toxic in the sediment toxicity tests are predicted to be non-toxic based upon the measured C_{free} values of the COCs and vice-versa. When your data are consistent (i.e., no false positives and no false negatives), one can be reasonably assured that the contaminants causing toxicity to benthic organisms have been correctly identified and that the developed pore water RGs for the contaminants will be protective of the benthic organisms at the site. Further, you have established a causal linkage between the CERCLA COCs at your site and the effects observed in the sediment toxicity tests on the sediments from your site.

5.1 Approaches for Aligning Pore Water RGs and Sediment Toxicity Testing Results

5.1.1 Exposure Response

When sediment toxicity tests are performed, each test provides one or more effect endpoints (e.g., survival, growth, and/or reproduction), for the tested sample. If one had a set of sediment samples that contained the complete range of contaminant concentrations, one would expect a sigmoidal shape response curve where at lower concentrations of the contaminant, no effects are observed; at high concentrations of the contaminant, unacceptable effects are observed on all test organisms; and at intermediate concentrations, a graded response is observed. Plotting of the individual test results would result in an exposure-response curve as shown in Figure 5-1 where toxic units of the contaminant are on x-axis and endpoint responses are on the y-axis. Note, Figure 5-1 is idealized for illustrative purposes! For a variety of reasons, the uniform spacing of the contaminant concentrations and uniformity in biological response will be rarely observed in practice.

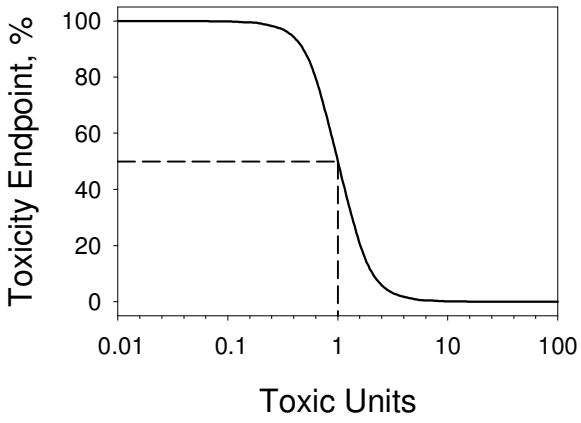

Figure 5-1. Illustrative idealized dose-response curve. Circles are test results for individual sediment samples and a smooth line has been fitted to the individual test results. The EC50 is shown by the dashed line.

In Figure 5-1, the midpoint in the response curve is centered on 1.0 toxic unit and for sediment samples with concentrations of the contaminant above and below its FCV, their responses in toxic units would reside on the line above and below the 1.0 toxic units midpoint, respectively. As discussed in the Introduction, equilibrium partitioning theory argues that the same exposure-response curve would be observed with a water only exposure of the same organism. In the Figure 5-1, the EC50 (effect concentration at 50% response for the endpoint of interest) is also shown. For survival, the EC50 is equivalent to LC50 (lethal concentration for 50% survival of the test organisms).

5.1.2 Exposure Response Curves Observed at Sediment Sites

At Superfund sites, sediment toxicity testing data typically do not imitate perfectly the illustrative dose-response curve in Figure 5-1. Causes for deviations from the illustrative curve include:

a) Not having a set of sediment samples with a broad range of contaminant concentrations;
b) Having sediment samples whose contaminant concentrations miss important portions of the overall exposure-response curve;
c) Presence of multiple COCs in varying proportions across the site, such that the exposure-response curve for a single COC is confounded by the effects of another COC; and
d) Data quality issues, e.g., QC issues with toxicity tests and/or passive sampling measurements (see Section 5.3. Method Uncertainties).

Data from 28-day sediment toxicity tests with *Hyalella azteca* on Hudson River sediments contaminated with PAHs are provided in Figure 5-2 (Kreitinger et al. 2007). These data illustrate a number of important points that might appear at your sites.

First, survival of the *H.* azteca when plotted against the concentration of the PAHs in the sediments on a dry weight (Figure 5-2A) does not follow the sigmoidal shape pattern. We expect this behavior because

the total concentration of the PAHs is poor measure of the bioavailable portion of the PAHs in the sediments. Second, survival of the *H.* azteca when plotted against the concentration of the PAHs in the sediments on an organic carbon basis (Figure 5-2B) does not follow the sigmoidal shape pattern. Depending upon the types and consistency of the organic carbon in the sediments at your site, sigmoidal dose-response behavior might or might not occur with organic carbon normalization. For the Hudson River example (Figure 5-2B), organic carbon normalization does not completely account for the bioavailability of the PAHs in the sediments. Third, when C_{free} concentrations in sediment pore water are expressed on a toxic units basis, the data follow the sigmoidal shape pattern shown in Figure 5-1, that is, at elevated survival, there are low TUs of contaminants and at low survival, there are high TUs of contaminants (Figure 5-2C). Kreitinger et al. (Kreitinger et al. 2007) computed the total toxic units using EPA's narcosis FCVs (Table 3-1 (US-EPA 2003c)) and their measured concentrations in the sediment pore water for the 18 parent PAHs and 16 alkylated PAH groups (Figure 5-2C). Fourth, in Figure 5-2C, non-toxic and toxic samples have toxic units ranging from 0.1 to 18 and from 110 to 310, respectively. The break point between non-toxic and toxic sediment samples occurs somewhere between 18 and 110 toxic units, and not at 1.0 toxic unit. The break between non-toxic and toxic samples at toxic units different from 1.0 is expected and data from your site will likely have this behavior as well. The reason for the departure from 1.0 toxic units for the break between non-toxic and toxic samples is that *H. azteca* are less sensitive than the (theoretical) species driving the FCV. As discussed in Section 3.4, the sensitivity of the test organism itself, in all likelihood, does not reside at the 5^{th} percentile value of the SSD, but rather at a higher percentile in the SSD. In addition, the FCV represents a very low level of chronic effect (rather than 50% effect), and includes consideration of all endpoints, lethal and sublethal). Coherence of the site exposure-response curve for the sediment toxicity data can be evaluated by calculating the expected toxicity (based on other data) for the tested species and COCs. In Appendix A, the EC50 for *H. azteca* has been derived from water-only toxicity testing of PAHs, and for the data in Figure 5-2C, toxicity data for *H. azteca* derived from the literature agrees fairly well with measured toxicity, i.e., the literature EC50 resides between the toxic and nontoxic samples. Finally, if one uses the toxicity of the PAHs to *H. azteca* to convert the concentrations in sediment pore water to toxic units, the 28-day *H. azteca* chronic survival data replots as shown in Figure 5-2D where the literature EC50 for PAHs and EC50 from the sediment toxicity tests contaminated with PAHs both reside at approximately 1.0 toxic unit. The agreement illustrated in Figures 5-2C and 5-2D is the same and the only difference is the labeling of the x-axis.

Figures 5-2C illustrates the case where a sigmoidal dose-response is obtained; the EC50 for the tested sediments does not reside at 1.0 TU; and the EC50 of the contaminants from toxicity tests with the pure chemical and the test species resides between the non-toxic and toxic sediment samples. When the EC50 of the pure chemical and test species aligns with the break between non-toxic and toxic samples, and there is a sigmoidal dose-response, consistency between the sediment toxicity testing data and toxicity of the COCs has been shown.

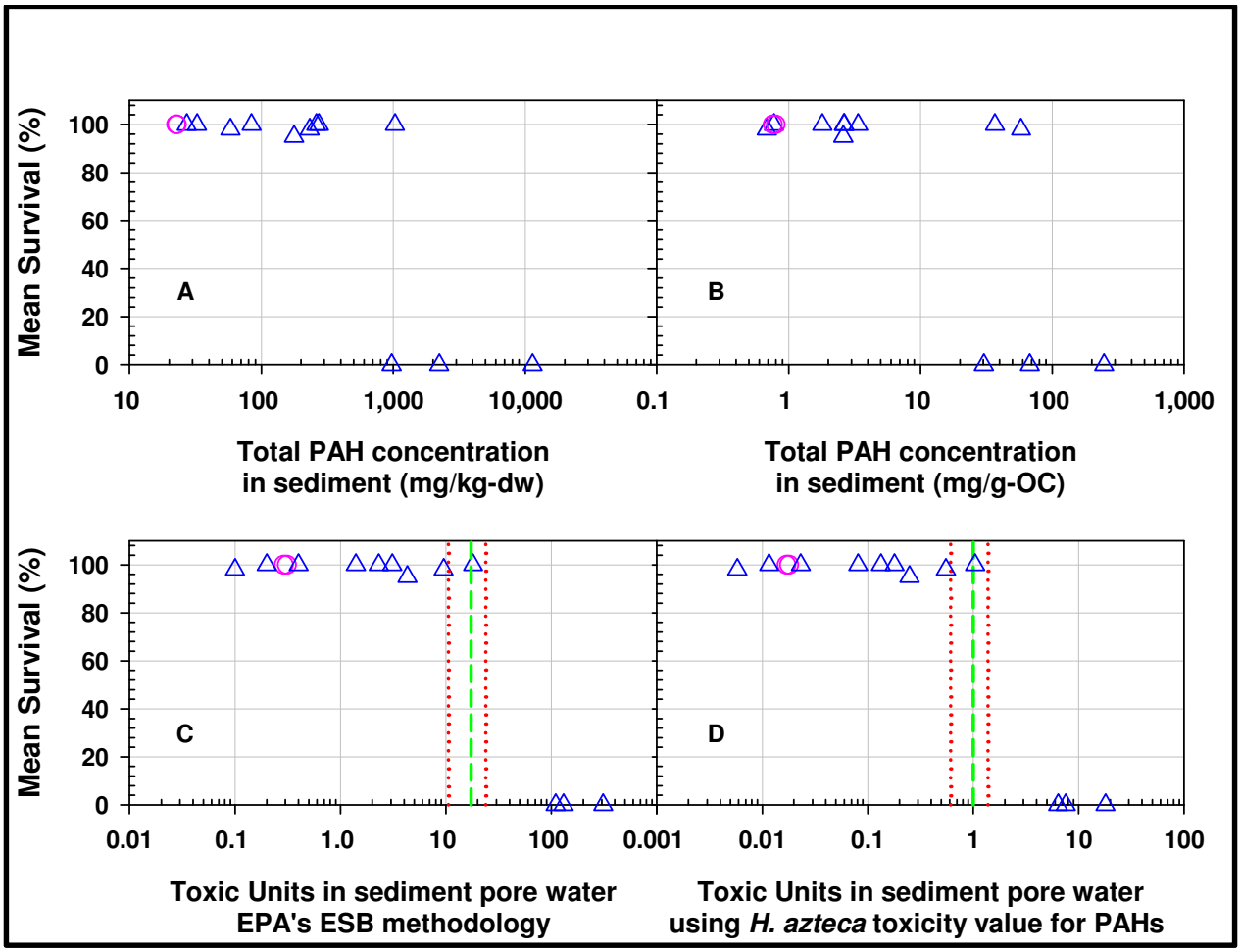

Figure 5-2. *Hyalella azteca* 28-d survival data for sediment toxicity tests with sediments from the Hudson River at Hudson, NY (Kreitinger et al. 2007) plotted against A) concentration of PAHs in sediment (mg/kg dw), B) concentration of PAHs in sediment on an organic carbon basis (mg/g OC), C) toxic units of PAHs in sediment pore water, and D) toxic units adjusted to the sensitivity of the *H. azteca*. Toxic units of measured C_{free} values in sediment pore water were derived using EPA's ESB methodology discussed in Section 4.3.2.2 (Figure C) and in Figure D, adjusted using the toxicity for *H. azteca*. Pink circle symbols are the sediment toxicity test controls. The ––– and ···· lines are the mean and 95% confidence levels for the EC50 for chronic survival derived from the water-only toxicity testing of PAHs.

Another common occurrence with sediment toxicity testing data is the attainment of incomplete dose-response curves. Figure 5-3 illustrates a case where all of the samples are nontoxic. The data in Figure 5-3 are for sediments from the Hudson River at Troy, NY (USA) and most of the data are in good agreement with the sediment test controls (considered nontoxic) (Kreitinger et al. 2007). Two field reference sediments were include in the samples tested and these were collected near the site from locations having low PAH concentrations and considered not affected by the PAH contamination (Kreitinger et al. 2007). These data illustrate the following points:
First, when toxicity data for a set of sediment samples has similar results for all samples, e.g., all samples are non-toxic or all samples are toxic, one needs to determine/obtain from the literature the toxicity of the COCs from pure chemical testing. With the toxicity of the COCs, you should determine if the sediment samples have the proper orientation relative to the COCs' EC50 from pure chemical testing. In Figure 5-3, the toxicity value for PAHs derived in Appendix A is consistent with the testing data, i.e., the TUs for the tested samples are less than the EC50 from water-only toxicity testing of PAHs. This consistency conforms to the sigmoidal dose-response pattern and we conclude that the data in Figure 5-3 are from the lower end of the sigmoidal dose-response curve where no effects are observed. Second, if one has a set of sediment samples where all samples are toxic, the TUs for the tested samples should be greater than the EC50 from water-only toxicity testing of the COCs. Although the data are consistent with a sigmoidal dose-response curve, the consistency does not absolutely insure that contaminants causing the toxicity in the sediment samples are the identified COCs. There may be unidentified contaminants in the sediment causing the toxicity in the sediments.

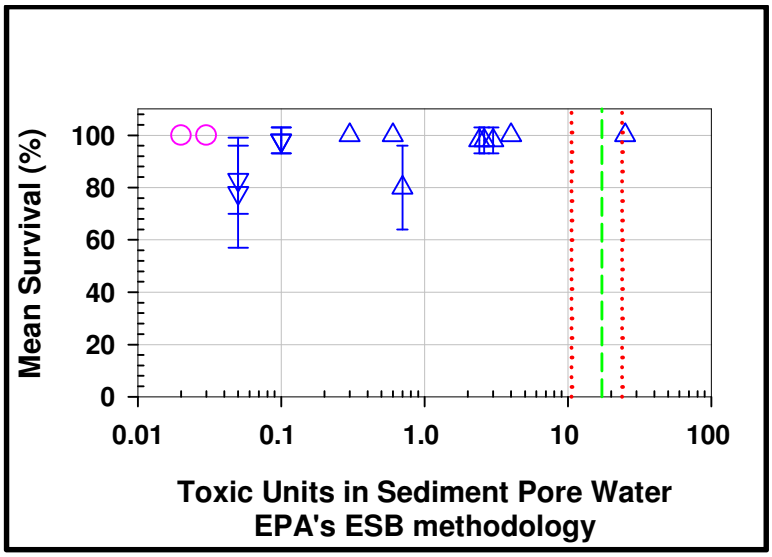

Figure 5-3. Measured survival data (± one standard deviation) for *Hyalella azteca* in 28-d sediment toxicity tests with sediments from the Hudson River at Troy, NY (Kreitinger et al. 2007). Toxic units of measured C_{free} values in sediment pore water were derived using EPA's ESB methodology (discussed in Section 4.3.2.2). Downwards triangle symbols are for field reference locations for the site and pink circle symbols are the sediment toxicity test controls. The controls are considered non-toxic, have zero toxic units, and are arbitrarily placed on the graph. The ---- and ····· lines are the estimated mean and 95% confidence levels for the EC50 for chronic survival derived from the water-only toxicity testing of PAHs (Appendix A).

Like the data in Figure 5-2, the data in Figure 5-3 conforms to the sigmoidal dose-response pattern, i.e., the non-toxic sediment samples have the proper orientation relative to the EC50 of the COCs from water-only toxicity testing of the chemicals.

A broader comparison of PAH toxicities has been performed by Hawthorne et al. (Hawthorne et al. 2007) where 97 sediment samples from six manufactured-gas plants and two aluminum smelter sites were investigated. Each sediment sample was toxicity tested using *Hyalella azteca* and subjected to passive sampling measurement. For these sediments, 28-d survival data for *Hyalella azteca* and the estimated sediment toxicity, using EPA's PAH FCVs along with their measured concentrations in the sediment pore water for the 18 parent PAHs and 16 alkylated PAH groups, are shown in Figure 5-4. Like the data of Kreitinger et al. (Kreitinger et al. 2007) in Figure 5-2, these data follow the sigmoidal shape pattern, i.e., at low predicted toxicity, high survival and at high predicted toxicity, low survival (Figure 5-4). Similar to the data of Kreitinger et al. (Kreitinger et al. 2007) above (Figures 5-2 and 5-3), the Hawthorne et al. (Hawthorne et al. 2007) toxicity data illustrates the case where the sediment test organism is less sensitive than the 5th percentile derived from the SSD for the PAHs (US-EPA 2003c). The toxicity value for PAHs derived in Appendix A is consistent with the testing data of Hawthorne et al. (Hawthorne et al. 2007) (Figure 5-4).

These data illustrate some of the variability one might observe at their site. Across these eight sites, there were only one or two potential outliers in the entire dataset. One of the samples with unusual toxicity was almost pure sand with very low organic carbon content, and the poor survival of the test organisms might have been related to the poor nutritional content of a sediment (Hawthorne et al. 2007). Like the data in Figures 5-2 and 5-3, the EC50 does not reside at 1.0 TU for the COCs in the sediments tested; the non-toxic sediment samples have the proper orientation relative to the EC50 of the PAHs derived from water-only toxicity testing of PAHs; and the data conforms to the sigmoidal dose-response pattern. The data of Hawthorne et al. (Hawthorne et al. 2007) can be replotted using toxicities predicted using PAH toxicity value derived for *H. azteca* in Appendix A instead of the EPA's FCV for PAHs. When replotted, the predicted toxicities shift such that EC50 in the toxicity data align around 1.0 TU for the data of Hawthorne et al. (Hawthorne et al. 2007) (Figure 5.5), and non-toxic sediment samples have the proper orientation relative to the EC50 of the PAH mixture, and the data conform to the sigmoidal dose-response pattern. The EC50 from Appendix A resides at ca. 20% survival endpoints in the probit regression and the *H. azteca* EC50 estimate comes from entirely independent data set.

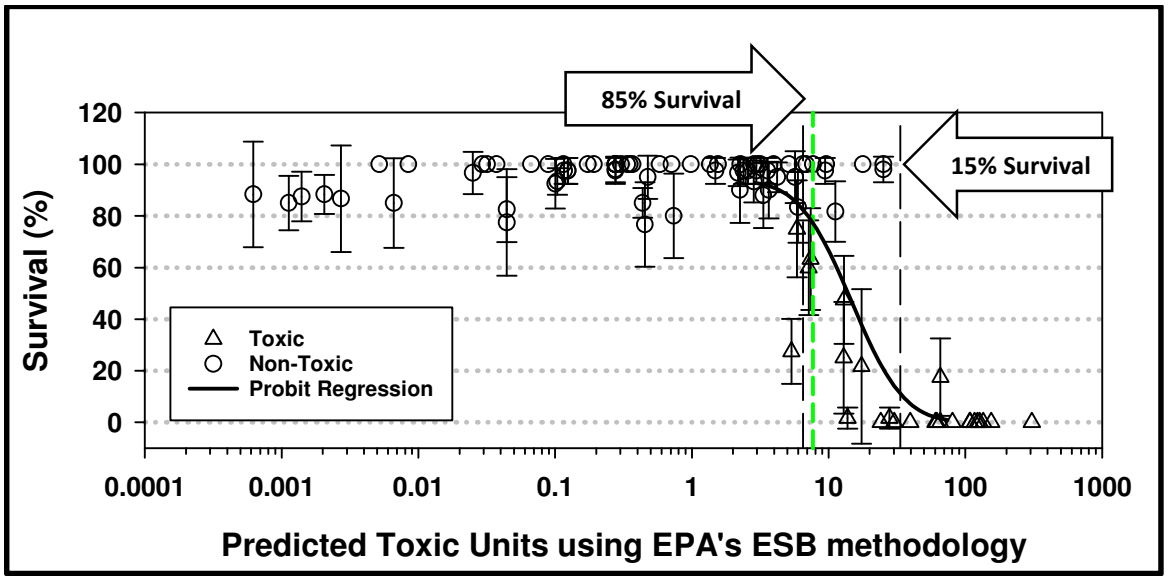

Figure 5-4. Measured toxicity survival data for *Hyalella azteca* in 28-d sediment toxicity tests with 97 sediments from six manufactured-gas plants and two aluminum smelter sites, and toxicity estimated from the concentrations of PAHs in the sediment pore water (Hawthorne et al. 2007). The *Hyalella azteca* EC50 (short dash line) was derived from the water-only toxicity testing data (Appendix A). The solid line is the probit regression fit of the data and 15% and 85% survivals lines (long dash) are from the probit regression. Adapted with permission from Hawthorne SB, Azzolina NA, Neuhauser EF, Kreitinger JP (2007). Predicting bioavailability of sediment polycyclic aromatic hydrocarbons to *Hyalella azteca* using equilibrium partitioning, supercritical fluid extraction, and pore water concentrations. *Environmental Science & Technology* 41:6297-6304. Copyright 2007 American Chemical Society.

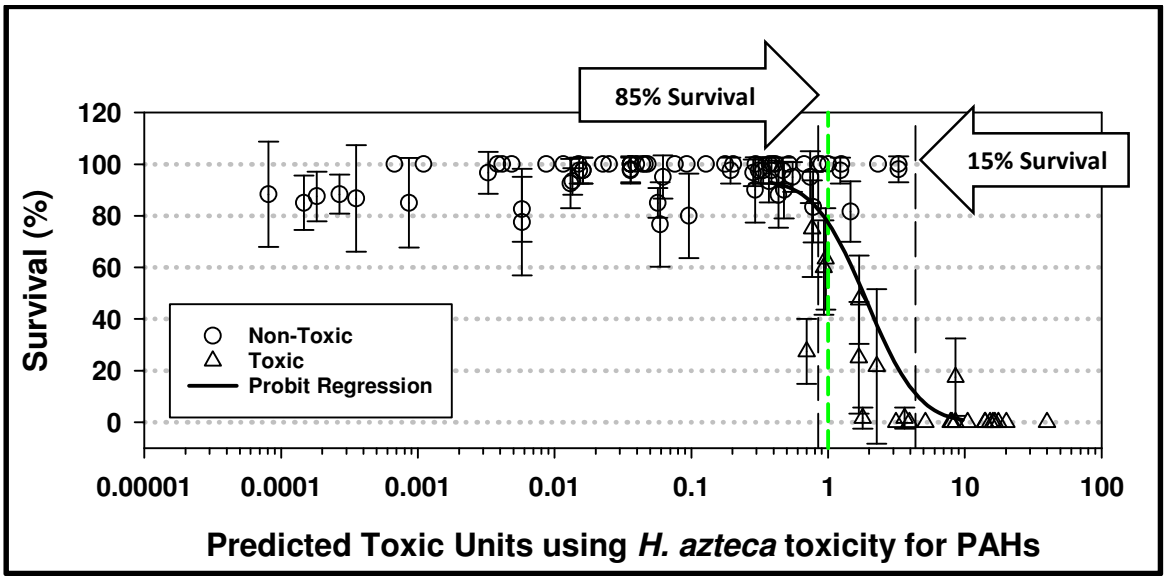

Figure 5-5. Measured toxicity survival data for *Hyalella azteca* in 28-d sediment toxicity tests with 97 sediments from six manufactured-gas plants and two aluminum smelter sites, and toxicity estimated from the concentrations of PAHs in the sediment pore water (Hawthorne et al. 2007). The *Hyalella azteca* EC50 (----) was derived from the water-only toxicity testing data (Appendix A). The solid line is the probit regression fit of the data and 15% and 85% survivals lines (long dash) are from the probit regression. Adapted with permission from Hawthorne SB, Azzolina NA, Neuhauser EF, Kreitinger JP (2007). Predicting bioavailability of sediment polycyclic aromatic hydrocarbons to *Hyalella azteca* using equilibrium partitioning, supercritical fluid extraction, and pore water concentrations. *Environmental Science & Technology* 41:6297-6304. Copyright 2007 American Chemical Society.

5.2.3 Approaches for Aligning Sediment Toxicity Results with Pore Water RGs

In general, a weight of evidence (WOE) approach should be used at your site to evaluate the alignment of sediment toxicity testing results with the pore water RGs developed for your site. The WOE approach will vary across sites because the amount of confidence needed in the agreement between the toxicity testing results and pore water RGs is highly dependent upon the significance of the decision(s) based upon the comparison. Some factors that one should consider include:

- How well does the sediment toxicity data conform to the expected sigmoidal dose-response curve?
- Does the EC50 from water-only toxicity testing of the COCs for the species used in the toxicity tests reasonability define the break between non-toxic and toxic sediment samples on the sigmoidal dose-response curve?
- Are all sediment toxicity testing results explainable based on their positions on the sigmoidal dose-response curve?
- Do outliers exists in the dose-response plot, and if so, are they explainable?

In considering the above factors:

- Was the nature and variability of the f_{OC} and K_{OC} values adequately defined for the site? Was this information used in the calculation of the toxic units for the COCs in the toxicity tested sediment samples?
- When the COCs are a mixture, e.g., PAHs, were changes in the composition of mixture across the site accounted for in the calculation of the toxic units for the COCs in the toxicity tested sediment samples?

The overall approach for aligning sediment toxicity testing results with the pore water RGs developed for your site is the comparison of the sediment toxicity testing results with the pore water concentration measurements (or equivalently, computed toxic units). These data need to form a sigmoidal dose-response curve and the break between non-toxic and toxic samples should be consistent with the EC50 from water-only testing of the COCs with the toxicity testing species. When these conditions exist, one has shown consistency between the toxicity testing results and the pore water RGs. When consistency exists in the data, one can be reasonably assured that the contaminants causing toxicity to benthic organisms have been correctly identified and that the developed pore water RGs for the contaminants will be protective of the benthic organisms at the site. Clearly, if the passive sampling measurements are for chemicals that have little or no role in the overall toxicity of the sediments, plotting of the sediment toxicity measurements against the passive sampler measurements should enable detection of the issue.

It is important to note that the evaluation of exposure-response is primarily intended to establish that the inferred risk to benthic organisms (as indexed by sediment toxicity) is attributable to the COC(s) that are the focus of the RG development. In doing so, the exposure response evaluation is often focused on an endpoint, (e.g., survival versus reproduction), a level of effect (e.g., 50% mortality in a less than life-cycle test) or organism that is not as sensitive as the level of protection intended by the FCV for the chemical. The importance of these differences must be considered in characterizing the level of risk posed by site contamination and the intended benefits of different RGs.

5.2 Method Uncertainties and Confounding Factors

Standardized operating procedures for passive sampling measurements are not currently available although guidance is available (US-EPA/SERDP/ESTCP 2017). The technique has evolved over the past decade (Ghosh et al. 2014; Greenberg et al. 2014; Lydy et al. 2014; Mayer et al. 2014; Parkerton and Maruya 2014), and there are a host of issues that could arise with the passive sampling technique. These issues including inaccurate $K_{Polymer}$ partition coefficients, nonattainment of equilibrium conditions when equilibration techniques are used, performance reference compounds that do not accurately match the partitioning behavior of the toxicants, inconsistencies in polymer batches resulting in varying partition coefficients, and detection limit issues. Some simple checks on the passive sampling measurements could include “Are the freely dissolved concentrations less than the chemicals’ aqueous solubilities?” and “Are the freely dissolved concentrations estimated using generic K_{OC}s greater than

those measured by passive sampling?" Additional checks and data evaluation procedures for the quality of passive sampling measurements will be provided in a forthcoming document, and the readers should consult this document (US-EPA/SERDP/ESTCP 2017).

In addition to the potential uncertainties associated with passive sampling measurements, sediment toxicity tests are performed with live organisms and these organisms are obtained from in-house cultures and facilities specializing in culturing the test organisms. As with any living organism testing system, occasional unusual results occur even though test controls are within performance specifications. Different cultures of live organisms might have slightly different sensitivities to the COCs and these sensitivity differences could slight shift the sigmoidal dose-response curve among testing laboratories. Some simple checks on the toxicity testing results could include comparing controls with controls from prior testing data from the testing facility and determining if organism source deviated from the testing laboratory's normal practices. The sensitivities of the organisms to reference toxicants and the site's COCs might also be evaluated. Clearly, the sediment toxicity test results should also meet the criteria specified in their testing protocol, and the reader should consult these documents for these criteria (US-EPA 1994; US-EPA 2000; US-EPA 2002a; US-EPA 2002b; US-EPA and US-ACE 2001).

There are situations where conformity with the expected sigmoidal dose-response curve might not appear or the sigmoidal dose-response is messy. One cause is the presence of other unidentified contaminants in the sediment samples. Unidentified contaminants could cause sediment samples to be much more toxic than estimated from the measured concentrations in sediment pore water for the identified contaminants. The unidentified contaminants could be additive with or exert toxicity independent of the identified contaminants in the samples. Sediment samples with unidentified contaminants will often appear as outliers from the expected sigmoidal dose-response curve. One needs to understand why outliers exist in the site data and further, their influence upon the overall conceptual model of sediment toxicity at the site, the site's CSM, and ultimately, remedy selection. Are the outlier samples located in one portion of the site? Are the outlier samples scattered across the site? Do the outlier samples have unusual composition, e.g., ammonia, sulfides, metals, high in oils/greases, tars, wood chips or sand, relative to the other samples at the site? Are the outliers an artifact of the quality of the toxicity testing and/or C_{free} data? Performing sediment Toxicity Identification Evaluations (TIEs) (US-EPA 2007b) on the outliers might be in order depending upon the site, location of the samples within the site, and/or the cost of the remedial action. The importance of understanding why the outliers exist cannot be under emphasized because the outliers could influence the remedy selection and the success of the remedy.

When multiple contaminants exist at your site and the contaminants are not additive toxicologically, plotting of toxicity testing endpoints against the predicted toxicities based upon the concentrations measured in the pore water should be performed for each contaminant separately. Separate plots would enable a better evaluation of the dose-response for the individual contaminants. At large sites where different contaminants are at different locations within the site, i.e., contaminant X is in locations A, and contaminant Y is in locations B, the data should be plotted separately to determine if a sigmoidal dose-response exists for each contaminant at its locations within the site. Plotting of toxicity data for both contaminants in one plot would simply confuse the interpretation of the data. Alternatively, exposure/response data can be plotted with the exposure axis being the maximum TU from any COC (or

additive mixture thereof). This approach may help identify cases where a sample showing toxicity at low concentrations of one COC might be explained by a high exposure to another COC, something that can be hard to evaluate in plots that show only one COC at a time.

At some sediment sites, PAHs reside in an oily matrix in the sediment, and the oily matrix can contain high levels of aliphatic hydrocarbons (e.g., alkanes and cycloparaffins). Aliphatic hydrocarbons are the major components of lubricants and greases, and are present in crude oil and numerous refined petroleum products. A confounding issue with PAHs might occur when high levels of aliphatic hydrocarbons are present in the sediments. For aliphatic hydrocarbons, their mechanism of toxicity for filter feeding benthic invertebrates, such as the freshwater amphipod *Hyalella azteca*, can stem from a physical effect, such as fouling of respiratory surfaces by the oil phase (Mount et al. 2015, unpublished results). A risk assessment on mineral oils by Verbruggen (Verbruggen 2004) reported EC50s of 500 (90% CI: 460-550) mg/kg-dw and 1800 (850-4000) mg/kg-dw for mortality, and 67 (0-180) mg/kg-dw and 130 (19-240) mg/kg-dw for growth for 10-d *Hyalella azteca* toxicity tests with two different oil mixtures. In most cases, the composition of mineral oil will not be highly reflective of the composition of the aliphatic hydrocarbons at your site. Consequently, the levels reported by Verbruggen (Verbruggen 2004) should be taken as indicative. Measurements of gasoline range organics (GROs) and diesel range organics (DROs), residual range organic (RROs) will provide some indication of the levels of aliphatic hydrocarbons, but these measurements can include aromatic hydrocarbons depending upon the analytical method and will complicate data interpretation. When toxicity testing data are substantially more toxic than predicted based upon the PAH content, we suggest you consider possibility of the aliphatic hydrocarbons as the contaminants when all other contaminant classes, e.g., pesticides, metals, …, have been eliminated as causes of toxicity in the sediment samples of interest.

APPENDIX A

DERIVATION OF 10- and 28-DAY PAH EFFECT CONCENTRATIONS FOR *HYALELLA AZTECA* FOR PURPOSES OF EVALUATING EXPOSURE-RESPONSE IN SEDIMENT TESTS

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1.0 Background and Purpose

This appendix was developed to provide an estimated response value for the amphipod, *Hyalella azteca*, when exposed to polycyclic aromatic hydrocarbons (PAHs) in 28-d sediment toxicity tests. These values are not intended to be cleanup values or otherwise used as regulatory values, they have been derived to aid in the interpretation of 28-d sediment toxicity test data, particularly to evaluate whether a measured PAH exposure in sediment or water is of an intensity that would be expected to cause effects to *H. azteca*. These are values expected to cause 50% effect in exposed organisms, they are not threshold effect values nor are then intended to assess effects on any organism other than *H. azteca*.

2.0 Technical Basis

The conceptual framework used to derive these values is that described by Di Toro et al. (Di Toro and McGrath 2000; Di Toro et al. 2000) and later used by U.S. EPA in deriving Equilibrium-partitioning Sediment Benchmarks (ESBs) for PAHs (US-EPA 2003c). This approach assumes that PAHs affect organisms like *H. azteca* via a narcosis mechanism of toxicity, which in turn asserts that 1) the toxicity of individual chemicals (including PAHs) increases with increasing octanol-water partition coefficient (K_{OW}); and 2) that the toxicity of a mixture of these chemicals can be predicted by summing their relative potencies (exposure concentration/effect concentration) across all the similar chemicals in the mixture. The Di Toro et al. (Di Toro and McGrath 2000; Di Toro et al. 2000) approach asserts that the slope of the relationship between effect concentration and K_{OW} has a common slope across all organisms, such that this "universal narcosis slope" can be used to normalize the toxicity of narcotic chemicals with different Kow values to common units and therefore compare them, even though their absolute toxicities vary. This approach is built on the theoretical construct of a critical body burden, and correspondingly that the relationship to K_{OW} is tied to the partitioning of chemical between the water and the organism (higher K_{OW} = higher partitioning to the organism = higher potency).

Although the approach is built around a body burden concept, the calculations are based on water column exposure concentrations, rather than measured body burdens. This is in part because of

the much greater availability of data for water column exposures than for residue-response studies; it also avoids directly addressing complications of metabolites and kinetics of chemical uptake. Finally, basing calculations on water column exposures is particularly appropriate for purposes of evaluating interstitial water-based evaluations of sediment exposure, since concentrations in (interstitial/pore) water are the exposure measure for such evaluations.

3.0 Data collection and analysis

3.1 Data collection and aggregation

Data relevant to this analysis were collected by searching the ECOTOX database (www.epa.gov/ecotox) using the species name "*Hyalella azteca*" and selecting the PAH chemicals subgroup. From there, papers containing water-only exposure data for *H. azteca* were identified and the data contained therein were collated. Some papers provided toxicity data for many time points; from these, emphasis was placed on 10-d and 28-d endpoints, as these correspond to the durations of common sediment toxicity test procedures.

The extracted endpoint was the reported LC50 or EC50 (though some reported EC50 values were reported on the basis of mortality). While the 10- and 28-d *H. azteca* sediment tests measure sublethal endpoints (growth) in addition to survival, for most *H. azteca* sediment toxicity data from PAH-contaminated sites the authors are aware of, survival is the primary responding endpoint. That is not to say that the values derived here implicitly account for sublethal effects, only that the derived values are expected to be applicable to many site data sets.

This search yielded ten LC50/EC50 values, 9 for 10-d exposures and one for a 28-d exposure (Table 1). Data coverage included 7 publications and 5 different PAHs. In some cases, values had to be visually interpolated from graphic presentations. If necessary, reported water concentrations were converted to µg/L units using the molecular weights listed in Table 1.

As explained above, to directly compare potencies across PAHs, data must be normalized to account for differing lipophilicity. This was performed using the method described by Di Toro et al. (Di Toro and McGrath 2000; Di Toro et al. 2000), which estimates a theoretical critical lipid concentration (C_ℓ^*),in units of µmol/g octanol, and calculated from the equation:

$$\text{Log}(C_\ell^*) = ((\text{log EC50 in } \mu\text{mol/L}) + 0.945 * \text{log } K_{OW} \text{ (L/kg octanol)} * 0.0001 \text{ kg/g} \quad (1)$$

Resulting values are shown in Table 1.

3.2 Selection of a 10-d *H. azteca* C_ℓ^* value

The overall range of C_ℓ^* values obtained for nine 10-d exposures is about a factor of 4 overall (range 9.6 to 34.7), but the distribution is skewed, with six of the nine values clustered in the range of 26.2 to 34.7, and three in the range of 9.6 to 17.1. Toxicity data are often aggregated using the geometric mean, but the observed distribution is even more skewed in log space, arguing against that approach. Instead, the median, rather than the mean, of 27.3 µmol/g octanol was selected as the estimated 10-d *H. azteca* C_ℓ^*.

3.3 Selection of a 28-d *H. azteca* C_ℓ* value

Only one applicable 28-d water only study was identified, which yielded a C_ℓ* value of 18.6 µmol/g octanol. The robustness of this value is uncertain because of having only a single value. An alternative means to estimate the 28-d C_ℓ* value is to apply an adjustment factor to the 10-d C_ℓ* value to reflect the greater toxicity expected with longer exposure duration. In the case of the single measured 28-d C_ℓ* value, the same study (Schuler et al. 2004) had a paired 10-d observation, which gave a 10-d C_ℓ* value of 34.7, for a 10-d/28-d ratio of 1.86. In addition, the Lee et al. (Lee et al. 2001) study contained daily EC50 values for up to 16 days of exposure for four different PAHs. Plotting the Lee et al. data (Lee et al. 2001) as the log of the daily EC50 values versus the log days yielded quite linear slopes. Linear regressions were fit to those slopes using the available data from days 7 to 16, then the resulting regressions were used to estimate 10-d EC50s and extrapolated to estimate 28-d EC50s. The resulting ratios of 10-d EC50 to 28-d EC50 were 1.69 for naphthalene, 1.41 for fluorene, 1.22 for phenanthrene, and 1.89 for fluoranthene. These four values were combined with the value of 1.86 for fluoranthene from the Schuler et al. (Schuler et al. 2004) study, yielding a geometric mean of 1.59, which when applied to the 10-d C_ℓ* value of 27.3 yields an estimated 28-d C_ℓ* value of 17.2 µmol/g octanol.

This 28-d C_ℓ* value is not only generally consistent with the single reported 28-d value of 18.6 (Table 1), but it is also reasonable that it is slightly lower than the Schuler et al. (2004) value, which seems appropriate given that the 10-d C_ℓ* value from the Schuler et al. (2004) study was the highest among those 10-d values.

4.0 Comparison to EPA PAH ESB

While the EPA ESB document for PAHs has the same general goal of estimating potency of PAHs to aquatic organisms, including *H. azteca*, and it is based on the same narcosis theory that the current derivation is, there are differences in how the PAH ESB was calculated that create differences between the estimated sensitivity of *H. azteca* in the PAH ESB document and the analysis above. In the PAH ESB document, the ESB had only a single *H. azteca* value in the acute toxicity database, a 4-d LC50 value of 44 µg/L for fluoranthene (Spehar et al. 1999). If one computes a 4-d C_ℓ* value from this, the resulting value of 13.9 µmol/g octanol is counterintuitively low compared with the higher 10-d C_ℓ* value of 27.3 computed here, as one would expect that C_ℓ* should decline with length of exposure. The PAH ESB derivation did not include any chronic *H. azteca* data as no life-cycle toxicity data were available for the species, but if one applied the generic acute-chronic ratio of 4.16 (US-EPA 2003c), the species specific chronic C_ℓ* estimate for *H. azteca* would be 3.34 µmol/g octanol, which is nearly as low as the actual ESB of 2.24 µmol/g octanol (US-EPA 2003c). Some have extended this argument to assert that a *H. azteca* toxicity test is essentially as sensitive as the PAH ESB and would therefore provide a comparable level of protection.

The data provided in Table 1 argue this is not the case, and that actual sensitivity of *H. azteca* to PAHs is higher than the ESB. We believe the underlying reason for the apparent discrepancy lies in a problem with the Spehar et al. (Spehar et al. 1999) acute value of 44 µg/L for fluoranthene. Recent research has shown that *H. azteca* is sensitive to the chloride content of the

dilution water, and that at chloride concentrations below about 15 mg/L, sensitivity of the common strain of *H. azteca* used in most laboratory studies (including the Spehar study) increases in a way not seen in other strains of *H. azteca* (Soucek et al. 2015). As the water source used for the Spehar study is known to have low chloride (about 1.5 mg Cl/L), it is very likely that the Spehar LC50 is biased low, something that was confirmed in the compilation of data for the current analysis. Among 4-d LC50 data obtained for our analysis, computed 4-d C_ℓ* values from five other studies ranged from 30.5 to 94.4 µmol/g octanol, far above the value of 13.9 from the Spehar study, and much more consistent with data from the 10-d and 28-d studies. The conclusion is that the sensitivity of *H. azteca* that might be inferred from the PAH ESB document is over-estimated, and is better represented by the current analysis.

Despite this difference, the potency of PAHs in sediments as calculated by the PAH ESB can be used to estimate effect concentrations specifically for *H. azteca* 10-d and 28-d toxicity tests. The PAH ESB is based on a final chronic value (expressed as C_ℓ*) of 2.24 µmol/g octanol (U.S. EPA 2003). Accordingly, one would expect the 10-d EC50 for *H. azteca* to occur at 27.3/2.24 = 12.2 times the ESB concentration (or 12.2 ESBTU) and the 28-d EC50 to be 17.2/2.24 = 7.68 times the ESB concentration (7.68 ESBTU). It is important to note that these values are <u>not</u> threshold values that would be protective of *H. azteca*; instead they are EC50 values that would be expected to have substantial adverse effect on *H. azteca*. To estimate a threshold for the *H. azteca* response in 10-d or 28-d toxicity tests, the values presented here would have to be adjusted down to go from an EC50 to an acceptably low level of effect.

5.0 PAH-specific water concentrations for evaluating 10-d and 28-d response

To predict the toxicity of a mixture of PAHs measured in interstitial water, one must calculate the ratios of the exposure concentration to the effect concentration for each individual PAH, then sum those ratios across all PAHs. PAH-specific values for making these calculations, based on the 10-d and 28-d C_ℓ* values derived above, are presented in Table 2. Fifty percent effect to *H. azteca* is predicted when the summed ratios equal 1. If the summed ratios are greater than 1, effects on *H. azteca* should be greater than 50%; if the summed ratios are less than 1, less than 50% effect is expected. It is critically important to understand that it is the <u>sum</u> of the ratios that is evaluated, not the ratios for individual chemicals.

Table 1 – Compiled 10-d and 28-d water column toxicity data and calculated critical lipid concentration (C_ℓ*) (based on Equation 1) for *Hyalella azteca*.

Chemical	Exposure Duration (day)	Endpoint	Value (µg/L)	MW (g/mol)	log K_{OW}	C_ℓ* µmol/g-octanol	Source
Fluoranthene	10	LC50	110	202	5.08	34.71	(Schuler et al. 2004)
Fluoranthene	10	LC50	105	202	5.08	33.21	(Driscoll and Landrum 1997)
Naphthalene	10	LC50	3032	143	3.36	31.46	(Lee et al. 2001)
Fluorene	10	LC50	486	166	4.21	27.76	(Lee et al. 2001)
Phenanthrene	10	LC50	233	178	4.57	27.34	(Lee et al. 2001)
Fluoranthene	10	LC50	83	202	5.08	26.20	(Wilcoxen et al. 2003)
Pyrene	10	LC50	77	202	4.92	17.07	(Lee et al. 2001)
Fluoranthene	10	EC50	45	202	5.08	14.17	(Suedel et al. 1993)
Fluoranthene	10	LC50	30	202	5.08	9.56	(Suedel and Rodgers Jr 1996)
Fluoranthene	28	LC50	59	202	5.08	18.62	(Schuler et al. 2004)

Table 2 – Estimated single chemical 10-d and 28-d EC50 values for *Hyalella azteca* for use in estimating responses to PAH mixtures.

Chemical	**10-d *Hyalella* estimated EC50 (µg/L)**	**28-d *Hyalella* estimated EC50 (µg/L)**
Naphthalene	2355	1,482
C1-Naphthalenes	997	627
C2-Naphthalenes	368	232
C3-Naphthalenes	135	85.2
C4-Naphthalenes	49.4	31.1
Acenaphthylene	3745	2,358
Acenaphthene	681	429
Fluorene	479	302
C1-Fluorenes	170	107
C2-Fluorenes	64.6	40.7
C3-Fluorenes	23.4	14.7
Phenanthrene	234	147
Anthracene	253	159
C1-Phenanthrenes	90.8	57.1
C2-Phenanthrenes	39.0	24.5
C3-Phenanthrenes	15.4	9.7
C4-Phenanthrenes	6.82	4.29
Fluoranthene	86.7	54.6
Pyrene	123	77.6
C1-pyrene/fluoranthenes	59.7	37.6
Benz(a)anthracene	27.2	17.1
Chrysene	24.9	15.7
C1-Chrysenes	10.4	6.57
C2-Chrysenes	5.89	3.71
C3-Chrysenes	2.05	1.29
C4-Chrysenes	0.86	0.54
Perylene	11.0	6.92
Benzo(b)fluoranthene	8.26	5.20
Benzo(k)fluoranthene	7.83	4.93
Benzo(e)pyrene	11.0	6.92
Benzo(a)pyrene	11.7	7.35
Indeno(1,2,3-cd)pyrene	3.36	2.11
Dibenz(a,h) anthracene	3.44	2.17
Benzo(g,h,i)perylene	5.36	3.37

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