

Deriving Sediment Interstitial Water Remediation Goals (IWRGs) at Superfund Sites for the Protection of Benthic Organisms from Direct Toxicity

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Table of Contents

Executive Summary	4
Section 1	5
Introduction	5
1.1 Background	5
1.2 Purpose and Scope	10
Section 2	11
Measuring the Freely Dissolved Concentrations of Nonionic Organic Chemicals in Sediment Interstitial Water	11
2.1 Measurement of freely dissolved chemical concentrations (C_{free}) in sediment interstitial water using passive sampling	11
2.1.1 Passive Sampler Fouling	12
2.2 Measurement of chemical concentrations in sediment interstitial water using solid phase microextraction: ATSM Method D7363-13 and EPA Method 8272	12
Section 3	14
Establishing Adverse Effects Concentrations in Sediment Interstitial Water for Benthic Organisms	14
3.1 Use of aquatic life criteria as an effect benchmark	14
3.2 Sensitivities of benthic and pelagic organisms	15
Section 4	22
Implementation of the IWRG Approach	22
4.1 Overall approach	22
4.2 Development of interstitial water to bulk sediment contaminant relationships	24
4.3 Derivation of IWRG for a sediment with one primary contaminant – Dieldrin example	25
4.4 Derivation of IWRGs for a sediment with a PAH mixture as the primary contaminant	26
4.5 Derivation of IWRGs for a sediment with other toxicant mixtures	31
Section 5	32
Comparison and Evaluation of Toxicity Testing Results and IWRGs	32
5.1 Derivation of EPA’s AWQC FCVs	33
5.2 Sensitivities of toxicity test organisms in relation to EPA’s AQWC FCVs	33
5.3 Comparing passive sampling measurements and sediment toxicity test data for consistency: Sigmoidal response exists	34
5.4 Comparing passive sampling measurements and sediment toxicity test data for consistency: Difficult to interpret data (non-sigmoidal responses exist).....	36
5.5 Method uncertainties	38

Section 6	40
Appendix	40
6.1 Relationship between toxicity of PAH mixtures and aliphatic hydrocarbons	40
6.2 Measuring water only toxicity value for toxicant(s)	40
Section 7	41
References	41

Executive Summary

This document contains a methodology for developing interstitial water remediation goals (IWRGs) for nonionic organic pollutants (toxicants) in sediments for the protection of benthic organisms. The document provides the basis for using the final chronic values (FCVs) from EPA's aquatic water quality criteria (AWQC) for the protection of aquatic life to set the IWRGs for toxicants in sediments. Concentrations of the toxicants in the sediment interstitial water are measured using passive sampling. This document also discusses how to evaluate the consistency between passive sampling measurements and sediment toxicity test 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 IWRGs for the toxicants will be protective of the benthic organisms at the site. The consistency evaluation is an important step in developing defensible IWRGs.

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 for classifying the likely toxicity of contaminated sediments were developed. 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 Probably Effects Concentration (PEC) developed by MacDonald and others ((MacDonald et al. 1996; MacDonald et al. 2000); see Mount et al. (Mount et al. 2003) for more detail). 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 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., $\mu\text{g}/\text{kg}$ 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) could 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 non-polar organic contaminants, early work demonstrated that sediment organic carbon controlled the partitioning of those contaminants between sediment solids and the interstitial water (sometimes called “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 $\log K_{OC} = a + b \times \log K_{OW}$ and $K_{OC} = b \times K_{OW}$ 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:

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

where C_s is the concentration of chemical in the bulk sediment ($\mu\text{g}/\text{kg}$ dry weight), f_{OC} is the organic carbon content of the sediment (fractional value), 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 interstitial water ($\mu\text{g}/\text{L}$).

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 interstitial 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 interstitial 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 interstitial water. As discussed above, sediment organic carbon was thought to be the primary sediment phase controlling partitioning between sediment solids and the interstitial 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 seemed very similar, as it had when expressed based on interstitial water (Figure 1-1c).

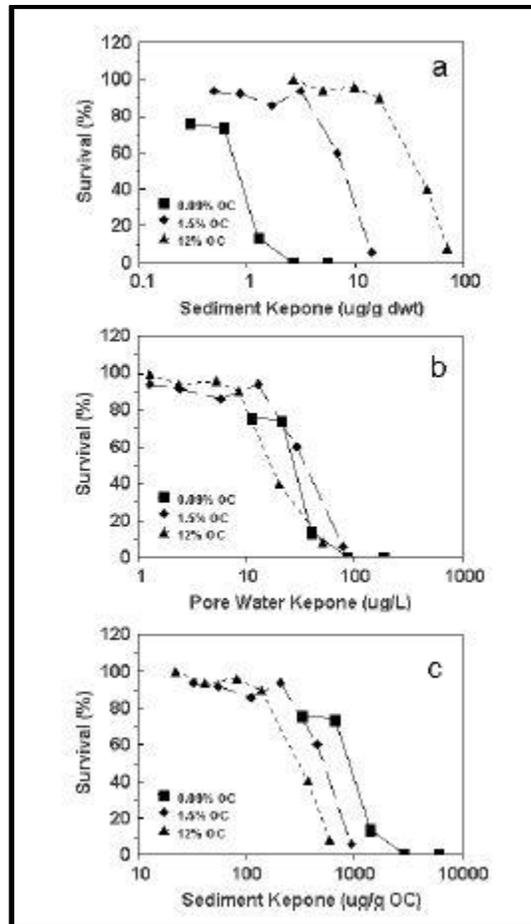


Figure 1-1. Toxicity of three Kepone-spiked sediments with different organic carbon content, expressed as Kepone in bulk sediment (a), Kepone in interstitial water (b), and organic carbon normalized Kepone in sediment (c). Redrawn from Adams et al. (1985).

Historically, measurement of concentrations of nonionic organic chemicals in sediment interstitial water has been analytically extremely challenging, and the method of choice has been centrifugation where the interstitial water is isolated from the bulk solids. As stated in the ASTM 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 interstitial 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 has been 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 interstitial water preparation and isolation that can result in an overestimation of the contaminant concentrations in the interstitial 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 in interstitial water can be very low, presenting challenges for analytical detection. These difficulties can be overcome with exceptional laboratory technique to produce accurate measurement of the freely dissolved concentrations of nonionic organic contaminants in sediments (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, there was considerable uncertainty as to whether the challenges of accurate isolation and analysis would preclude reliance on interstitial water as a routine measurement for sediment assessment.

Rather than relying on direct analysis of interstitial water, focus shifted to basing guidelines on the more easily measured bulk sediment concentrations, and predicting chemical concentration in interstitial 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 concentration in interstitial water corresponds closely with chemical activity, this rationalizes the concept that bioavailability and toxicity are proportional to concentration in interstitial water as demonstrated by Adams and others. It's worth noting that despite its emphasis on chemical activity/concentration in interstitial water EqP does not assume that interstitial water is the only route of exposure to organisms. What it assumes is that the chemical activity (which can be thought of 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 whether exposure is via sediment ingestion, interstitial water, or any combination of the two.

As implied by the Adams experiment, the bioavailable chemical in the sediment is equivalent to the freely dissolved chemical concentration (C_{free}) in the sediment interstitial water (Ankley et al. 1996; Di Toro et al. 2005; Di Toro et al. 1991; US-EPA 2000a; US-EPA 2003a; US-EPA 2009). Freely dissolved chemical in water is chemical held in solution by water molecules only, and is not associated with DOC, particulate organic carbon (POC), or colloids in the water phase. The freely dissolved concentration in water can never exceed the aqueous solubility of the chemical. In this document, bioavailable chemical and freely dissolved chemical are equivalent.

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 interstitial 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 low in dissolved organic carbon and other binding phases, it can generally be expected that most of the chemical in these experiments is present 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 chemical concentration in the interstitial water equaling that of the water only exposure. Thus, EqP can be used to estimate contaminant concentrations in sediments associated with specific levels of toxicity (or non-toxicity) by estimating the sediment concentration that would be in equilibrium with the same level of toxicity as determined 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 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 2003b; US-EPA 2003c; US-EPA 2003d; 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., $\mu\text{g/g}$ -organic carbon). For metals, the ESBs are expressed on a $\mu\text{mole/g}$ -organic carbon basis in the bulk sediment after considering sequestration of metals by acid volatile sulfides (AVS) or on a $\mu\text{g/L}$ basis when metals are measured directly in the sediment interstitial 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 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 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; Lydy et al. 2014; Maruya et al. 2009; Mayer et al. 2014). The passive sampling technique does not require isolation of the sediment interstitial water from the bulk sediment but rather is performed on the whole sediment 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. Polymers include low density polyethylene, polyoxymethylene and polydimethylsiloxane. During the deployment time, the contaminants diffuse from the interstitial 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 interstitial 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 interstitial water brings the EqP approach full circle; rather than basing the assessment on bulk sediment concentrations and predicting partitioning to interstitial water, chemical activity of sediment contaminants can be measured directly via passive sampling of interstitial water, and those concentrations can be used directly 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 derive Interstitial Water Remediation Goals (IWRGs) for the protection of benthic organisms. Like the ESBs that provide much of technical background, IWRGs 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 does not address effects that result from accumulation of chemical through the food chain and is not designed to explicitly protect higher trophic level benthic species (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, some phthalates, and several low molecular weight organic compounds, many pesticides, and some phthalates. Values for polychlorinated biphenyls (PCBs), chlorinated dioxins and chlorinated furans are not included because it is presumed their primary ecological risks would occur via accumulation and adverse effects to organisms at higher trophic levels. Although ESBs have been developed for cation metals (Cu, Cd, Zn, Pb, Ni, Ag), IWRGs 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 IWRG approach requires two basic elements: a) a method for measuring or inferring the freely dissolved concentration of contaminant in interstitial water; and b) a 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 IWRGs.

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

As discussed in the Introduction, centrifugation has been a common technique for isolating interstitial 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 interstitial water. The passive sampling technique is simple to perform in the laboratory and has lower potential for sampling handling and processing artifacts in comparison to the centrifugation technique.

2.1 Measuring Freely Dissolved Chemical Concentrations (C_{free}) in Sediment Interstitial 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 interstitial 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 interstitial water can be determined. In equation form, C_{free} is computed:

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

where, $C_{Polymer}$ is the concentration of the chemical in the equilibrated polymer material and $K_{Polymer}$ 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 same at a single time point in the equilibration process, equilibrium has been obtained (Mayer et al. 2014). For many target contaminants of interest (e.g., PCBs and PAHs), 28-days is often assumed to be adequate time for a passive sampler to obtain equilibrium.

There will be cases where equilibrium conditions are not obtained in 28-days. Causes of non-equilibrium conditions include slow diffusion kinetics for highly hydrophobic chemicals like dibenz[a,h]anthracene, slow desorption kinetics from black carbon like phases to the interstitial 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). By measuring the loss of the PRCs from the sampler during their equilibration, one can determine if 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, their actual freely dissolved concentrations 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 interstitial water. Two US-EPA documents provide details on the passive sampling approach (US-EPA 2012a; US-EPA 2012b). 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 is a methodological issue with the passive sampling technique. For fouling by biological growth on the surface of the sampler, PRCs can be used to correct for the effects 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 2016).

At some sites, oils, greases, and NAPL phases will be present, and samplers that come in to contact with these phases are compromised. Measurements from compromised sampler must not be used. When in contact with a contaminated NAPL, the sampler equilibrates with the NAPL rather than the C_{free} in the aqueous phase. As a result, compromised samplers will not provide accurate estimates of the concentrations of chemicals in the sediment interstitial water. In cases where NAPL fouling is an issue, we suggest that the solid phase microextraction method, discussed in the following section, be applied. This methodology will not provide the C_{free} but will generate the best measure of interstitial water concentrations available with current sampling technologies under these circumstances.

2.2 Measuring Chemical Concentrations in Sediment Interstitial 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 interstitial 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 interstitial 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 interstitial 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 interstitial water is isolated from

the sediment or sediment slurry by centrifugation and treated with alum to precipitate and remove colloidal organic carbon (COC). A fiber is then added to the isolated and COC-reduced interstitial water. In this application, the SPME fiber is acting like an organic solvent in that the fiber is extracting any dissolved contaminants from the interstitial water sample into the PDMS polymer coating on the fiber. The fiber is then extracted and the extract analyzed for target contaminants. This process creates an operationally defined form of interstitial water (i.e., interstitial water minus colloidal matter precipitated by alum).

Because of uncertainties introduced by the centrifugation and flocculation steps and the lack of true equilibrium sampling, there is a general preference for passive sampling as a means to measure C_{free} in interstitial water. However, research conducted using the Hawthorne method (Hawthorne et al. 2005) has shown it to be effective in addressing contaminant bioavailability, so it may be used in implementing the IWRG approach if there is confidence that the interstitial water measurements are of sufficient scientific quality for the assessment.

Establishing Adverse Effects Concentrations in Sediment Interstitial Water for Benthic Organisms

3.1 Use of Aquatic Life Criteria as an Effect Benchmark

As outlined in the introduction, implementation of the IWRG approach requires the selection of a chemical concentration in water that defines a threshold above with the likelihood of adverse effects is unacceptable. 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. Because concentrations of most sediment contaminants do not change rapidly over time, 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. IWRGs as proposed here, are intended to provide this same level of protection, and therefore also 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 the developing AWQCs, and often sufficient data are not available to derive a FCV for a chemical. For some of the common sediment toxicants that don't have AWQC, there are methods 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 values among available toxicity data to the FCV derived when enough data were available to meet the requirements of 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 toxicants are provided in Table 3-1.

Polycyclic aromatic hydrocarbons (PAHs) are common sediment toxicants, and have several characteristics that present challenges in the development of IWRG. 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 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 2003d). 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 2003d). 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 basis of 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

aggregate potency of the mixture. Additional details on the derivation of water column potency estimates (used here as IWRGs) are provided in the PAH ESB document (US-EP A 2003d). Section 4 of this document describes how IWRG calculations for PAHs are performed.

Table 3-1 provides IWRG 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-specific differences in sensitivity, 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 IWRGs 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 IWRGs can be used instead of the GLI SCV for chemicals expected to act through the narcosis mechanism. If narcosis IWRGs 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 IWRG must be assessed on an aggregate 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 2003d; US-EPA 2008).

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 IWRGs assumes that there is no inherent bias in applying these values in contexts where benthic organisms are the explicit protection 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 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).

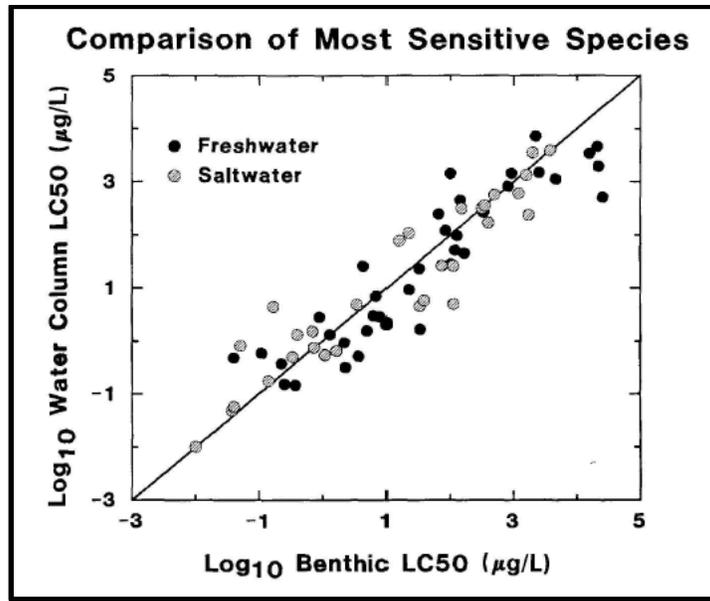


Figure 3-1. A comparison of the minimum LC50 for infaunal and epibenthic species (x-axis) and water column (y-axis) species. Each data point represents a particular chemical in either a freshwater and saltwater exposure. The diagonal line indicates a 1:1 relationship. The data are from AWQC or draft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

Figure 3-1 combines data across chemicals, but evaluates only the most sensitive organism for each chemical. Another way to address the benthic vs pelagic sensitivity question is to look at the distribution of values within a single chemical. Figures 3-2 to 3-4 show the distribution of LC50 values for dieldrin (US-EPA 2003b), endrin (US-EPA 2003c), and PAH mixtures (US-EPA 2003d). 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 that for all three plots there are benthic species whose sensitivity is at or near the sensitive end of the distribution. Statistical analysis of these distributions can be found in the reference source documents.

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

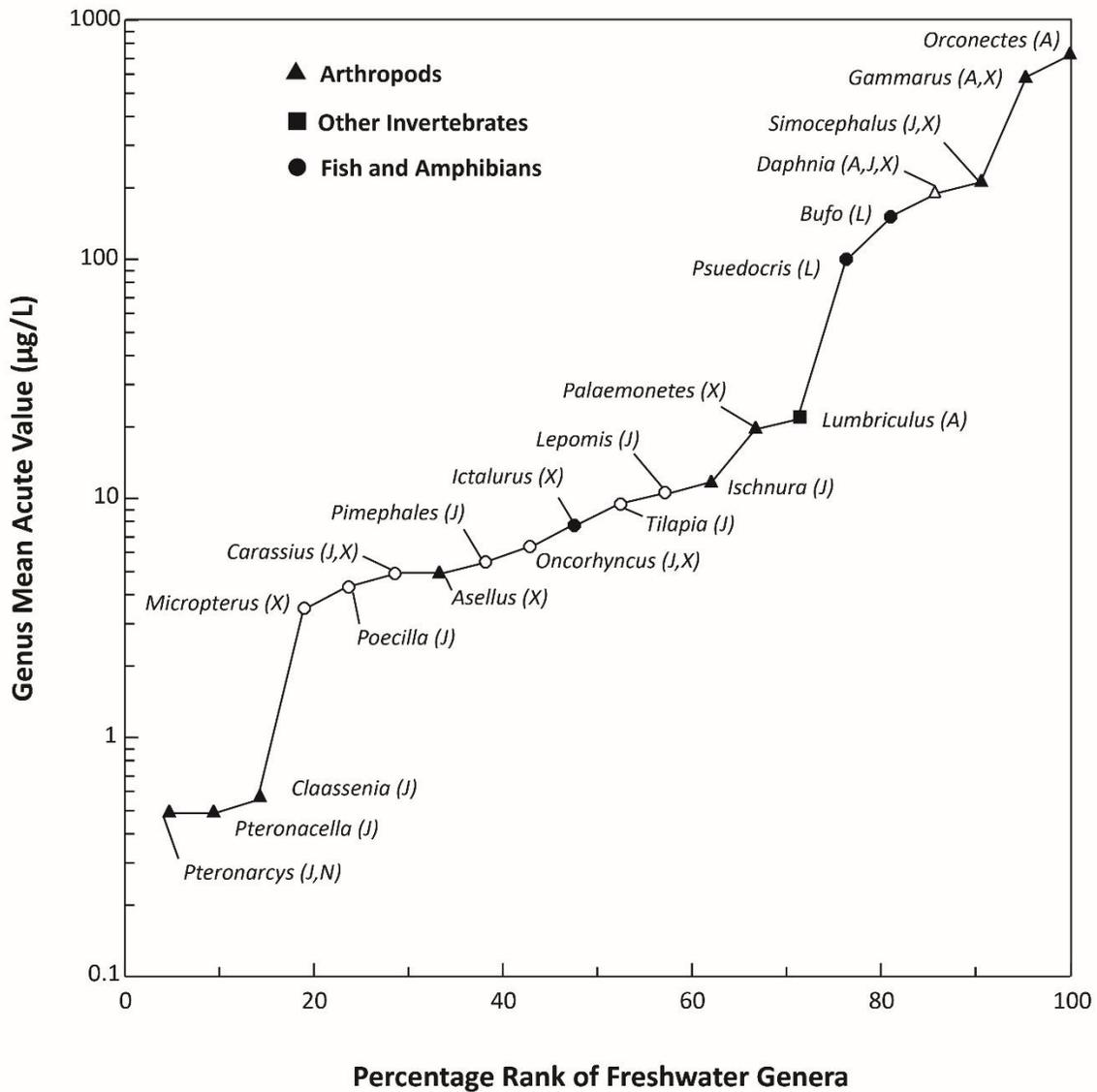


Figure 3-2. Species Sensitivity Distribution for Dieldrin of Freshwater Genera for Acute Toxicity (US-EPA 2003b). Genus mean acute values from water-only acute toxicity tests using freshwater species versus percentage rank of their sensitivity. Symbols representing benthic species are solid; those representing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

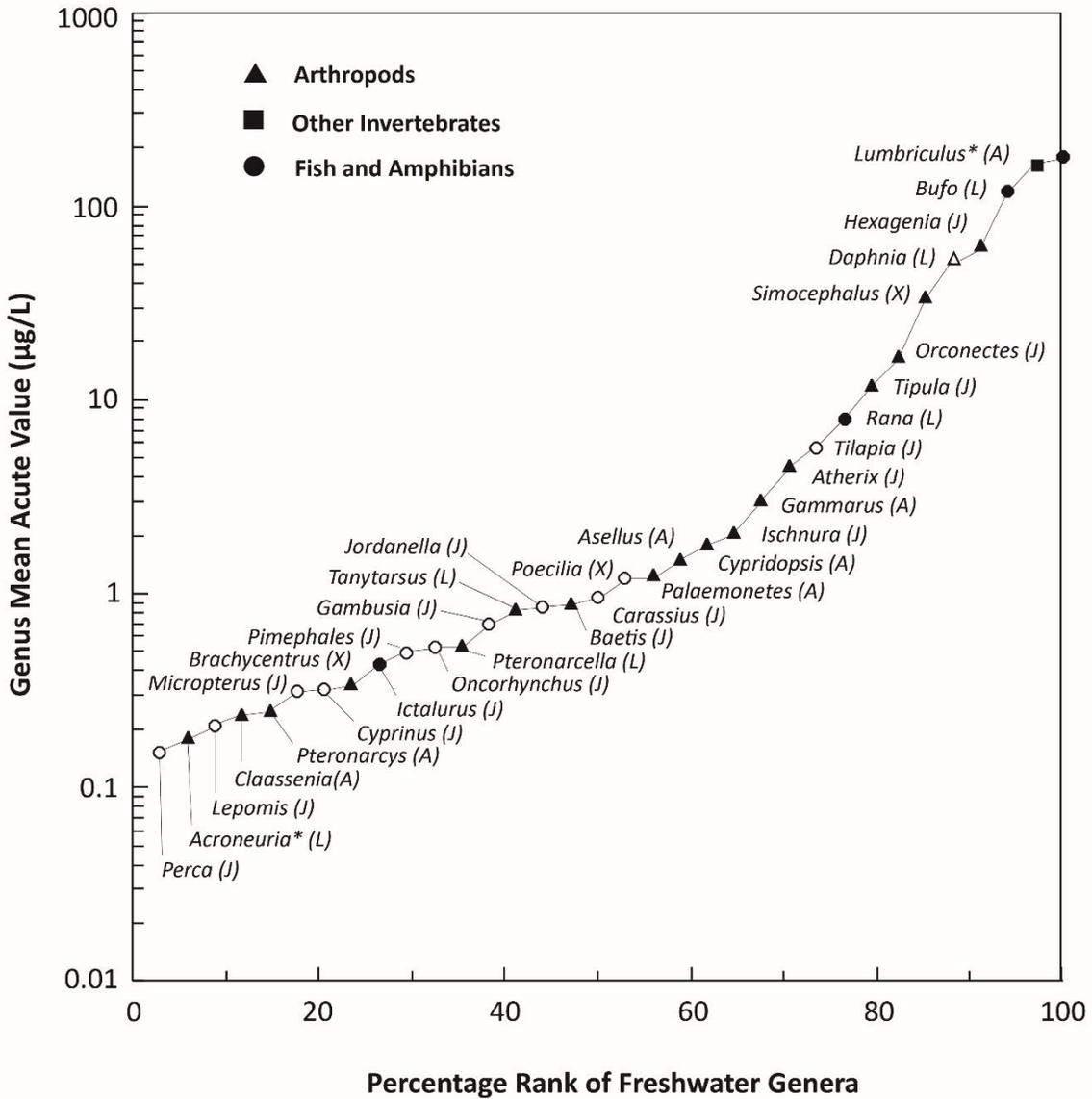


Figure 3-3. Species Sensitivity Distribution for Endrin of Freshwater Species for Acute Toxicity (US-EPA 2003c). Genus mean acute values from water-only acute toxicity tests using freshwater species versus percentage rank of their sensitivity. Symbols representing benthic species are solid; those representing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

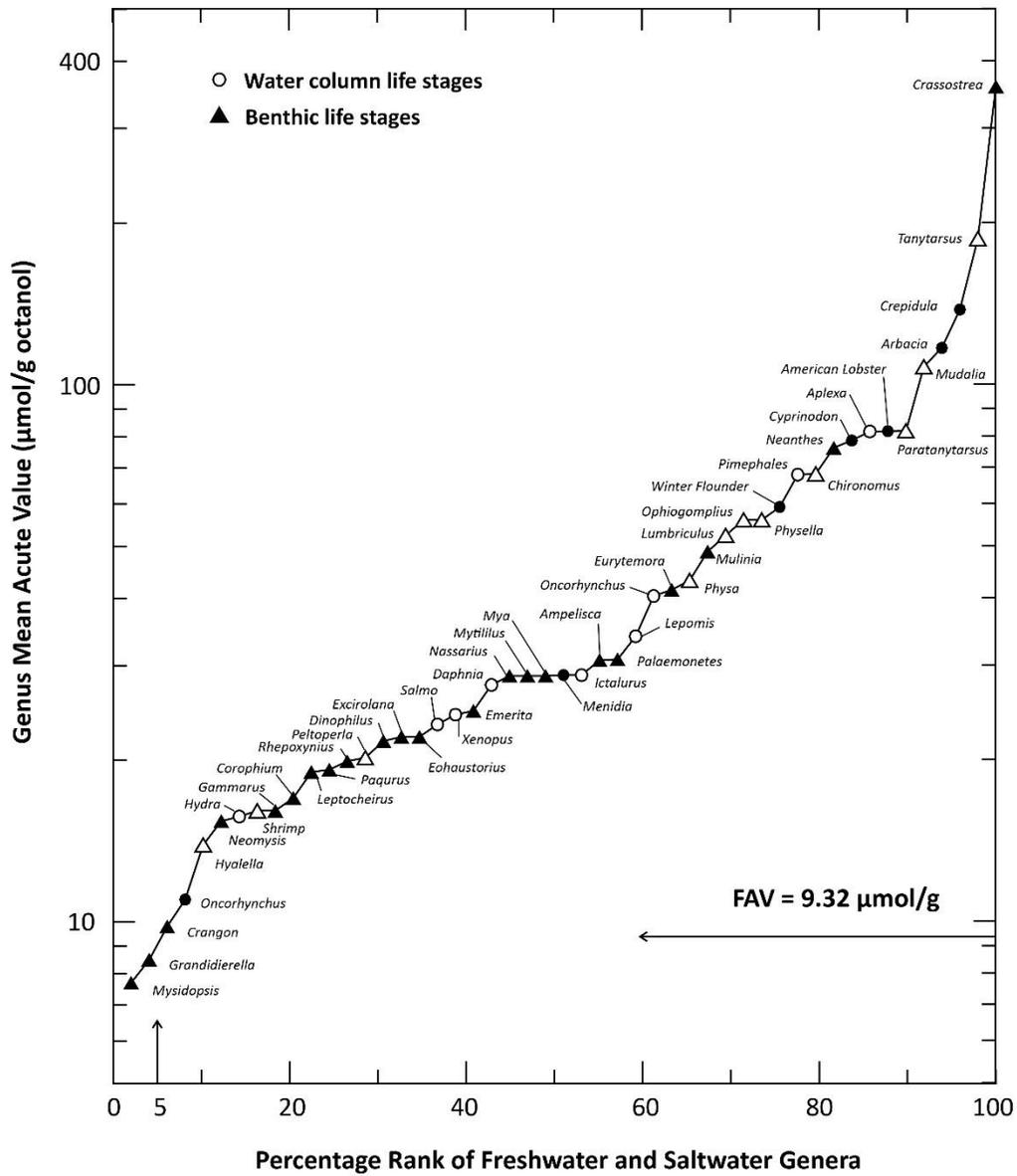


Figure 3-4. Species Sensitivity Distribution for PAH Mixtures for Acute Toxicity (US-EPA 2003d). GMAVs at a $\log_{10}K_{OW}$ of 1.0 from water-only acute toxicity tests using freshwater and saltwater genera versus percentage rank of their sensitivity.

Table 3-1. Conventional and narcosis water-only chronic toxicity values ($\mu\text{g/L}$) (FCVs and SCVs) for a selection of nonionic organic chemicals (Burgess et al. 2013).

Chemical	Log K_{ow}	Conventional FCV or SCV ($\mu\text{g/L}$)		Narcosis FCV or SCV ($\mu\text{g/L}$)
		Freshwater	Marine	
Ethers				
4-Bromophenyl phenyl ether	5.00	SCV = 1.5	SCV = 1.5	19
Low Molecular Weight Compounds				
Benzene	2.13	SCV = 130	SCV = 130	5300
Chlorobenzene	2.86	SCV = 64	SCV = 64	880
1,2-Dichlorobenzene	3.43	SCV = 14	SCV = 14	330
1,3-Dichlorobenzene	3.43	SCV = 71	SCV = 71	330
1,4-Dichlorobenzene	3.42	SCV = 15	SCV = 15	340
Ethylbenzene	3.14	SCV = 7.3	SCV = 7.3	790
1,1,2,2-Tetrachloroethane	2.39	SCV = 610	SCV = 610	3700
Tetrachloroethene	2.67	SCV = 98	SCV = 98	2000
Tetrachloromethane	2.73	SCV = 240	SCV = 240	1600
Toluene	2.75	SCV = 9.8	SCV = 9.8	1600
Tribromomethane (Bromoform)	2.35	SCV = 320	SCV = 320	6000
1, 1, 1-Trichloroethane	2.48	SCV = 11	SCV = 11	2400
Trichloroethene	2.71	SCV = 47	SCV = 47	1400
m-Xylene	3.20	SCV = 67	SCV = 67	700
Pesticides				
Alpha-, Beta-, Delta-BHC	3.78	SCV = 2.2	NA	^a
Gamma-BHC, Lindane	3.73	FCV = 0.08	NA	^a
Biphenyl	3.96	SCV = 14	SCV = 14	190
Diazinon	3.70	FCV = 0.1699	FCV = 0.8185	^a
Dibenzofuran	4.07	SCV = 3.7	SCV = 3.7	170
Dieldrin	5.37	FCV = 0.06589	FCV = 0.1469	^a
Endosulfan mixed isomers	4.10	FCV = 0.056	FCV = 0.0087	^a
Alpha-Endosulfan	3.83	FCV = 0.056	FCV = 0.0087	^a
Beta-Endosulfan	4.52	FCV = 0.056	FCV = 0.0087	^a
Endrin	5.06	FCV = 0.05805	FCV = 0.01057	^a
Hexachloroethane	4.00	SCV = 12	SCV = 12	160
Malathion	2.89	SCV = 0.097	FCV = 0.1603	^a
Methoxychlor	5.08	SCV = 0.019	NA	^a
Pentachlorobenzene	5.26	SCV = 0.47	SCV = 0.47	11
Toxaphene	5.50	FCV = 0.039	FCV = 0.2098	^a
1, 2, 4-Trichlorobenzene	4.01	SCV = 110	SCV = 110	120
Phthalates				
Butyl benzyl phthalate	4.84	SCV = 19	NA	^a
Diethyl phthalate	2.50	SCV = 210	NA	^a
Di-n-butyl phthalate	4.61	SCV = 35	NA	^a
Polycyclic Aromatic Hydrocarbons^b				
Naphthalene	3.356	NA	NA	193.5
C1-naphthalenes	3.80	NA	NA	81.69
Acenaphthylene	3.223	NA	NA	306.9

Acenaphthene	4.012	NA	NA	55.85
C2-naphthalenes	4.30	NA	NA	30.24
Fluorene	4.208	NA	NA	39.3
C3-naphthalenes	4.80	NA	NA	11.1
Anthracene	4.534	NA	NA	20.73
Phenanthrene	4.571	NA	NA	19.13
C1-fluorenes	4.72	NA	NA	13.99
C4-naphthalenes	5.30	NA	NA	4.048
C1-phenanthrene/anthracenes	5.04	NA	NA	7.436
C2-fluorenes	5.20	NA	NA	5.305
Pyrene	4.922	NA	NA	10.11
Fluoranthene	5.084	NA	NA	7.109
C2-Phenanthrene/anthracenes	5.46	NA	NA	3.199
C3-fluorenes	5.70	NA	NA	1.916
C1-pyrene/fluoranthenes	5.287	NA	NA	4.887
C3-phenanthrene/anthracenes	5.92	NA	NA	1.256
Benz(a)anthracene	5.673	NA	NA	2.227
Chrysene	5.713	NA	NA	2.042
C4-Phenanthrenes/anthracenes	6.32	NA	NA	0.5594
C1-Benzanthracene/chrysenes	6.14	NA	NA	0.8557
Benzo(a)pyrene	6.107	NA	NA	0.9573
Perylene	6.135	NA	NA	0.9008
Benzo(e)pyrene	6.135	NA	NA	0.9008
Benzo(b)fluoranthene	6.266	NA	NA	0.6774
Benzo(k)fluoranthene	6.291	NA	NA	0.6415
C2-benzanthracene/chrysenes	6.429	NA	NA	0.4827
Benzo(ghi)perylene	6.507	NA	NA	0.4391
C3-benzanthracene/chrysenes	6.94	NA	NA	0.1675
Indeno(1,2,3-cd)pyrene	6.722	NA	NA	0.275
Dibenz(a,h)anthracene	6.713	NA	NA	0.2825
C4-benzanthracene/chrysenes	7.36	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 2003d). FCV = final chronic values. SCV = secondary chronic values.

Implementation of the IWRG Approach:

4.1 Overall Approach

Most sediment assessments begin with data on contaminant concentrations in bulk sediment, from which initial screening for contaminants of concern is done. The IWRG approach involves collection of paired measurements of bulk sediment and interstitial water measurements; these interstitial water measurements are compared to IWRGs to evaluate the degree of contamination in relation to ecological risk and evaluation of remedial alternatives. In most cases, these IWRGs will be converted back to bulk sediment concentrations for purposes of remedial design consideration. In addition, these paired measurements provide information on the site- (and sample-) specific partitioning of contaminants between the bulk sediment and interstitial water.

This process is represented in four steps as illustrated in Figure 4-1. Beginning in the upper left, the first step is the characterization of the contamination and properties of the sediments. In the figure, sediment samples/locations are illustrated using boxes A, B, and C, and analyses of the samples would result in concentrations of the contaminants, organic carbon content, and other sediment parameters, e.g., oil/grease, AVS, pH, and NH_3 . These measurements provide concentrations in the bulk sediment on a $\mu\text{g}/\text{kg}$ dry weight basis, and may be used with screening criteria to determine contaminants for further evaluation. In the second step (upper right), the sediment samples are then subjected to passive sampling measurements (as described in Section 2) to determine the concentration of the chemicals in the sediment interstitial water ($\mu\text{g}/\text{L}$). Passive sampling data serve two purposes; in addition to providing concentrations to compare to IWRGs, paired measurements from bulk sediment and interstitial water provide information on the site- (and sample-) specific partitioning of contaminants between the bulk sediment and interstitial water. For contaminants of concern in the sediment interstitial water, the third step is to develop appropriate IWRGs ($\mu\text{g}/\text{L}$) as discussed in Sections 4.2, 4.3, and 4.4 below. Comparing these IWRGs to results of passive sampling will establish which site contaminants and samples indicate exposures above the IWRG, with the associated implications for the site assessment and remedial evaluation. While this comparison of site sediments to IWRGs involves interstitial water, in many cases it will be desirable to convert IWRGs into bulk sediment concentrations (fourth step, lower left in Figure 4-1) for purposes of remedial design and/or to make use of additional site characterization data (e.g., samples for which only bulk sediment concentrations are available). This conversion can be done by back-calculation from IWRGs using appropriate site-specific K_{OC} ($K_{\text{OC:SS}}$) and f_{OC} values resulting in bulk sediment concentrations equivalent to the IWRG ($C_{\text{S:IWRG}}$ in $\mu\text{g}/\text{kg}$ dry weight).

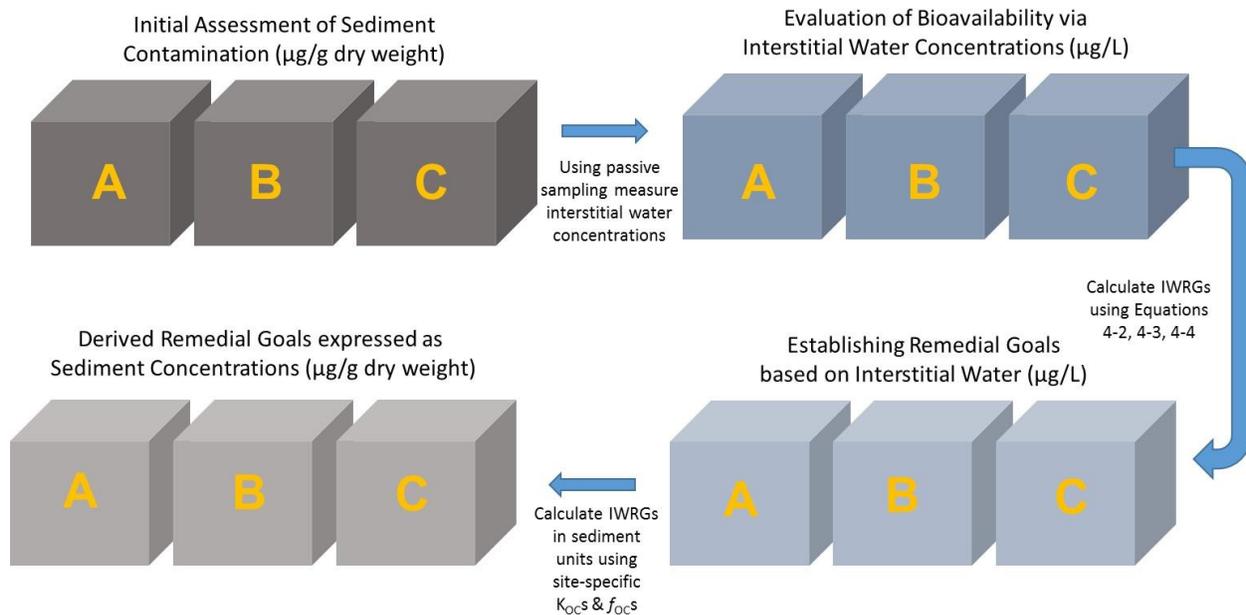


Figure 4-1. Overall approach for deriving sediment remedial goals. The boxes represent different sampling locations at the contaminated sediment site. The approach starts in the upper left corner (Initial Assessment) and proceeds clockwise to result in remedial goals expressed on concentrations in the sediment on bulk basis ($\mu\text{g/kg}$ dry weight). Letters represent different locations within the overall site.

The fourth step in this process, converting IWRGs from an interstitial water basis to a bulk sediment basis, assumes that remedial design will be pursued based on concentrations in bulk sediment. It is possible that some assessment questions might be addressed directly based on interstitial water measurements, such as the spatial extent of contamination above the IWRG. Applying IWRG to define the vertical extent of contamination or remedial action requires either that a K_{OC} be assumed for deeper sediments and the evaluation is based on bulk sediment chemistry, or that passive sampling be performed on samples from deeper sediments and the IWRG applied directly. Both approaches have logistical implications and some technical uncertainties (e.g., are K_{OC} values from surficial sediments applicable to deeper sediments); the choice between the two can be made based on site-specific considerations.

4.2 Development of Interstitial Water to Bulk Sediment Contaminant Relationships

If measurements on bulk sediments are used in the assessment and/or remedial design, it requires a method for converting from concentrations in the sediment interstitial water (C_{free}) (Third Step in Figure 4-1) to concentrations in the bulk sediment (Fourth Step in Figure 4-1). As discussed in the Introduction, sediment-water partitioning of nonionic organic chemicals is expressed using the sediment-water partition coefficient (K_{OC}), and the K_{OC} is the ratio of the concentration in the sediment on an organic carbon basis (C_{SOC} , $\mu\text{g}/\text{kg}$ of organic carbon) to C_{free} ($\mu\text{g}/\text{L}$):

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

where C_s is the concentration of chemical in the sediment on a dry weight basis ($\mu\text{g}/\text{kg}$ dry weight) and f_{OC} is the fraction of organic carbon in the sediment. Clearly, K_{OC} can only be determined when organic carbon content of the sediment and concentrations in the sediment interstitial water and bulk sediment are measured, which they typically are (First Step in Figure 4-1).

Sample-specific K_{OC} values are calculated individually for each sample. However, the resulting set of K_{OC} values must then be translated into values that are used to convert IWRG values for interstitial water into their equivalent bulk sediment concentration. Depending upon the nature and complexity of the site, K_{OC} s might vary widely as demonstrated by Hawthorne et al. (Hawthorne et al. 2006) or might have only a narrow range of values. If the variability is small, then selecting a single value to apply should be straightforward.

If the site-specific K_{OC} s vary widely, additional analysis will be required to select K_{OC} values to convert IWRG values to equivalent bulk sediment concentrations. Variability in K_{OC} should be evaluated in the context of additional site or sediment characteristics to determine if correlates can be found and used to inform the selection of an appropriate K_{OC} value. For example, if spatial patterns in K_{OC} are found, it may be that less variability exists in areas where IWRG values are exceeded, and those K_{OC} values may be more applicable. The site history and/or conceptual site model have also provide information on site characteristics that may parse variability in K_{OC} . Alternatively, correlates may be found within other sediment characteristics, such as f_{OC} , grain size, hydrocarbon content (e.g., total petroleum hydrocarbons [TPH] or oil and grease), or contamination level. If variability in K_{OC} cannot be reduced through such analysis, then an appropriate value should be selected from the distribution of values in a way that reflects a level of confidence (or conservatism) consistent with overall objectives of the assessment or remedial alternative. It may be instructive to consider the scope of contamination using different assumed K_{OC} values to determine how sensitive the assessment is to K_{OC} ; if contamination gradients are sharp, uncertainty regarding K_{OC} may have a comparatively small influence on the overall assessment and/or remedial alternatives.

Because the conversion of the IWRG from interstitial water to bulk sediment is based on K_{OC} , the corresponding bulk sediment concentration is dependent not only on the K_{OC} , but also on the organic carbon content of the sediment (f_{OC}). If the sediments to which the IWRG will apply have a relatively narrow range in f_{OC} , calculation of the bulk sediment concentration can use that single value. If f_{OC} varies substantially within the area to which the IWRG will be applied, it may be feasible to subdivide

areas according to their organic carbon content and calculate different bulk sediment goals for different areas. Alternatively, a value may be selected from within the range of applicable f_{OC} values based on risk management considerations (lower f_{OC} values result in lower bulk sediment concentrations).

Once the applicable K_{OC} value is selected, bulk sediment concentrations equivalent to the IWRG ($C_{S:IWRG}$; $\mu\text{g}/\text{kg}$ dry weight) can be calculated as:

$$C_{S:IWRG} = K_{OC:SS} \times f_{OC} \times C_{free:IWRG} \quad (4-2)$$

Where $K_{OC:SS}$ ($\mu\text{g}/\text{kg}$ dry weight) is the selected site-specific K_{OC} , and $C_{free:IWRG}$ is the IWRG expressed as concentration in water ($\mu\text{g}/\text{L}$).

4.3 Derivation of IWRG for a Sediment with One Primary Contaminant – Dieldrin Example

The example setting is a riverine Superfund site with sediments contaminated with dieldrin; site sediments show toxicity to benthic organisms in toxicity tests, and additional studies have shown that the cause of this toxicity is dieldrin. Dieldrin has an FCV of $0.06589 \mu\text{g}/\text{L}$ (Table 3-1) and several site sediments show interstitial water concentrations of dieldrin in excess of the IWRG. For those sediments exceeding the IWRG, the site-specific log K_{OC} values averaged 5.21 ± 0.11 (mean \pm SD); this degree of variability is considered sufficiently low that a single $K_{OC:SS}$ value is used to calculate a remedial goal based on dieldrin concentration in bulk sediment ($C_{S:IWRG}$ in equation 4-2). For this case, the site IWRG ($C_{free:IWRG}$) would be set equal to the FCV from EPA's AWQC, which is $0.06589 \mu\text{g}/\text{L}$ in the sediment interstitial water (Table 3-1). In terms of the four sequential step process outlined in Figure 4-1, this IWRG would apply to all locations/samples (illustrated by boxes A, B, and C in the Figure) in the third Step. The range in organic carbon content of site sediments is also comparatively small at $1.7 \pm 0.3\%$ ($f_{OC} = 0.017 \pm 0.003$), and the average value was considered sufficiently representative. To convert this IWRG expressed on a $\mu\text{g}/\text{L}$ basis to a bulk sediment basis, the values above are applied in Equation 4-2:

$$C_{S:IWRG} = K_{OC:SS} \times f_{OC} \times C_{free:IWRG}$$

$$C_{S:IWRG} = 10^{5.21} \text{ L water/kg OC} \times 0.017 \text{ kg OC/kg sediment} \times 0.06589 \mu\text{g dieldrin/L water}$$

$$C_{S:IWRG} = 182 \mu\text{g dieldrin/kg sediment (rounded)}$$

For simplicity and clarity, this example has low variability in both K_{OC} and f_{OC} . As discussed previously, if one or both of these values showed large variability, then additional consideration would be necessary to select appropriate values. This could result in a range of $C_{S:IWRG}$ values, or different values applied to different types of sediments or spatial areas within the overall site as judged appropriate for the situation.

4.4 Derivation of IWRGs for a Sediment with a PAH Mixture as the Primary Contaminant

PAHs are one of the most common sediment toxicants 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 2003d). 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 2003d). Table 3-1 lists the narcosis FCVs/SCVs; readers can consult the ESB document (US-EPA 2003d) 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 an interstitial water containing $\frac{1}{2}$ the toxic concentration of PAH A, and $\frac{1}{2}$ the toxic concentration of PAH B, the combination would be toxic. In practice, PAH mixtures occurring in field sediments consist of dozens of PAH structures, so the IWRG calculation is more involved than the simple example above. Another important aspect of assessing sediments contaminated with PAHs using IWRGs 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 misses alkylated PAHs (e.g., methyl-, dimethyl-, ethyl-substituted PAHs like 1-methylnaphthalene or 3,6-dimethylphenanthrene) that often represent from 50% to 90% of the overall potency of common PAH mixtures. For that reason, application of the IWRG approach to PAH-contaminated sediments should be done only when passive sampling includes the suite of 34 PAH structures described in the PAH ESB document (US-EPA 2003d) and listed in Table 4-1. Analytical methods are available for sediments and interstitial water measurements of the 18 parent PAHs and 16 alkylated groups (e.g., EPA 8270) when the alkylated PAHs are included (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 2003d). 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 interstitial 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 IWRG 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 4-1

will have its own measured interstitial 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 IWRG is exceeded. For each individual PAH, the measured concentration in interstitial water (column 3 in Table 4-1) is divided by its corresponding FCV/SCV from Table 3-1 (column 5 in Table 4-1); the result is the fractional contribution of that PAH to the overall sediment potency (Column 6), which is the interstitial water toxic units (IWTU):

$$IWTU_i = C_{free,i}/FCV_i \quad (4-3)$$

where $C_{free,i}$ is the freely dissolved concentration measured in the interstitial 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 IWTU of each chemical:

$$IWTU_{Mixture} = \sum_{i=1}^j IWTU_i \quad (4-4)$$

where $IWTU_i$ is computed using equation 4-3 for each of the “j” chemicals in the mixture.

Using an example from Table 4-1, the measured concentration of naphthalene in this interstitial water was 2.89 $\mu\text{g/L}$, the PAH-specific FCV/SCV is 193 $\mu\text{g/L}$, and the resulting ratio is 0.0150, which is $IWTU_{\text{naphthalene}}$. These ratios are then calculated for each of the individual PAHs, and the ratios are added together to the overall toxic units (relative to the IWRG) present. In the example in Table 4-1, this sum ($\Sigma IWTU$) is 58.68, indicating that the PAH exposure in this sediment greatly exceeds the PAH IWRG, 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 IWRG values back to bulk sediment concentrations. 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 4-1 shows the calculation based on a single sample; later in this section, other options are discussed. For this example, $\Sigma IWTU = 58.68$, meaning that this mixture exceeds the IWRG by 58.68-fold; put differently, interstitial water concentrations would have to be reduced to 1/56.68 or 1.704% of their measured concentration to meet the IWRG. Column 7 of Table 4-1 shows the concentration in sediment interstitial 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 4-2 to give a PAH-specific $C_{S:IWRG}$ values for each PAH in $\mu\text{g/kg}$ dry weight (column 10).

In practice, it may be challenging to implement the detailed approach shown in Table 4-1 across multiple samples, for several reasons, including:

- a) the composition of the PAH mixture will likely vary across samples, requiring some way to define an “average” composition;

- b) K_{OC} values are likely to vary not only across samples, but among PAHs within samples in a way that may not be systematic;
- c) Determining whether bulk sediment concentrations meet IWRGs will likely require some way of averaging across PAHs as individual PAHs may be above or below the $C_{S:IWRG}$; and
- d) There may be a need to evaluate compliance with $C_{S:IWRG}$ in samples for which only a subset of PAHs are measured (e.g., only priority pollutant PAHs).

The paragraphs that follow describe several alternatives that may be less involved ways to implement the IWRG approach for PAH mixtures.

One possibility is to apply the 1/IWTU ratio not to the interstitial water concentrations but directly to the measured bulk sediment concentrations. Using Table 4-1 as the example, instead of multiplying the measured interstitial water concentrations (column 3) by 1/56.68, apply that factor directly to the measured bulk sediment concentration (column 2). Using naphthalene as an example, this would mean dividing the bulk sediment concentration of 3.33 $\mu\text{g/g dwt}$ by 56.68 to obtain a $C_{S:IWRG}$ of 0.057 which yields the same value as was obtained by equation 4-2 (column 10; small difference due to rounding error). These values could then be averaged across samples to derive average $C_{S:IWRG}$ values, if they are sufficiently constant across the site. If these calculations are based on dry weight concentrations, averaging these values across multiple samples lumps variation attributable to mixtures, K_{OC} , and f_{OC} . Detailed evaluation of individual samples like that shown in Table 4-1 can be used to assess the relative influence of each of these factors, and it is possible to account for these if they vary greatly across the site. For example, if bulk sediment concentrations are expressed on an organic carbon normalized basis:

$$C_{OC} (\mu\text{g/kg OC}) = C_S (\mu\text{g/kg sediment}) / f_{OC} (\text{kg OC/kg sediment}) \quad (4-5)$$

the resulting organic carbon normalized concentration can be applied with location-specific f_{OC} .

Another alternative is to aggregate the PAH-specific $C_{S:IWRG}$ values into an aggregate measure like “total PAHs”. If the PAH mixture composition is relatively stable, the uncertainty introduced by adding the PAH masses together may be relatively small, and might simplify the assessment. This aggregation could be done with or without organic carbon normalization as described above. A variant of this approach is to select particular PAHs that would be summed, perhaps those which show the greatest contribution to overall potency of the PAH mixture. For example, in Table 4-1, much of the overall potency is attributable to the PAHs listed from phenanthrene to fluoranthene/pyrene; accordingly, a reasonably robust approach might be based on concentrations of that subset of PAHs if the overall composition is reasonably consistent across the spatial area of concern. This “indicator PAH” approach may be particularly useful when attempting to combine data from samples with all 34 PAHs measured with data from samples with only priority pollutant PAHs analyzed.

Table 4-1. Example calculation of interstitial water toxicity and IWRGs for a sediment with a PAH Mixture as the known toxicants.

PAH	Measured Concentration				1.704% = 1/58.68			Site-Specific Log K _{oc} ^c	Bulk Sediment IRWGs
	Sediment µg/g (dw)	Interstitial Water (C _{free}) ^a µg/L	Aqueous Solubility ^b µg/L	Narcosis FCV/SCV µg/L	Interstitial Water Toxic Units ^c	IWRGs µg/L	IWRG Toxic Units		
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 2003d). ^c ½ detection limit used for non-detect values.

4.5 Derivation of IWRGs for a Sediment with Other Toxicant Mixtures

With the exception of PAHs as discussed in Section 4.4, IWRGs 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 vary 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 IWRG values on a chemical by chemical basis. However, those that share a toxicological mechanism, like the narcotic effect of PAHs, are likely to show additive toxicity. The degree to which mixture effects should factor into the IWRG approach will be a site-specific decision, based on the types of chemicals present, and their relative concentrations and potencies.

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 IWTU, with an expected combined potency of 1.8 IWTU. While this would be an exposure higher than intended by an IWRG of IWTU = 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 IWTU = 30.6 TU.

In real world mixtures, it is probably that the contributions of individual chemicals to overall mixture toxicity will vary, and would not all be right near the IWRG. Using the dieldrin/endrin example, if the IWTU for dieldrin was generally 20% or less of the IWTU for endrin, then the magnitude of the resulting uncertainty would be small even if mixture effects were ignored. In the example in Table 4-1, the highest IWTU for a single PAH was 12.5 IWTU for C3-Phenanthrenes/Anthracenes, compared to the summed IWTU of 56.68, which would be about a 5-fold underprotection if mixture effects were ignored and all PAHs were compared to their IWRG values individually.

The potential importance of considering mixtures can be evaluated from the passive sampler data by comparing the assessment conclusions if IWRGs 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.

If a mixture approach is chosen, the approach is parallel to that shown in section 4.4. IWTUs are calculated individually for each component of the mixture (Equation 4-4), then summed across the mixture (Equation 4-5), and the IWRG is a summed ratio of 1.00.

Comparison and Evaluation of Toxicity Testing Results and IWRGs

At Superfund sites with contaminated sediments, sediment toxicity tests (US-EPA 1994; US-EPA 2000b; US-EPA 2002a; US-EPA 2002b; US-EPA and US-ACE 2001) are performed in the RI/FS phase to evaluate if the sediments at the site are toxic to benthic organisms. In this section, the results from sediment toxicity tests, the developed IWRGs for the identified sediments toxicants, interstitial water chemical concentration measurements (C_{free}) for the toxicants, and toxicity data from water-only exposures for the toxicants are compared and contrasted. This analysis is performed in order to assess their consistency in describing the overall toxicity observed to benthic organisms for the sediments from the site. When data are consistent with each other, one can be reasonably assured that causes of toxicity to the benthic organisms in the sediment have been correctly identified and quantified, and that the developed IWRGs for these toxicants will be protective of benthic organisms at the site.

Standardized procedures for passive sampling measurements are not currently available. 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 close to 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 2016).

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 or facilities specializing in culturing the test organisms. As with any live organism testing system, occasional unusual results occur even though test controls are within performance specifications. 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. Clearly, the sediment toxicity test results should also meet the criteria specified in their testing protocol, and reader should consult these documents for these criteria (US-EPA 1994; US-EPA 2000b; US-EPA 2002a; US-EPA 2002b; US-EPA and US-ACE 2001).

After one has high confidence in both passive sampling and toxicity testing results, the interstitial water concentration measurements (or equivalently, computed toxic units) should be checked for consistency with the sediment toxicity test measurements. 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 may enable

detection of the issue. These comparisons/checks are discussed below after two short sections on EPA's FCVs, i.e., derivation of FCVs and sensitivities of test organism to FCVs.

5.1 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 interstitial 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 average acute to chronic toxicity ratio (ACR) for the chemical of interest.

5.2 Sensitivities of Toxicity Test Organisms in Relation to EPA's AWQC 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 5-1) 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 $\mu\text{mole/g}$ octanol (US-EPA 2003d). 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 IWRG (based on the FCV or comparable effect level) and the results of sediment toxicity tests. Finally, for chemicals whose IWRG 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 interstitial water, it is possible to calculate species/chemical-specific interstitial water effect concentrations based on the results of water column exposures using the same chemical, species, and endpoint. To do this, estimate species/chemical-specific IWTU by replacing the FCV with the applicable effect concentration from a water-only toxicity test and recalculating IWTUs.

Table 5-1. PAH mixture species sensitivity distribution genus mean acute values for marine amphipods <i>Ampelisca abdita</i> , <i>Eohaustorius estuarius</i> , <i>Leptocheirus plumulosus</i> , and <i>Rhepoxynius abronius</i> , and for freshwater species <i>Chironomus tentans</i> and <i>Hyalella azteca</i> .		
Species	Genus Mean Acute Value ($\mu\text{mole/ g octanol}$)	Percentage Rank of Genera
5 th Percentile distribution value	FAV = 9.32	5.0%
<i>Hyalella azteca</i>	13.9	10.2%
<i>Leptocheirus plumulosus</i>	19.0	22.4%
<i>Rhepoxynius abronius</i>	19.9	26.5%
<i>Eohaustorius estuarius</i>	22.1	32.6%
<i>Ampelisca abdita</i>	30.7	55.1%
<i>Chironomus tentans</i>	68.4	79.5%

5.3 Comparing Passive Sampling Measurements and Sediment Toxicity Test Data for Consistency: Sigmoidal Response Exists

When sediment toxicity tests are performed, each test provides an effect endpoint, e.g., survival, growth, and/or reproduction, for the tested sediment sample. Provided enough sediment samples are tested and the concentrations of the toxicant(s) vary across the sediment samples, one should observe a sigmoidal shaped response curve where at lower concentrations of the toxicant(s), no effects are observed, and at higher concentrations of the toxicant(s), adverse effects are observed to occur on all test organisms. Data from sediment toxicity tests with *Hyalella azteca* on Hudson River sediments contaminated with PAHs (Kreitinger et al. 2007) follow the sigmoidal shape pattern (Figure 5-1), i.e., at low toxicity (low concentration of toxicants), high survival and at high toxicity (high concentration of toxicants), low survival. In Figure 5-1, the x-axis is on a toxic units basis for the PAH mixture, and Kreitinger et al. (Kreitinger et al. 2007) computed the total toxic units using EPA's narcosis FCVs (Table 3-1 (US-EPA 2003d)) and their measured concentrations in the sediment interstitial water for the 18 parent PAHs and 16 alkylated PAH groups.

What is readily noticeable from Figure 5-1 is that the 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; resultantly, the *H. azteca* are less sensitive than the species driving the FAV. As discussed in Section 5.2, the sensitivity of the test organism itself, in all likelihood, does not reside at the 5th percentile value of the SSD, but rather at a higher percentile in the SSD. Assuming both sets of data are of high quality, the effect concentration for the sediment test organism for the chemical/mixture of interest should be derived. For the PAH data in Figure 5-1, Kreitinger et al. (Kreitinger et al. 2007) derived an EC50 for survival with a mean of 25 and 95% confidence interval of 18 to 51 toxic units for the *H. azteca* based upon a study by Driscoll and Landrum (Driscoll and Landrum 1997) with water-only toxicity testing of the chemical. The measured effect level with the sediments should agree with derived and/or measured effect levels from water-only chemical testing. For the data in Figure 5-1, toxicity for *H. azteca* derived from the literature agrees fairly well with measured toxicity. When they agree, one has demonstrated

consistency between the toxicity test and passive sampling measurements. If they don't agree, then efforts to resolve why they are different should be conducted.

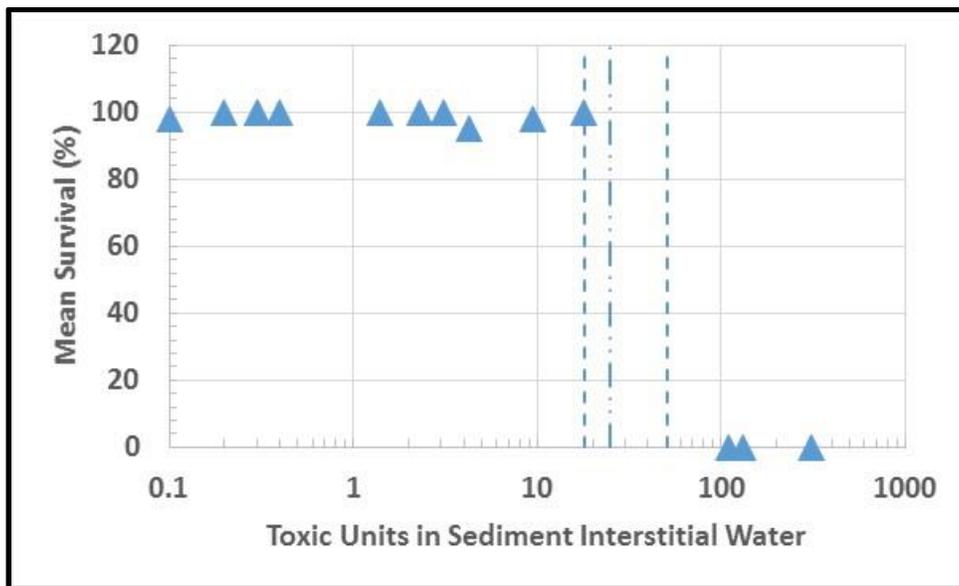


Figure 5-1. Measured sediment toxicity survival data for *Hyalella azteca* in 28-d sediment toxicity test with sediments from the Hudson River at Hudson, NY, and toxicity estimated from the concentrations of PAHs in the sediment interstitial water using FCV/SCVs for PAHs (Kreitinger et al. 2007). The — · — and --- lines are the mean and 95% confidence levels for the EC50 derived from the water-only toxicity testing data of Driscoll and Landrum (Kreitinger et al. 2007).

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. For these sediments, 28-d survival data for *Hyalella azteca* and the estimated sediment toxicity, using EPA's PAH FCVs and their measured concentrations in the sediment interstitial water for the 18 parent PAHs and 16 alkylated PAH groups, are shown in Figure 5-2. Like the data of Kreitinger et al. (Kreitinger et al. 2007) in Figure 5-1, these data follow the sigmoidal shape pattern, i.e., at low toxicity, high survival and at high toxicity, low survival (Figure 5-2). Similar to the data of Kreitinger et al. (Kreitinger et al. 2007) above, 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 2003d). The FAV and FCV for PAHs is 9.32 $\mu\text{mole/g}$ octanol and 2.24 $\mu\text{mole/g}$ octanol, respectively (US-EPA 2003d). Given the 25.4 $\mu\text{mole/g}$ octanol acute toxicity value for *H. azteca* and the FCV of 2.24, the *H. azteca* test species is approximately 11 fold less sensitive in comparison to the FCV toxicity derived from the SSD.

The data from Hawthorne et al. (Hawthorne et al. 2007) also illustrates the power of using interstitial water concentrations for sediment contaminants to classify the samples as being nontoxic and toxic when the toxicants are known. At these eight sites, the toxicants were PAHs, and there are

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). The measured effect level with the sediments should agree with derived and/or measured effect level from water-only chemical testing. For the data in Figure 5-2, toxicity data for *H. azteca* derived from the literature agrees well with measured toxicity, and the toxicity data sorts into nontoxic and toxic sediments with almost no/few outliers. The outliers are explainable. With this level of agreement, one has demonstrated consistency between the toxicity test and passive sampling-based estimates of interstitial water concentrations. If they don't agree (i.e., numerous unexplainable outliers and/or sediments not sorted into nontoxic and toxic groups), then efforts to resolve why they are different should be conducted.

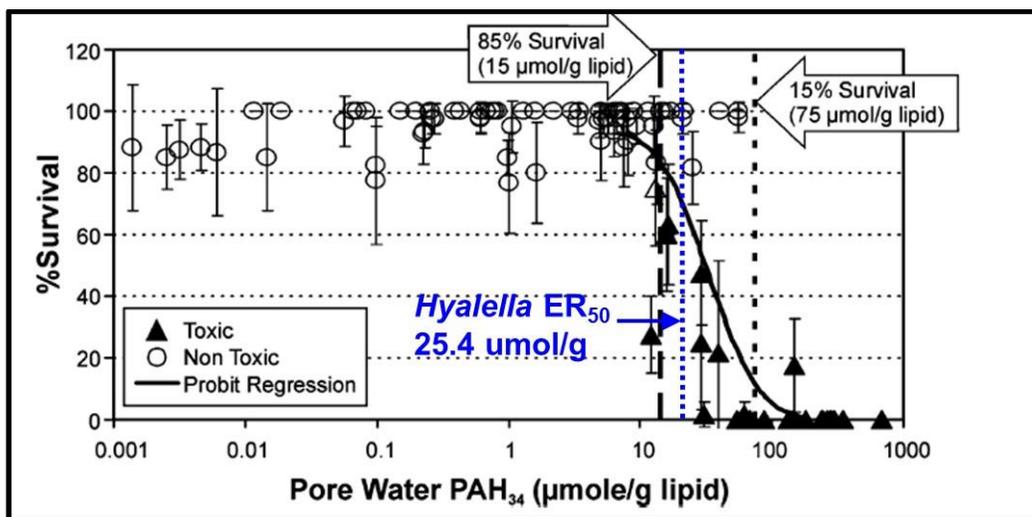


Figure 5-2. Measured acute toxicity survival data for *Hyalella azteca* in 28-d sediment toxicity test with 97 sediments from six manufactured-gas plants and two aluminum smelter sites, and toxicity estimated from the concentrations of PAHs in the sediment interstitial water (Hawthorne et al. 2007). The *Hyalella azteca* ER₅₀ was derived from the water-only toxicity testing data of Driscoll and Landrum (Driscoll and Landrum 1997).

5.4 Comparing Passive Sampling Measurements and Sediment Toxicity Test Data for Consistency: Difficult to Interpret Data (Non-Sigmoidal Responses Exist)

There will be sites where the sigmoidal response pattern may not appear or where there are a handful of outliers from the generalized sigmoidal response pattern. This section discusses and provides guidance for situations that are difficult to interpret because the sediment toxicity testing data do not conform to the sigmoidal response pattern.

Figure 5-3 illustrates the case when an incomplete dose-response curve is obtained. The data in Figure 5-3 are from a manufactured-gas plant site with PAH contamination on the Hudson River at Tory,

NY (Kreitinger et al. 2007). The toxicity data are for mean growth of *Hyalella azteca* in 28-d sediment toxicity tests and the toxicity estimated in the sediment interstitial water using EPA's PAH FCVs for narcosis. In evaluating the toxicity data with an incomplete response curve, one needs to determine where the data reside on the response curve. For the data in Figure 5-3, most of the data are in reasonable agreement with the sediment test controls (considered non-toxic). Resultantly, the toxicity testing data are from the lower end of the sigmoidal response curve where no effects are observed. In cases like this, one might consider additional sediment sampling and testing to obtain a complete dose-response curve; potentially using samples from locations nearer the sample with ≈ 25 toxic units. Even with an incomplete dose-response curve, one should derive effects level from water-only chemical testing for the toxicants. With such information, one can place the measured toxicities in context of the estimated effects level. As shown in the Figure 5-3, some of non-toxic samples have estimated toxicities of more than 1 toxic unit, suggesting that the *H. azteca* are less sensitive and don't reside on the 5th percentile of the species sensitivity distribution. For the PAH data in Figure 5-3, Kreitinger et al. (Kreitinger et al. 2007) derived an EC50 for growth with a mean of 25 and 95% confidence interval of 18 to 51 toxic units for the *H. azteca* based upon a study by Driscoll and Landrum (Driscoll and Landrum 1997). The portion of the dose-response curve obtained with the samples in Figure 5-3 agrees reasonably well with the derived EC50 break point between non-toxic and toxic samples. With this level of agreement, one has demonstrated consistency between the toxicity tests and interstitial water-based toxicity estimates. If they don't agree, then efforts to resolve why they are different should be conducted.

Cases of incomplete response curves where only the higher portion of the response curve are obtained (i.e., all sediments are toxic) will occur at some sediment sites. Clearly, if the sediments are predicted to be not toxic using EPA's FCVs with the measured C_{free} data, the incorrect toxicant(s) or not all of toxicant(s) have been identified. In this situation, additional efforts on identifying the additional and/or correct toxicant(s) in the sediments are required, and we recommend the use of sediment TIE methodology (US-EPA 2007b) for these efforts.

In the case where the sediment are predicted to be toxic and all sediments are toxic in the sediment toxicity tests, some care or caution is warranted because one may or may not have the correct and/or all of the toxicant(s) identified. We suggest that additional sampling and testing of sediment samples with lower concentrations of the identified toxicant(s) be performed in order to obtain a more complete response curve for the site. With a more complete response curve, one can place the measured toxicities in context of the water-only effects threshold between non-toxic and toxic samples for the known toxicants. If the break point in the measured and estimated (from the FCV and C_{free} data) toxicities align, then consistency has been demonstrated between the toxicity tests and interstitial water-based toxicity estimates. If not, efforts to resolve the differences should be performed, e.g., are there unidentified toxicants in the samples and are there data quality issues?

When toxicity endpoints are plotted against their estimated toxicities using EPA's FCVs, outliers from the generalized response pattern may be caused by the presence of other toxicants in those samples. These toxicants might make the sediment more toxic than predicted based upon the identified toxicants in the samples. These toxicants could be additive with or exert toxicity independent of the identified toxicants in the samples. 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 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., 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 TIE work (US-EPA 2007b) on the outliers might be in order depending upon the site and/or location of the samples within the site. 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.

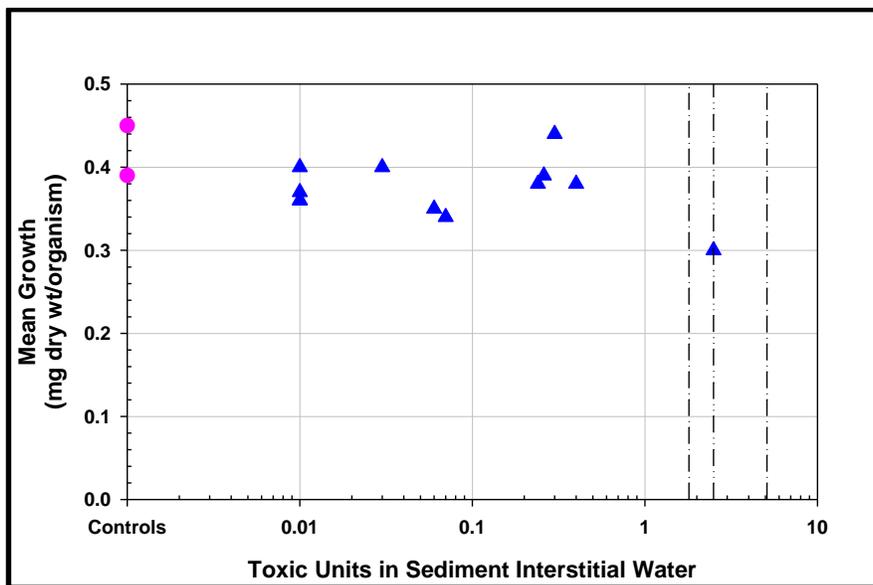


Figure 5-3. Measured chronic toxicity data for *Hyalella azteca* in 28-d sediment toxicity test with sediments from the Hudson River at Troy, NY, and toxicity estimated from the concentrations of PAHs in the sediment interstitial water using EPA’s PAH FCVs (Kreitinger et al. 2007). Pink circle symbols are the sediment toxicity test controls. The controls are considered non-toxic and have zero toxic units. The —·— and --- lines are the mean and 95% confidence levels for the EC50 derived from the water-only toxicity testing data of Driscoll and Landrum for *H. azteca* (Kreitinger et al. 2007).

5.5 Method Uncertainties

This guidance is based upon laboratory measurements of the freely dissolved concentrations (C_{free}) of the chemical in sediment interstitial waters, and the ability to define or establish adverse effects concentrations in sediment interstitial water. The guidance provided in this document, in most cases, will be quite difficult to apply with *in-situ* measurements of interstitial water. The complexities, difficulties, and costs of *in-situ* measurements often result in limited data, e.g., a handful of

measurements, and in these cases, evaluation of potential remedial options and activities becomes very tenuous. However, *in-situ* measurements capture actual field conditions that laboratory (*ex-situ*) measurement are unable to replicate with very much accuracy.

As with any method, replication of measurements is needed in order to understand variability because sediments often exhibit high spatial and temporal variability (Stemmer et al. 1990). Therefore, replicate samples should be collected to determine variances in sediment characteristics. For sediments being sampled using the passive sampling methodology, there are three types of passive sampler replication are recommended.

- Multiple passive samplers are simultaneously placed in one sediment sample.
- Replicate samples from the same batch of sediment should be sampled using passive samplers.
- Replicate samples from the same sampling location should be sampled using passive sampler

These measurements will define the variances associated with the passive sampling measurement technique and those arising from sample collection and homogenization.

For sediment toxicity test methods, eight replicates are recommended for routine testing with freshwater species (US-EPA 2000b) while 5 replicates are recommended for marine species (US-EPA 1994; US-EPA and US-ACE 2001). Additional guidance on replication is provided in EPA's sediment testing manuals and should be consulted for further information.

Appendix

This appendix provides information on two important facets related to this document. The first is on the importance of aliphatic hydrocarbons in causing toxicity in sediments. The second is on how to generate water-only effects data for toxicant(s) of interest.

6.1 Relationship between Toxicity of PAH Mixtures and Aliphatic Hydrocarbons

There are many sources of PAHs to the environment (Burgess et al. 2003a). At some 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. Consequently, when PAHs are suspected as the toxicants, comparison of the toxicity predicted based upon the measured concentrations in the sediment interstitial water and the toxicity measured in sediment toxicity tests must be performed. The mechanism of toxicity for filter feeding benthic invertebrates such as the freshwater amphipod *Hyalella azteca* might stem from a physical effect, such as fouling of respiratory surfaces by the oil phase (Mount et al. 2015, unpublished results). Urban industrial waterways with numerous years of industrial inputs and ship traffic are especially prone to having high level of aliphatic hydrocarbons. Resultantly, the presence of PAH mixtures in a sediment does not *automatically* equate to the presence of risk or toxicity in the sediment when high levels of aliphatic hydrocarbons are present. Methods like toxicity identification evaluation (TIE) can be very useful for characterizing the causes of sediments toxicity and resolving if PAHs or aliphatic hydrocarbons are the causes of sediment toxicity (US-EPA 2007b).

6.2 Measuring Water Only Toxicity Value for Toxicant(s)

Water-only toxicity effects concentration(s) may be derived by performing aquatic toxicity tests with the chemical(s) of interest in water-only exposures especially if the FAVs or FCVs are not available for a given chemical. EPA acute or chronic water toxicity test methods (US-EPA 1996a; US-EPA 1996b; US-EPA 1996c; US-EPA 1996d) or equivalent are required. These methods provided high quality chronic toxicity data when properly implemented. Proper implementation will require measured concentrations in the water over the duration of the toxicity test. Results based upon nominal concentrations of the toxicants are unacceptable. With the newly measured toxicity value(s), these value(s) would then be used to derive a FCV or SCV for the chemical or mixture of chemicals of interest. Note, performing water-only toxicity tests will be costly and time consuming. Resultantly, this approach is only recommend in those situations where the costs and time commitments warrant such efforts.

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