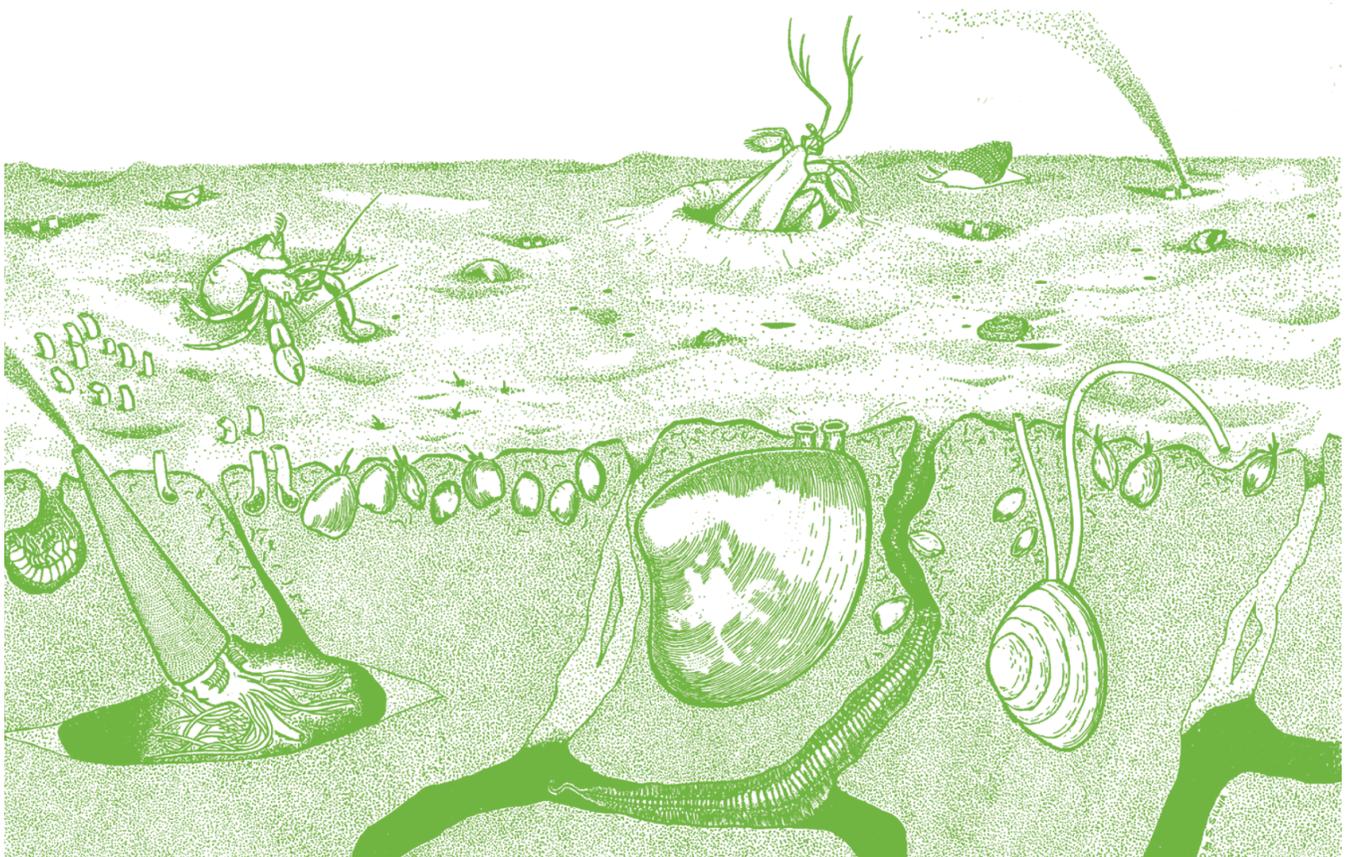


Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Procedures for the Determination of the Freely Dissolved Interstitial Water Concentrations of Nonionic Organics



Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Procedures for the Determination of the Freely Dissolved Interstitial Water Concentrations of Nonionic Organics

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Notice

The Office of Research and Development (ORD) has produced this ESB document to provide procedures for the determination of the freely dissolved concentrations of nonionic organic chemicals for deriving sediment interstitial water toxic units (IWTUs). ESBs may be useful as a complement to existing sediment assessment tools. This document should be cited as:

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This document, and the other ESB documents, can also be found in electronic format at the following web address:

<http://www.epa.gov/nheerl/publications.html>

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It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Abstract

This document describes procedures to determine the concentrations of nonionic organic chemicals in sediment interstitial waters. In previous ESB documents, the general equilibrium partitioning (EqP) approach was chosen for the derivation of sediment benchmarks because it accounts for the varying bioavailability of chemicals in different sediments and allows for the incorporation of the appropriate biological effects concentration. This provides for the derivation of benchmarks that are causally linked to the specific chemical, applicable across sediments, and appropriately protective of benthic organisms.

In contrast to the previous ESB documents, the emphasis of this ESB document is to provide a summary of procedures for determining the freely dissolved concentrations of nonionic organic chemicals for deriving sediment interstitial water toxic units (IWTUs). In the last ten years, technologies have been developed allowing for the accurate estimation and measurement of the concentrations of nonionic organic chemicals in sediment interstitial waters. When the general EqP model (i.e., one-carbon model) was first proposed for deriving ESBs, methods for directly measuring interstitial water concentrations of nonionic organic chemicals were often overly technically difficult, cost prohibitive, or simply not available. The procedures described here are an alternative or complement to using the one-carbon general model for deriving ESBs. The one-carbon general model estimates the bioavailability of nonionic organic contaminants based on their measured sediment concentrations and sediment organic carbon content. The new technologies and resulting procedures described in this document include a two-carbon model incorporating black carbon along with natural organic carbon for making EqP-based predictions, direct measurements of interstitial water contaminants adjusted for dissolved organic carbon, and passive samplers to measure interstitial water concentrations directly or via the sediment. These procedures allow for the more accurate determination of the freely dissolved and potentially bioavailable concentrations of nonionic organic chemicals. These concentrations along with the final chronic values (FCVs), secondary chronic values (SCVs), or other relevant water-only toxicity values are used to derive IWTUs. Depending upon the toxicological endpoint, if the IWTUs are greater than one, benthic organisms may not be protected and adverse effects may result.

This document is not intended as a methods manual but rather provides an overview of procedures for determining freely dissolved concentrations of nonionic organic chemicals. Throughout this document, the scientific literature cited provides greater methodological detail.

ESB documents have been developed for two pesticides (endrin, dieldrin), polycyclic aromatic hydrocarbon (PAH) mixtures, metal mixtures, and a selection of 32 nonionic organic chemicals.

The ESBs do not intrinsically consider the antagonistic, additive or synergistic effects of other sediment contaminants in combination with the individual nonionic organic chemicals discussed in this document or the potential for bioaccumulation and trophic transfer of these chemicals to aquatic life, wildlife or humans. However, for narcotic chemicals, additivity can be used to sum toxic effects.

Foreword

Under the Clean Water Act (CWA), the U.S. Environmental Protection Agency (EPA) and the States develop programs for protecting the chemical, physical, and biological integrity of the Nation's waters. To support the scientific and technical foundations of the programs, EPA's Office of Research and Development has conducted efforts to develop and publish equilibrium partitioning sediment benchmarks (ESBs) for some of the 65 toxic pollutants or toxic pollutant categories. Toxic contaminants in bottom sediments of the Nation's lakes, rivers, wetlands, and coastal waters create the potential for continued environmental degradation, even where water column contaminant levels meet applicable water quality standards. In addition, contaminated sediments can lead to water quality impacts, even when direct discharges to the receiving water have ceased.

The ESBs and associated methodologies presented in this document provide a means to estimate the concentrations of a substance that may be present in sediment while still protecting benthic organisms from the effects of that substance. These benchmarks are applicable to a variety of freshwater and marine sediments because they are based on the biologically available concentration of the substance in the sediments. These ESBs are intended to provide protection to benthic organisms from direct toxicity resulting from this substance under site conditions. The ESBs do not intrinsically consider the antagonistic, additive, or synergistic effects of other sediment contaminants in combination with the nonionic organic chemicals discussed in this document or the potential for bioaccumulation and trophic transfer of these chemicals to aquatic life, wildlife, or humans. However, in some cases, the additive toxicity for specific classes of toxicants (e.g., polycyclic aromatic hydrocarbon mixtures and other narcotic organic chemical) is addressed.

ESBs may be useful as a complement to existing sediment assessment tools, to help evaluate the extent of sediment contamination, to identify chemicals causing toxicity, and to serve as targets for pollutant loading control measures. This document provides technical information to EPA Program Offices, including Superfund, Regions, States, the regulated community, and the public. Decisions about risk management are the purview of individual regulatory programs, and may vary across programs depending upon the regulatory authority and goals of the program. For this reason, each program will have to decide whether the ESB approach is appropriate to that program and, if so, how best to incorporate this technical information into the assessment process. While it was necessary to choose specific parameters for the purposes of this document and other ESB documents, it is important to realize that the basic science underlying this document can be adapted to a range of risk management goals by adjusting the input parameters. At the same time, the ESBs do not substitute for the CWA or other EPA regulations, nor are they regulation. Thus, they cannot impose legally binding requirements on EPA, States, or the regulated community. EPA and State decision makers retain the discretion to adopt approaches on a case-by-case basis that differ from this technical information where appropriate. It is recommended that the ESBs not be used alone but with other sediment assessment methods to make informed management decisions based on a weight of evidence approach. EPA may change this technical information in the future. This document has been reviewed by EPA's Office of Research and Development (Atlantic Ecology Division, Narragansett, Rhode Island), undergone an external peer review, and has been approved for publication.

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Executive Summary

The purpose of this document is to provide guidance on procedures to determine the freely dissolved concentrations of nonionic organic chemicals in sediment interstitial waters. These data when combined with FCVs, SCVs or other relevant water-only toxicity data can be used to derive interstitial water toxic units (IWTUs). This methodology is issued in support of the published ESBs for endrin and dieldrin (U.S. EPA, 2003b,c), PAHs mixtures (U.S. EPA, 2003d), and other nonionic organic chemicals (U.S. EPA, 2008). The procedures used to determine the freely dissolved concentrations of nonionic organic chemicals are intended to supplement the procedures described for calculated ESBs based on the general equilibrium partitioning (EqP) theory as described in the ESB Technical Basis Document (U.S. EPA, 2003a).

The EqP approach was chosen because it accounts for the varying biological availability of chemicals in different sediments and allows for the incorporation of the appropriate biological effects concentration (Di Toro et al., 1991; U.S. EPA, 2003a). This provides for the derivation of benchmarks that are causally linked to the specific chemical, applicable across sediments, and appropriately protective of benthic organisms.

General EqP theory holds that a nonionic chemical in sediment partitions between sediment organic carbon, interstitial (pore) water, and benthic organisms. At equilibrium, if the concentration in any one phase is known, then the concentrations in the others can be predicted. The ratio of the concentration in water to the concentration in organic carbon is termed the organic carbon-water partition coefficient (K_{OC}), which is expected to be a constant for each chemical. The ESB Technical Basis Document (U.S. EPA, 2003a) demonstrates that biological responses of benthic organisms to nonionic organic chemicals in sediments are different across sediments when the sediment concentrations are expressed on a dry weight basis, but similar when expressed on a μg chemical/g organic carbon basis ($\mu\text{g}/\text{g}_{OC}$). Similar responses were also observed across sediments when interstitial water concentrations were used to normalize biological availability. The Technical Basis Document (U.S. EPA, 2003a) further demonstrates that if the effect concentration in water is known, the effect concentration in sediments on a $\mu\text{g}/\text{g}_{OC}$ basis can be accurately predicted by multiplying the effect concentration in water by the chemical's K_{OC} .

The U.S. Environmental Protection Agency (EPA) currently recognizes that the ESBs may be under- or overprotective when differences occur in the bioavailability of the chemical in the site sediment because of alternate partitioning phases (e.g., black carbon). In such cases, the bioavailability of chemicals can be influenced by the site-specific partitioning behavior of sediment carbon that may be substantially different than for typical diagenic organic carbon. The procedures described in this document assume that the true concentration of bioavailable chemical can be reasonably measured or estimated from the concentration of freely dissolved chemical in interstitial water. This assumption does not imply that exposure occurs only from interstitial water, rather that the freely dissolved concentration of NOCs in interstitial water is a better surrogate than the bulk concentration for the fraction of chemical in the sediment that is available to partition into interstitial water and into organisms. In the last ten years, technologies have been developed allowing for the accurate estimation and measurement of the concentrations of nonionic organic chemicals in

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sediment interstitial waters. When the EqP model was first proposed for deriving ESBs, methods for directly measuring interstitial water concentrations of nonionic organic chemicals were often overly technically difficult, cost prohibitive, or simply not available. This document includes examples that demonstrate the calculation of interstitial water toxic units using various approaches including: a “two-carbon” model that estimates the concentrations of chemical in interstitial water by taking into account the influence of black carbon, direct measurement of chemical in isolated samples of interstitial water, and deploying passive samplers in interstitial water and whole sediment. This document concludes with a proposed tiered implementation framework that may be useful in a weight of evidence application of this guidance.

The ESBs, based on the one-carbon general model, can be used to calculate ESBs for any toxicity endpoint for which there are water-only toxicity data; it is not limited to any single effect endpoint. ESBs have been calculated using FCVs from water quality criteria (U.S. EPA, 2003b,c), SCVs derived from existing toxicological data (U.S. EPA, 2008), and from narcosis theory (U.S. EPA, 2003d). The FCVs, SCVs and other relevant water-only toxicity data can be used to derive interstitial water toxic units (IWTUs).

These values are intended to be the concentration of each chemical in water that is protective of the presence of aquatic life. The ESBs should be interpreted as a chemical concentration below which adverse effects are not expected. At concentrations above the ESB (i.e., > 1.0 toxic unit), assuming equilibrium between phases, effects may occur with increasing severity as the degree of exceedance increases. This document is intended to provide guidance for determining the freely dissolved interstitial water concentrations of NOCs for deriving IWTUs. The document is not intended to be a methods manual; whenever possible, relevant scientific literature is cited that provides greater methodological detail. Further, especially for the passive samplers, as they are used more frequently, standardized manuals for the procedures discussed here are likely to be available in the near future. A sediment-specific site assessment (e.g., toxicity testing) would provide further information on bioavailability and the expectation of toxicity relative to the ESB along with associated uncertainties. The procedures in this document are intended to complement such sediment-specific assessments. In general, the ESBs apply only to sediments having $\geq 0.2\%$ total organic carbon by dry weight and nonionic organic chemicals with $\log K_{OWs} \geq 2$.

The ESBs do not intrinsically consider the antagonistic, additive, or synergistic effects of other sediment contaminants in combination with the nonionic organic chemicals discussed in this document or the potential for bioaccumulation and trophic transfer of these chemicals to aquatic life, wildlife, or humans. However, for narcotic chemicals, ESB values may be used in a framework to evaluate the potential effects of chemical mixtures. Consistent with the recommendations of EPA’s Science Advisory Board, publication of these documents does not imply the use of ESBs as stand-alone, pass-fail criteria for all applications; rather, ESB exceedances could be used to trigger the collection of additional assessment data. Similarly, ESBs are supportive of recommendations by Wenning et al. (2005) to apply a weight of evidence approach when evaluating contaminated sediments.

Glossary of Abbreviations

ASTM	American Society for Testing and Materials
BC	Black carbon
C ₁₈	Octadecyl matrix used in solid chromatography
C _d	Freely-dissolved interstitial water concentration of contaminant
C _{d,PAHi,FCVi}	Freely-dissolved interstitial water effect concentration of a specific PAH
C _{DOC}	Chemical concentration associated with dissolved organic carbon
C _{IW}	Total interstitial water concentration of contaminant
C _{OC}	Chemical concentration in sediments on an organic carbon basis
C _{OC,PAHi}	PAH-specific chemical concentration in sediment on an organic carbon basis
C _{OC,PAHi,FCVi}	Effect concentration of a specific PAH in sediment on an organic carbon basis calculated from the product of its FCV and K _{OC}
C _{OC,PAHi,Maxi}	Maximum solubility limited PAH-specific concentration in sediment on an organic carbon basis
C _{PS}	Passive sampler concentration of contaminant
C _{Td}	Total dissolved concentration of a contaminant in interstitial water
CHN	Carbon, hydrogen and nitrogen elemental analyzer
CWA	Clean Water Act
DDTs	Dichlorodiphenyltrichloroethane and degradation products
DOC	Dissolved organic carbon
EPA	United States Environmental Protection Agency
EqP	Equilibrium partitioning
ESB	Equilibrium partitioning Sediment Benchmark; for nonionic organic contaminants, this term usually refers to a value that is organic carbon-normalized (more formally ESB _{OC}) unless otherwise specified
ESBTU	Equilibrium Partitioning Sediment Benchmark Toxic Units
ESBTU _{FCV}	Equilibrium Partitioning Sediment Benchmark Toxic Units based on the Final Chronic Value
FCV	Final chronic value
f _{BC}	Fraction of black carbon in sediment
f _{NSOC}	Fraction of natural sedimentary organic carbon
f _{OC}	Fraction of organic carbon in sediment
GC/MS	Gas chromatograph/mass spectrometer
g _{OC}	Gram organic carbon

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IW	Interstitial water (also known as pore water)
IWTU	Interstitial water toxic units
IWTU _{FCV}	Interstitial water toxic units based on the Final Chronic Value
IWTU _{SCV}	Interstitial water toxic units based on the Secondary Chronic Value
K _{BC}	Black carbon-water partition coefficient
K _{DOC}	Dissolved organic carbon-water partition coefficient
K _{OC}	Organic carbon-water partition coefficient
K _{OW}	Octanol-water partition coefficient
K _P	Sediment-water partition coefficient
K _{PDMS}	Polydimethylsiloxane-water partition coefficient
K _{PED}	Polyethylene device-water partition coefficient
K _{POM}	Polyoxymethylene-water partition coefficient
K _{PS-d}	Passive sampler-water partition coefficient
NAPL	Non-aqueous phase liquid
NSOC	Natural sedimentary organic carbon
NOC	Nonionic organic chemical
OC	Organic carbon
ORD	U.S. EPA, Office of Research and Development
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyls
PDMS	Polydimethylsiloxane
PED	Polyethylene device
POM	Polyoxymethylene
PRC	Performance reference compound
SCV	Secondary chronic value
SIM	Selected ion mode in analyses using GC/MS
SPE	Solid phase extraction
SPMD	Semi-permeable membrane device
SPME	Solid phase microextraction
TIE	Toxicity Identification Evaluation
TNT	Trinitrotoluene
TOC	Total organic carbon
TU	Toxic Unit
WQC	Water Quality Criteria

Section 1

Introduction

1.1 General Information

The purpose of this document is to provide guidance on procedures that can be used to determine the freely dissolved interstitial water concentrations of nonionic organic chemicals to derive interstitial water toxic units, reflective of environmental conditions. The procedures are intended to be used with any water-only toxicity values (e.g., FCVs, SCVs, other relevant water-only data) and are not limited to the equilibrium partitioning sediment benchmarks for endrin and dieldrin (U.S. EPA, 2003b,c), mixtures of polycyclic aromatic hydrocarbons (PAHs) (U.S. EPA, 2003d), and a selection of nonionic organic chemicals (U.S. EPA, 2008) discussed here (see Table 2.1 for a list of selected nonionic organic contaminants).

A thorough understanding of the “Technical Basis for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Nonionic Organics” (U.S. EPA, 2003a), the ESB documents for endrin and dieldrin (U.S. EPA, 2003b,c), as well as documents for mixtures of PAHs (U.S. EPA, 2003d), and selected nonionic organic chemicals (U.S. EPA, 2008), and “Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and their Uses” (Stephan et al., 1985) is recommended. Importantly, it is strongly suggested that these procedures for determining the sediment interstitial water concentrations should be used with other sediment assessment lines of evidence (e.g., Toxicity Identification Evaluations (TIEs) (U.S. EPA, 2007)), benthic community surveys, sediment toxicity testing) as well as risk assessment procedures.

1.2 Review of the General Equilibrium Partitioning Approach

The general EqP approach assumes that (1) the partitioning of the nonionic organic chemical between natural sedimentary organic carbon and interstitial water is at or near equilibrium; (2) the concentration in the phases can be predicted using appropriate partition coefficients and the measured concentration in the other phases (assuming the freely-dissolved interstitial water concentration can be accurately measured); (3) organisms receive equivalent exposure from water-only exposures or from any equilibrated phase: either from interstitial water via respiration, from sediment via ingestion or other sediment-integument exchange, or from a mixture of exposure routes; (4) for nonionic chemicals, effect concentrations in sediments on a normalized basis can be predicted using the partition coefficients and effects concentrations in water; (5) the FCV or SCV concentration (or other relevant water-only value) is an appropriate effects concentration for freely-dissolved chemical in interstitial water; and (6) ESBs derived as the product of a partition coefficient and FCV or SCV are protective of benthic organisms.

ESB concentrations presented in previous documents (e.g., U.S. EPA, 2003b,c,d, 2008) are expressed as $\mu\text{g chemical/g sediment organic carbon}$ ($\mu\text{g/g}_{\text{OC}}$) and not on an interstitial water basis because (1) interstitial water was considered too difficult to sample and (2) significant amounts of the dissolved chemical may be associated with dissolved organic carbon (DOC); thus, total concentrations in interstitial water may overestimate exposure.

As discussed in Section 1.3 and Section 2, in the last several years, the first assumption used in the one-carbon general model that nonionic organic contaminants always partition between only two phases (i.e., natural sedimentary organic carbon and interstitial water) has been demonstrated to not be entirely true in all sediments and that other sedimentary partitioning phases occur in sediments (Luthy et al., 1997; Cornelissen et al., 2005a). Further, because of advances in technology, some contaminated sediment measurements like interstitial water contaminant concentrations and assessing the effects of DOC on contaminant partitioning can now be made more accurately. While the one-carbon general model has been shown to operate successfully in many applications (e.g., Swartz et al.; 1990, DeWitt et al., 1992; Hoke et al., 1994), the recognition of multiple sedimentary phases and recent advances in interstitial water measurements make the direct derivation of interstitial water toxic units feasible.

1.3 Rationale for Development of Procedures for Determining Freely Dissolved Concentrations

As noted above, current ESB documents use a one-carbon EqP model which assumes organic contaminants partition between the aqueous and natural sedimentary organic carbon phases (see Section 2). Under some environmental conditions and ESB applications, these assumptions may be inaccurate. ESBs may be under- or overprotective if the sediment or chemical quality characteristics at the site alter the bioavailability and, consequently, the toxicity of the sediment-bound chemical relative to that predicted by the one-carbon EqP theory. Therefore, it is appropriate and more accurate that the ESBs be used with directly determined freely dissolved concentrations of nonionic organic chemicals to derive interstitial water toxic units. Further, in recent years, technologies have been developed using passive sampling to determine these freely dissolved interstitial water

concentrations of chemicals instead of estimating them from sediment associated concentrations as is performed in the one-carbon EqP approach (Maruya et al., 2012).

1.4 Freely Dissolved Concentration Procedures

The reason for using the various bioavailability-based procedures described in this document is that although testing of various sediments has demonstrated the applicability of the one-carbon EqP approach (U.S. EPA, 2003a), EqP theory based on a one-carbon model may not accurately predict contaminant partitioning for certain sediments and sites. Unique sediment phases (i.e., the mixture of pyrogenic carbon called black carbon), chemical speciation, or chemical form may make the chemical more or less bioavailable than EqP predicts, thereby altering the toxicity of the sediment. For example, in some sediments, the partitioning of PAHs cannot be explained by EqP based on natural sedimentary organic carbon (Maruya et al., 1996; McGroddy et al., 1996). Instead, accurate predictions of partitioning behavior may require the use of both an organic carbon-water partition coefficient (K_{OC}) and a black carbon-water partition coefficient (K_{BC}) (see Section 2) (Gustafson et al., 1997; Cornelissen et al., 2005a). Further, to derive accurate interstitial water toxic units based on existing water-only toxicity data (e.g., FCV), quantification of partitioning at these sites may require direct measurement of the freely dissolved concentration of the nonionic organic chemical in interstitial water (see Section 2).

Application of these ESB procedures may indicate improvements to the one-carbon general model that will require implementation over time. Further, because these procedures can be technically complex and sometimes costly, it is important that they be conducted only by those who are well qualified and experienced, and potentially only as a second-tier assessment approach (see Section 4).

This document focuses on black carbon as an important alternate sedimentary phase. However, other phases may be present in sediments including incompletely degraded petroleum (Jonker et al., 2003). The effects of petroleum and other non-aqueous phase liquids (NAPLs) on contaminant bioavailability are not considered in this document due to the lack of approaches, at this time, for accurately addressing their effects.

1.5 Data Quality and Uncertainties

Data sources and manipulations used to generate black carbon-water and passive sampler-water partition coefficients (i.e., K_{BC} , K_{PS-d}) presented in this document are discussed in detail in Section 2. Due in part to the relatively recent development and application of many of the passive sampling technologies as well as black carbon partitioning for estimating bioavailability, the magnitude of the accuracy, precision and uncertainties associated with these partition coefficients is not well known. Recent intensive evaluations of partition coefficients for solid phase microextraction (SPME), polyoxymethylene (POM), and polyethylene (PE) (DiFilippo and Eganhouse, 2010; Endo et al., 2011; Lohmann, 2012) are good examples of the types of analyses needed to parameterize these data quality assurance measures in the future. There is also a need to encourage the organization of expert workshops and funding of quality assurance-related research to provide guidance on these issues. For example, determining when contaminants have achieved equilibrium between the passive samplers and the dissolved phase is currently a critical challenge in the use of passive samplers. Further, as the number of values for K_{BC} and K_{PS-d} increase in the scientific literature some values may need to be retired and replaced with values that are more scientifically-sound and robust. Similarly, as new toxicological data and models become available (e.g., Di Toro et al., 2007; McGrath and Di Toro, 2009), older data and models may need to be reassessed or removed

from the data base. Further, the relationship between predicted toxicological effects and physicochemical parameters like K_{OW} , may also need to be reassessed. For example, McGrath and Di Toro (2009), recently suggested to not use log K_{OW} values greater than 6.4 to predict toxicological effects using the target lipid model, frequently used with narcotic chemicals, because of the uncertainties in the model's predictions above that K_{OW} value. Such a cut-off would affect five of the chemicals specifically discussed in this document (i.e., high molecular weight PAHs). At this time, this guidance does not recommend users to apply this cut-off but does want to make users aware of this type of discussion in the scientific literature. In contrast to the passive samplers, black carbon, and toxicological models, the accuracy, precision and uncertainties associated with other aspects of the procedures discussed in this document; such as, sediment and interstitial water instrumental analysis for contaminants and sediment characteristics (e.g., DOC) are well understood and have been discussed in detail elsewhere.

This document was reviewed as part of a formal external peer review coordinated at the U.S. EPA National Health and Environmental Effects Research Laboratory, Research Triangle Park, North Carolina, and Atlantic Ecology Division, Narragansett, Rhode Island. Any detected errors of omission, substance or calculation discovered during the peer review process were corrected.

1.6 Overview

This document presents procedures for determining the freely dissolved concentration of nonionic organic chemicals for calculating interstitial water toxic units. Section 2 of the document provides background and guidance on the procedures. Section 3 illustrates examples of the use of the procedures. The implementation of the procedures is discussed in Section 4. Section 5 lists the references for this document. Finally,

Equilibrium Partitioning Sediment Benchmarks (ESBs): Freely Dissolved Concentrations

the focus of this document is to provide the reader with an overview of the current approaches for determining the freely dissolved concentrations of nonionic organic chemicals in sediment interstitial waters. The document is not intended to serve as a methods manual. In the different sections of the document, relevant scientific literature is cited to provide the reader with more in-depth information.

Section 2

Procedures for Determining Freely Dissolved Interstitial Water Concentrations

2.1 Introduction

Current ESB documents for the nonionic organics endrin, dieldrin, PAH mixtures, and compendium chemicals (U.S. EPA, 2003 a,b,c,d, 2008) use a two-phase EqP model to derive ESB values. This model assumes sediment contaminants partition between natural sedimentary organic carbon and the freely dissolved phase in interstitial water. In this document, this model is called the “one-carbon” model. The procedures in this document are intended for determining the freely dissolved concentration of chemicals in sediment interstitial waters. These concentrations can then be used with current ESBs and other relevant water-only toxicity values. For example, as recently discussed by Di Toro et al. (2007) and McGrath and Di Toro (2009), the target lipid model used to calculate the FCVs for PAHs (U.S. EPA, 2003d) can also be modified to calculate “mode of action” based FCVs. The mode of action FCV considers the 5th percentile of the distribution of the critical target lipid body burdens using the target lipid model, a chemical class variable, and an empirically-derived geometric mean acute to chronic ratio. When applied in combination, the freely dissolved interstitial water concentration and water-only toxicity value are used to derive interstitial water toxic units that more directly consider contaminant bioavailability. The procedures capture the partitioning of organic contaminants to specific phases in the sediment in addition to natural sedimentary

organic carbon. These alternate phases may include, but are not limited to, interstitial DOC and different forms of BC. These phases are discussed below. The objective of this document is to generate an assessment of sediment toxicity that is more accurate in terms of environmental bioavailability. The focus of this document is on the performance of assessments for nonionic organic contaminants.

2.1.1 Rationale

As noted above, U.S. EPA’s sediment guidelines or benchmarks (ESBs) for nonionic organic chemicals are based on the one-carbon general equilibrium partitioning model. The general model uses a two-phase approach: particulate-associated chemical and dissolved interstitial water chemical, where the total concentration in the sediment matrix equals the concentration in the particulate phase plus the concentration freely-dissolved in interstitial water under equilibrium conditions. With this model, the dissolved phase concentration (C_d) ($\mu\text{g/L}$) of a nonionic organic contaminant can be calculated as follows:

$$C_d = \frac{C_p}{K_p} \quad (2-1)$$

where, C_p is the particulate contaminant concentration ($\mu\text{g/Kg}$ dry) and K_p is the sediment-water partition coefficient (L/Kg).

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Substituting K_p with the product of the fraction of natural sediment organic carbon (f_{OC}) (Kg organic carbon (OC) /Kg dry) and organic carbon-water partition coefficient (K_{OC}) (L/Kg OC) (for more discussion of selecting K_{OC} , see U.S. EPA, 2003b,c,d, 2008), Equation 2-1 can be rewritten as:

$$C_d = \frac{C_p}{f_{OC}K_{OC}} \quad (2-2)$$

Using Equation 2-2, the conventional ESB can be determined. For example, for PAH mixtures (U.S. EPA, 2003d), in this one-carbon model, the estimated C_d for each of 34 PAHs are divided by water quality criteria (WQC) final chronic values (FCVs), secondary chronic values (SCVs) or any other relevant water-only value to derive the ESB toxic units (ESBTUs) (see Section 2.5 for more discussion on how to calculate interstitial water toxic units). It should be noted that in the conventional ESB procedure using the one-carbon general model, ESBTUs are often derived from the quotient of the contaminant organic carbon normalized sediment concentration ($\mu\text{g}/\text{Kg OC}$) and the organic carbon normalized toxicity value ($\mu\text{g}/\text{Kg OC}$). See U.S. EPA (2003b,c,d, 2008) for more discussion of the conventional ESB procedures and selection of water-only toxicity values.

If additional sorbing phases exist in sediment, it is possible that the EqP model (i.e., Equation 2-2) for C_d may not always be accurate. In these cases, the toxicity of the sediment may not be accurately predicted by the one-carbon model because, in addition to natural sedimentary organic carbon, black carbon, or other properties of the sediments may alter bioavailability (Figure 2-1). To accurately consider the effect of these phases and properties in a sediment assessment, use of the procedures described in this document is warranted.

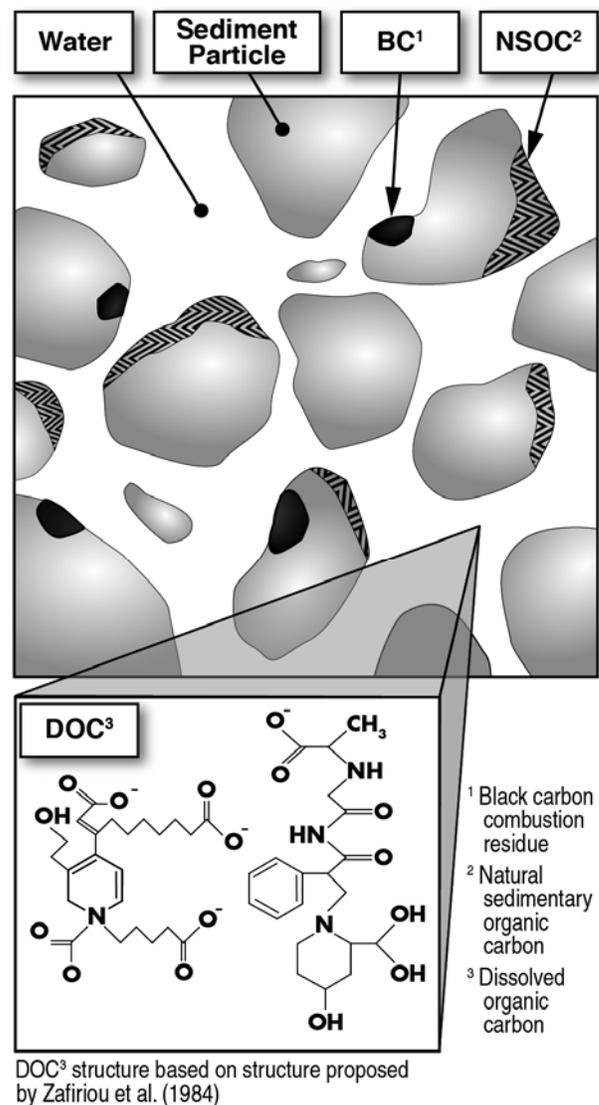


Figure 2-1. Magnified and exploded view of different types of sediment particle phases.

In this section, approaches are presented to estimate or measure the bioavailable, freely dissolved interstitial water concentration (i.e., C_d), which can be compared to the WQC FCV, SCV, or any relevant water-only toxicity value. See U.S. EPA (2003d, 2008) for more discussion of the ESB procedures and the selection of water-only toxicity values. FCVs and SCVs for many nonionic chemicals can be found in U.S. EPA (2003b,c,d, 2008), Suter and Mabrey (1994), Suter and Tsao (1996), and Great Lakes Water Quality Initiative (1995) as well as other sources (Di Toro et al., 2007; McGrath and Di Toro, 2009). The approaches EPA recommends in this document for estimating or measuring the freely dissolved chemical concentration in interstitial water require procedures appropriate for obtaining and chemically analyzing interstitial water or sampling the interstitial water or whole sediments with passive samplers. The approaches assume that the contaminant is distributed into multiple phases: freely dissolved, DOC-associated, natural sedimentary organic carbon, and BC. Recent research and technological advances have made the measurement or collection of these samples feasible. Further, the freely dissolved concentrations can be determined in various ways: (1) estimated using a two-carbon model that takes into account the association of contaminants with BC, (2) extracted directly from interstitial waters, (3) estimated by passive sampling of whole sediments, and (4) estimated by passive sampling of interstitial waters. The procedures presented below employ the best technologies available at the time this document was prepared for obtaining interstitial water, chemically analyzing interstitial water contaminant concentrations, passive sampling interstitial water and whole sediment, and estimating or measuring the freely dissolved concentration of contaminants. The last part of this section (2.5) describes an approach for using the freely dissolved concentrations

collected with the procedures listed above to derive interstitial water toxic units (IWTUs). If the IWTUs are greater than one, benthic organisms may not be protected and adverse effects may result.

2.2 Using a Two-Carbon Model for Determining Freely Dissolved Interstitial Water Concentrations

The comparison of dissolved contaminant concentrations derived from carbon-normalized concentrations in bulk sediment to FCVs or SCVs as described in Section 2.1 (i.e., Equation 2-2), may be inaccurate at some sites if the characteristics of the sediment or the contaminant reduces the partitioning into the interstitial water, thereby reducing bioavailability and toxicity. For example, several studies have demonstrated that partitioning of PAHs cannot always be explained by the conventional two phase “one-carbon” EqP model (Equation 2-2) (McGroddy et al., 1995; Maruya et al., 1996). Additional studies suggest that PAHs that are occluded in or sorbed to forms of black carbon exhibit reduced partitioning (Gustafsson et al., 1997; Bucheli and Gustafsson, 2000; Accardi-Dey and Gschwend, 2002; Arp et al., 2009) and limited bioaccumulation by benthic invertebrates (Vinturella et al., 2004a; Rust et al., 2004) which suggests bioavailability is being reduced.

Highly condensed forms of pyrogenic carbon (e.g., soot) and residues of incomplete combustion (e.g., charcoal), commonly termed BC, are ubiquitous in the aquatic environment. It is estimated that BC constitutes approximately 10% of sedimentary organic carbon in ordinary sediments (Middelburg et al., 1999). In sediments from contaminated sites, the contribution of BC may exceed 50% due to the fossil-fuel related residues of historic industrial activity. The sorption of nonionic organic contaminants to BC has been observed to be up to 10–1,000 times stronger

than the sorption to natural sedimentary organic carbon (NSOC), which includes diagenetic organic carbon, such as plant material (Burgess et al., 2004). The sorption to BC is often nonlinear following a Freundlich isotherm, with the effect of BC being strongest at low contaminant concentrations (Accardi-Dey and Gschwend, 2002).

Concentrations of BC in sediment are commonly measured using a chemothermal oxidation (CTO) method (Gustafsson et al., 1997, 2001; Accardi-Dey and Gschwend, 2003). The method involves quantification of BC and total organic carbon (TOC) using a carbon, hydrogen, nitrogen elemental analyzer (CHN): (1) removal of inorganic carbonates via acidification; (2) removal of NSOC in a furnace under air flow (375°C, 24 hours); and finally; (3) quantification of remaining carbon as BC using a CHN. Other methods are available for measuring BC but are less commonly used with contaminated sediments (e.g., chromic acid digestion, microscopic inspection).

2.2.1 Two-Carbon Model

Unlike the model in Equation 2-2, the freely dissolved concentration of nonionic organic contaminants in interstitial water can be estimated using a “two-carbon” model that accounts for association of nonionic organic contaminants with the fraction of BC (f_{BC}) in sediment and the fraction of NSOC (f_{NSOC}). A two-carbon model accounts for linear absorption into the NSOC in sediment and nonlinear adsorption to BC. The two-carbon model can be used to calculate the freely dissolved concentration of each nonionic organic contaminant in interstitial water using the following relationship:

$$C_d = \frac{C_p}{f_{NSOC} K_{OC} + f_{BC} K_{BC} C_d^{n-1}} \quad (2-3)$$

where, f_{NSOC} is the weight fraction of NSOC in sediment (Kg NSOC/Kg dry), calculated from the difference between TOC and BC, f_{BC} is the weight fraction of BC in sediment (g BC/g dry), K_{BC} is the BC to water partition coefficient (L/Kg BC), and n is the Freundlich exponent, which accounts for nonlinear sorption behavior ($n = 0.6$) (Accardi-Dey and Gschwend, 2002). The value of n will vary depending on the nonionic organic contaminant. For example, to date, 0.6 has been used for PAHs with log K_{OWs} of approximately 4.00 to 5.50. Because C_d appears on both sides of the equation, an iterative approach must be used to solve for C_d . Computer-based statistical protocols such as the “Goal Seek” function in Excel[®] (Microsoft, Seattle, WA, USA) are available for this purpose.

2.2.2 Estimation of K_{BC}

Values of K_{BC} have been reported for several PAHs in spiked sediments (Accardi-Dey and Gschwend, 2003; Burgess et al., 2004) as well as for PAHs and chlorinated compounds in native sediments (Lohmann et al., 2004, 2005; Vinturella et al., 2004b; Hawthorne et al., 2007). Because K_{BC} values are not available in the literature for many nonionic organic contaminants, one study developed a linear regression relationship between the octanol-water partition coefficient (K_{OW}) and experimentally-derived values of K_{BC} for 17 PAHs (Accardi-Dey and Gschwend, 2003) to estimate K_{BC} values for PAHs for which experimental data was not available (Kane Driscoll and Burgess, 2007). Use of estimated values of K_{BC} in a two-carbon model thus far has been successful in predicting interstitial water concentrations (e.g., Armitage et al., 2008; Accardi-Dey and Gschwend, 2003) or in screening-out sediments that were not toxic to aquatic invertebrates (e.g., Driscoll et al., 2009); however more data are needed. For example, another study of 114 sediments reported that

the two-carbon model showed no significant improvement over the one-carbon general model for predicting the distribution of PAHs between sediment and interstitial water with K_{BC} ranging over three orders of magnitude (Hawthorne et al., 2007). Additional studies have demonstrated that various types of carbonaceous materials, such as coal tar pitch, exhibit a range of partitioning behavior. Further, the size of the black carbon particle affects the magnitude of the K_{BC} (Hong et al., 2003; Ghosh et al., 2003; Khalil et al., 2006; Ghosh, 2007; Ghosh and Hawthorne, 2010).

As a result of the lack of empirical values and current level of uncertainty associated with predicted K_{BC} values, provisionally, this document uses the relationship developed by Driscoll et al. (2009) for 17 PAHs:

$$\text{Log}K_{BC} = 3.41 + 0.54 \text{Log}K_{OW} \quad (2-4)$$

K_{OW} values for a range of nonionic organic contaminants can be found in Mackay et al. (1992a,b), Karickhoff and Long (1995), and U.S. EPA (2003d, 2008). Other predictive relationships are also available (e.g., Koelmans et al., 2006; van Noort, 2003).

Table 2-1 provides a list of calculated provisional $\log K_{BC}$ values for several nonionic organic contaminants based on Equation 2-4. As noted in Section 1.5, as the number of available empirical K_{BC} values increases, Equation 2-4 should be updated. Further, K_{BC} should only be used for nonionic organic contaminants that are planar and not non-planar chemicals unless the K_{BC} s were derived specifically for those non-planar chemicals (see discussion in Section 4).

2.3 Direct Measurement of Interstitial Water Concentrations

Over the last several decades, a variety of methods have been developed to estimate or measure concentrations of freely dissolved

chemicals in interstitial water. Earlier methods calculated the freely dissolved concentration from the difference between the total (i.e., freely dissolved and DOC-associated) and DOC-associated phases. More recent methods use passive sampling devices to directly measure the freely dissolved concentration in interstitial water or whole sediment.

2.3.1 Direct Collection of Interstitial Water by Centrifugation

The problems associated with adequately collecting and processing interstitial water samples are well documented (Adams, 1991; Schults et al., 1992; Ankley and Schubauer-Berigan, 1994; ASTM, 1994; Ozretich and Schults, 1998; Adams et al., 2003; Carr and Nipper, 2003). Artifacts from the procedures can preclude accurate determination of interstitial water contaminant concentrations. Further, in general, eliminating and/or avoiding these artifacts when centrifuging can be quite difficult experimentally. The procedures cited below have been shown to minimize artifactual effects of interstitial water sample collection and analysis for contaminants.

If performed with a minimum of artifacts, centrifugation without subsequent filtration results in an acceptable sample of interstitial water which can be used to make an accurate measurement of the freely dissolved concentration of nonionic organic contaminants in sediments (Adams et al., 2003). Substantial artifacts include the formation of dissolved and colloidal organic matter during interstitial water preparation and isolation which can result in an over-estimation of interstitial water nonionic organic contaminant concentrations and potential bioavailability especially for those contaminants with high K_{OW} s. Another substantial artifact is absorption and loss of NOCs to laboratory equipment surfaces. The objective of centrifugation is to obtain

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interstitial water containing contaminants operationally defined as freely dissolved. Therefore, any combination of gravitational force and time that settles the particles is acceptable. For example, a procedure applied by Lee et al. (1994) and Swartz et al. (1994) on marine sediments was shown to effectively reduce losses of organic contaminants to laboratory equipment surfaces (Ozretich and Schults, 1998). The procedure also allowed for the chemical analysis of DOC (U.S. EPA, 2000) and total contaminant concentrations (i.e., freely dissolved fraction plus the fraction associated to DOC). Conversely, the total interstitial water can be sub-sampled for direct measurement of the DOC-bound contaminants (see Section 2.3.2).

Centrifugation of the sediment and sub-sampling of the interstitial water should be performed within two hours of each other to avoid complications from the potential formation of new artificial particles caused by oxidation of reduced iron. It is clear that cleanly sampled interstitial water is important, as the presence of a particle of sediment, as noted above, could result in erroneously high concentrations; on the other hand, if the time periods before extractions are extended, by filtering and excessive sample handling, erroneously low concentrations would result because of contaminant sorption to laboratory equipment surfaces.

2.3.2 Calculating the Freely-Dissolved Concentration

Regardless of the extraction method used, it is critical that the instrumental analysis can detect contaminant concentrations below the FCV, SCV or other relevant water-only effect concentrations (i.e., ~0.01 µg/L for a great deal of the toxic nonionic organic chemicals). With the interstitial water concentration data for total contaminant and DOC concentrations, the freely dissolved interstitial water

concentration of a nonionic organic chemical can be determined in the following three ways:

1. It can be assumed that the measured total interstitial water concentration (C_{IW}) for a nonionic organic chemical with a low to intermediate $\log K_{OW}$ value (i.e., 2.5 to 4.0) is equivalent to the dissolved concentration (C_d); that is, the freely dissolved interstitial water concentration equals the total measured interstitial water concentration. However, this approach is problematic and is not recommended because high concentrations of DOC can be present in isolated interstitial water. Even low K_{OW} nonionic organic chemicals are known to associate with this material, causing a reduction in their bioavailability. Therefore, contaminant concentrations measured in interstitial water isolated by centrifugation would contain both the freely dissolved and the DOC-associated chemical, over-estimating the true bioavailability of the nonionic organic chemicals. The magnitude of the over-estimation would depend on the concentration of the DOC and affinity of the DOC for the chemicals of interest. This affinity is represented by the dissolved organic carbon partition coefficient (K_{DOC}):

$$K_{DOC} = \frac{C_{DOC}}{C_d} \quad (2-5)$$

where, C_{DOC} is the contaminant concentration associated with the DOC.

2. It can be determined that the freely dissolved interstitial water concentration is the difference between the interstitial water concentration and the DOC-associated concentration. For example, solid phase extraction (SPE) using C_{18} selectively isolates the freely dissolved chemical on the column while the DOC-associated chemical passes through the column media. The freely dissolved chemical can then be eluted from the column with an organic solvent

Procedures for Determining Freely Dissolved Interstitial Water Concentrations

(Landrum et al., 1984; Ozretich et al., 1995). The application of this method depends on the DOC-associated concentration being operationally defined as the chemical passing through the column. However, use of this procedure doubles the number of samples that need to be analyzed, and may require monitoring of DOC retention by the column (Ozretich et al., 1995). In a similar procedure, both the DOC-associated chemical and freely-dissolved chemical concentrations can be directly measured (Burgess et al., 1996) rather than by being determined by difference from the interstitial water chemical concentration. This approach should be used only if acceptable mass balances (approximately 90% or greater) of the DOC-associated, freely dissolved, and total chemical are demonstrated.

- Using Equations 2-6 and 2-7 below, C_d can be calculated from the measured total interstitial water concentration (C_{IW}), the DOC concentration, and the contaminant K_{DOC} :

$$C_d = \frac{C_{IW}}{(DOC K_{DOC} + 1)} \quad (2-6)$$

as can the percentage of the total contaminant that is freely dissolved (% C_d):

$$\% C_d = \frac{1}{(DOC K_{DOC} + 1)} 100 \quad (2-7)$$

This method depends on determination of DOC (kg/L) and K_{DOC} . Determining the concentration of DOC in water is a routine analysis (see above) (U.S. EPA, 2000), and K_{DOC} values can be found in Burkhard (2000). Burkhard (2000) derived the following expression based on the analysis of several interstitial water studies:

$$\text{Log } K_{DOC} = -0.88 + 0.99 \text{ Log } K_{OW} \quad (2-8)$$

As noted earlier, K_{OW} values for a range of nonionic organic contaminants can be found in Mackay et al. (1992 a,b), Karickhoff and Long (1995), and U.S. EPA (2003d, 2008).

As an example, using Equation 2-8, K_{DOC} values from the endrin and dieldrin ESB documents (U.S. EPA, 2003a,b) were compared with K_{OC} values (Table 2-2), and the percentage of the total compound that is freely-dissolved calculated using Equation 2-7 for a range of DOC concentrations likely to be encountered in interstitial water (Table 2-3). In this example, the greatest percentage of endrin or dieldrin that would be associated with DOC using K_{DOC} is approximately 51% and 34%, respectively at 70 mg DOC/L. An example of using this procedure is also presented in Section 3.

2.4 Use of Passive Samplers for Determining Freely Dissolved Interstitial Water Concentrations

Recently, a variety of passive sampling methods have been developed to directly measure the concentrations of freely dissolved chemical in contaminated sediments (Figure 2-2). Some methods sample interstitial water generated by centrifugation while others sample directly from sediment matrix, either in the laboratory or in the field. Laboratory experiments have been conducted by tumbling sediments with passive samplers (Lohmann et al., 2005; Fernandez et al., 2009a,b; Hawthorne et al., 2009, 2011) or by static placement of the passive sampler into sediment (Lohmann et al., 2005; Fernandez et al., 2009a,b). All methods are similar in that an organic polymer is used to absorb nonionic organic contaminants from sediment and interstitial waters. Once the contaminant achieves equilibrium between the polymer, sediment, and interstitial water, partition coefficients can be used to calculate the interstitial water dissolved phase

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concentrations (C_d) of contaminants of interest. Chemical analysis of passive samplers starts with a simple organic solvent extraction similar to a sediment extraction (e.g., U.S. EPA Method 3540). Because of their small size, solid phase microextraction fibers (SPMEs) can also be directly injected with thermal desorption into the analytical

instrument (i.e., GC/MS). The freely dissolved concentration can then be used to calculate the interstitial water toxic units associated with the sediment (see Section 2.5).

2.4.1 Types of Passive Samplers

Several of the more commonly used passive samplers in North America are discussed below:

Semi-permeable membrane devices (SPMDs) are composed of flat, low-density polyethylene (LDPE) tubing that contains a thin film of a pure, high molecular weight synthetic lipid (triolein). The polymer structure of the LDPE allows for the diffusion of nonionic organic chemicals within and through the tubing, which are then sequestered in both the lipid and LDPE phases. SPMD is an established method for assessing freely dissolved concentrations in water (Huckins et al., 1993; Huckins et al., 2006) that has more recently been used to measure concentrations of freely dissolved organic contaminants in sediments, soils and ground water (Macrae and Hall, 1998; Gustavson and Harkin, 2000; Rantalainen et al., 2000; Wells and Lanno, 2001; Williamson et al., 2002; Leppanen and Kukkonen, 2000, 2006; Schubauer-Berigan et al., 2012).

Polyethylene devices (PEDs) consist of flat strips of LDPE lacking the inner triolein layer used in SPMDs (Lohmann et al., 2004; Adams et al., 2007; Tomaszewski and Luthy, 2008). The thickness of PEDs varies from 25 μm (Fernandez et al., 2009a,b) to >100 μm , and strips up to 50 cm in length have been used (Booij et al., 2003a). PEDs can reach equilibrium faster than SPMDs due to their smaller sorption capacity (Booij et al., 2002). Conversely, PEDs have greater contaminant capacity than some other passive samplers (e.g., solid phase microextraction (SPME)) but require a longer time to reach equilibrium. Performance reference compounds (PRC)

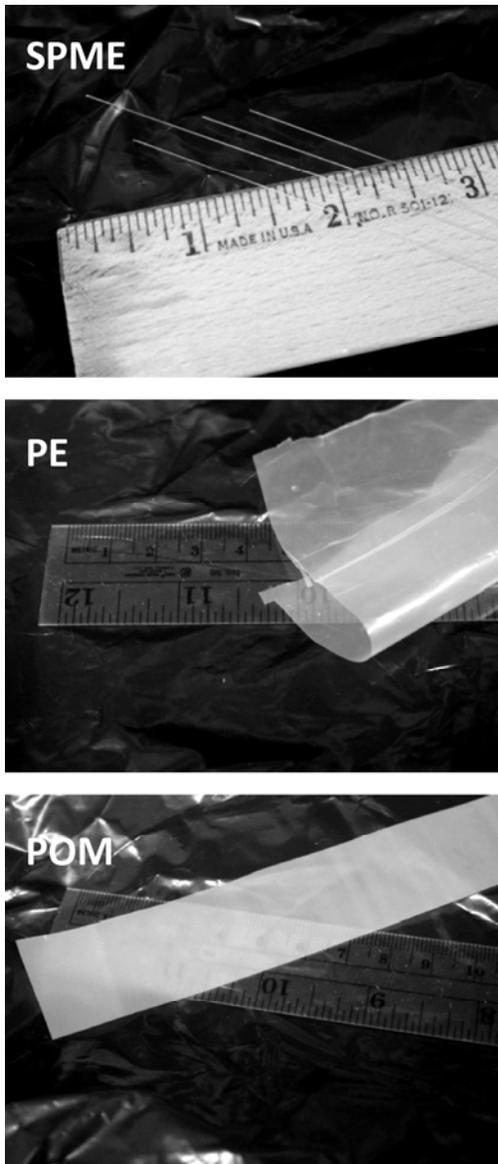


Figure 2-2. Photographs of selected passive samplers, including SPME, PE, and POM.

incorporated into the PED (as well as polyoxymethylene (POM) and SPMDs) before deployment can be used to estimate the extent to which equilibrium is reached during deployment, and to estimate adjusted equilibrium concentrations (Fernandez et al., 2009b). Biofouling of PED can be a concern as a barrier to exchange and equilibration but PRCs offer correction for this effect. Because they are inexpensive, robust, and easily deployable, PEDs have been used to measure interstitial water concentrations in laboratory and field applications, (Lohmann et al., 2004, 2005; Tomaszewski and Luthy, 2008; Fernandez et al., 2009a,b; Gschwend et al., 2011). Further, PED accumulation of PAHs and polychlorinated biphenyls (PCBs) has also shown good correlation to bioaccumulation by a benthic polychaete (Vinturella et al., 2004a; Friedman et al., 2009). In static sediment deployments, PEDs may deplete the surrounding interstitial water of contaminants if too much PE is used.

Solid phase microextraction (SPME) devices are composed of fused silica fibers that are coated with a layer of absorbing polymer. Polydimethylsiloxane (PDMS), which is typically used as a coating material, is thermally stable, and absorbed contaminants can be either thermally desorbed or extracted with solvent. Polyacrylate coatings have also been used to sample TNT (Conder et al., 2004). PDMS SPME fibers reach equilibrium rapidly in water, although their small capacity can result in elevated detection limits in comparison to other passive samplers. Time to reach equilibrium when deployed in sediment can be longer, ranging from 14 to 110 days (Maruya et al., 2009). The fibers are fragile, but can be protected for deployment in the field (Maruya et al., 2009) and used to determine vertical profiles of contaminants in sediment (Lu et al., 2011). SPME has been used to measure interstitial water concentrations in several laboratory and field

studies (Mayer et al., 2000a,b; Hawthorne et al., 2006; Maruya et al., 2009; Gschwend et al., 2011). Freely dissolved concentrations determined using SPME have been shown to be good predictors of sediment toxicity (Kreitinger et al., 2007; Xu et al., 2007) as well as bioaccumulation (Kraaij et al., 2003).

Polyoxymethylene (POM) is like the PED but is a harder plastic polymer with strong partitioning and greater capacity than PDMS. Studies have shown strong and reproducible partitioning of nonionic organic contaminants to POM, with sorption of contaminants being similar to the polymer coatings used for SPMEs (Jonker and Koelmans, 2001; Jonker et al., 2003; Cornellisen et al., 2008; Hawthorne et al., 2009, 2011). One advantage is that the surface of POM is hard and smooth, which allows any particulate matter accumulated on the sampler during the deployment to be physically wiped off after recovery (Jonker and Koelmans, 2001). Like PEDs, POM may deplete interstitial water concentration in static sediment deployments; consequently, the ratio of sampler to sediment organic carbon may need to be limited.

As mentioned earlier, passive samplers discussed here represent some of the more common devices used in the North America. Recently, published comparisons of some of these samplers provide very useful information for selecting which type of passive sampler is most appropriate for a given application (e.g., Gschwend et al., 2011; Oen et al., 2011; U.S. EPA, 2012). Because of their limited use in sediments, SPMDs will not be discussed further. Other samplers not discussed here can be found described in the cited literature (e.g., Stuer-Lauridsen, 2005; Vrana et al., 2005; Ouyang and Pawliszyn, 2007; Seethapathy et al., 2008; Allan et al., 2009; Rusina et al., 2010; Lohmann et al., 2012).

2.4.2 Procedures for Whole Sediments

Passive samplers can be exposed to whole sediments by a variety of methods. For example, laboratory exposures have been conducted by tumbling small pieces of pre-cleaned PED with a sediment slurry, with time to reach equilibrium ranging from 1 to 60 days for chemicals with $\log K_{OW} < 7$ (Booij et al., 2003a; Lohmann et al., 2005; Hawthorne et al., 2009; Gschwend et al., 2011). Passive samplers can also be exposed to static sediments, either in the laboratory or in the field. Time to reach equilibrium in static sediments is expected to be longer than in tumbled sediment, due to the decrease in transport resistance associated with tumbled sediment slurries (Booij et al., 2003a).

If equilibrium is not achieved during deployment, information on the uptake kinetics or the extent of equilibrium is required in order to estimate equilibrium concentrations. As noted above, in these instances, PRCs can be incorporated into the sampler prior to deployment to provide information on equilibrium status (Fernandez et al., 2009b). Experimental evidence indicates that the compound-specific rate at which PRCs dissipate from the passive sampler to the environment is related to the rate of uptake of chemically similar target compounds from the environment (Huckins et al., 2002; Booij et al., 2002; Thomaszewski and Luthy, 2008; Fernandez et al., 2009b). Thus, the concentrations of PRCs in the sampler before and after deployment can be used to estimate the equilibrium concentration of target chemicals from non-equilibrium concentrations measured in the sampler after retrieval. Guidance on the use of PRCs is still being developed but for losses of PRC less than 10% during a deployment, because of the uncertainties potentially associated with such low losses, those PRC data should not be used to adjust the equilibrium status of target contaminants.

2.4.2.1 Calculation of Freely Dissolved Concentrations using Passive Samplers

Starting with the measured concentration of contaminants in the passive sampler based on chemical analysis, the dissolved phase concentration is calculated as follows:

$$C_d = \frac{C_{PS}}{K_{PS-d}} \quad (2-9)$$

where, C_{PS} is the passive sampler concentration of a chemical ($\mu\text{g}/\text{Kg}$ passive sampler) and K_{PS-d} is the passive sampler – water partition coefficient (L/Kg passive sampler). As discussed in Section 2.4.2, there may be the need to adjust C_{PS} if the passive sampler deployment was insufficient in duration to achieve equilibrium conditions (Fernandez et al., 2009b). Values for K_{PS-d} are passive sampler specific and can be found in the literature (Jonker and Koelmans, 2001; Leslie et al., 2002; Booij et al., 2003b; Zeng et al., 2004; Lohmann et al., 2005; Adams et al., 2007; Cornelissen et al., 2008; Fernandez et al., 2009a,b; Maruya et al., 2009; Perron et al., 2009; DiFilippo and Eganhouse, 2010; Lohmann and Muir, 2010; Endo et al., 2011; Lohmann, 2012). However, whenever possible, laboratory confirmation of literature-based K_{PS-d} values for a given polymer is recommended highly. Table 2-1 provides calculated provisional K_{PS-d} values for PEDs, PDMS, and POM based on the following relationships from Lohmann and Muir (2010), DiFilippo and Eganhouse (2010) and Endo et al. (2011), respectively:

$$\text{Log } K_{PED} = -0.59 + 1.05 \text{ Log } K_{OW} \quad (2-10)$$

$$\text{Log } K_{PDMS} = 0.07 + 0.83 \text{ Log } K_{OW} \quad (2-11)$$

$$\text{Log } K_{POM} = -0.60 + 1.01 \text{ Log } K_{OW} \quad (2-12)$$

Several authors have reported that as K_{OW} increases, the relationship between K_{PS-d} and K_{OW} begins to demonstrate curvilinear behavior often at $\log K_{OWS}$ of greater than 6.5 or 7.0. The result is that the K_{PS-d} decreases in value. Our understanding of why this behavior occurs is incomplete and research to better understand this phenomena is underway. Conversely, for chemicals in Table 2-1 with partition coefficients less than $\log 2.00$, the use of PEDs, PDMS and POM-based passive samplers may not be effective because of weak partitioning to the polymers. For chemicals demonstrating this relatively low level of hydrophobicity, direct extraction and analysis of the interstitial water may be more effective.

2.4.3 Procedures for Interstitial Waters

A standardized and commercially-available method for using SPME to isolate PAHs from interstitial water is available (Hawthorne et al., 2005; ASTM, 2010). The method was developed to analyze 24 PAHs, consisting of the two- to four-ring parent and alkylated PAHs which contributed 95% of the ESBTUs measured in 120 samples of interstitial water from uncontaminated and contaminated sediments (Hawthorne et al., 2006). In this method, approximately 40 mL of sediment is centrifuged for 30 min at 1,000 g. Dissolved organic carbon (DOC) which interferes with the analysis, is removed from the produced interstitial water by flocculation with the addition of aluminum potassium sulfate (i.e., alum) followed by sodium hydroxide (Ghosh et al., 2000). Two rounds of flocculation and centrifugation are conducted no more than 24 hours prior to extraction of interstitial water for nonionic organic contaminant analysis. Immediately after flocculation, deuterated-PAH internal standards are mixed with a 1.5-mL aliquot of the interstitial water, which is then extracted for 30 mins. using a commercially available PDMS SPME fiber. Under these conditions, 30 minutes is sufficient to depletively sample

the interstitial water sample. The internal standards are used to quantify the target PAHs and compensate for incomplete extraction in the same way as a liquid-liquid extraction. Following the sorption period, the SPME fiber is immediately thermally desorbed in a GC/MS. The PAHs are detected and quantified using the selected ion monitoring (SIM) mode. The SPME fiber can be reused after cleaning for fifteen minutes to one hour (for heavily contaminated samples) under helium at elevated temperatures (Hawthorne et al., 2006).

Because this method removes some, but not all, of the DOC, both target PAHs and internal standards partition between the interstitial water and the DOC before extraction and analysis. The concentration of a target PAH is determined on the basis of its deuterated PAH internal standard and represents a “total dissolved” PAH concentration (C_{Td}) that includes both the freely dissolved PAHs and some PAHs associated with DOC. Because contaminant K_{DOC} increases with hydrophobicity, this overestimate of the freely dissolved concentration is much greater for four- to six-ring PAHs than for the two- and three-ring PAHs. For example, the “total dissolved” concentrations of five- and six-ring PAHs were as much as 7-fold higher than the freely dissolved concentration, whereas differences for two- and three-ring PAHs were insignificant (Hawthorne et al., 2005). However, because the lower molecular weight PAHs are present in interstitial water at much higher concentrations than the higher molecular weight PAHs, there was no significant difference in the sum of the ESBTUs regardless of whether “total dissolved” or freely dissolved PAH concentrations were determined. Using the C_{Td} value, interstitial water toxic units can be calculated.

This method is currently available for PAHs but the fundamental approach is viable with other nonionic organic contaminants. For example, Friedman et al. (2011) used a similar approach to calculate interstitial water concentrations of PCBs sampled with PEDs and adjusted for DOC.

Based on the discussion in this section, Table 2-4 summarizes a selection of the advantages and disadvantages of each approach for determining freely dissolved interstitial water concentrations.

2.5 Derivation of Interstitial Water Toxic Units

In the previous three subsections (2.2, 2.3, 2.4), approaches for determining organic contaminants were described. In this subsection, that data will be used to derive the interstitial water toxic units. The C_d for the freely dissolved concentrations of each nonionic organic contaminant is divided by its corresponding FCV, SCV or relevant water-only toxicity value to derive interstitial water toxic units (IWTUs) (Equations 2-13, 2-14). C_d values can be generated from the use of the two-carbon model (Section 2.2.1), direct measurement of interstitial waters after adjustment for DOC (Section 2.3), or passive samplers (Section 2.4). In deriving the IWTUs, the estimated interstitial water concentration of each contaminant (C_d) is also compared to the limit of water solubility for that contaminant in deionized water. If C_d is less than the limit of water solubility, then C_d is divided by the

corresponding FCV (or SCV) to calculate the $IWTU_{FCV}$ (or $IWTU_{SCV}$) for that contaminant. If C_d exceeds the available limit of water solubility, then the limit of water solubility is divided by the corresponding FCV (or SCV) to derive an IWTU value for that contaminant. Water solubility values for several nonionic organic contaminants can be found in Mackay et al., (1992a,b) as well as for PAHs in U.S. EPA (2003d, reported in Appendix E). For chemicals with a narcosis mode of action, the IWTUs for all contaminants may be summed to derive the $\sum IWTU$ (see U.S. EPA, 2003d, 2008 for more discussion of narcosis).

Using the FCV or SCV, the interstitial water toxic units are determined as follows:

$$IWTU_{FCV} = \frac{C_d}{FCV} \quad (2-13)$$

or

$$IWTU_{SCV} = \frac{C_d}{SCV} \quad (2-14)$$

If the IWTU for a nonionic organic contaminant or $\sum IWTU$ for a mixture of narcotic nonionic organic contaminants is less than or equivalent to 1.0, the concentration of the contaminant or mixture of contaminants, respectively, in the sediment is acceptable for the protection of benthic organisms from chronic toxic effects. Conversely, if the IWTUs exceed 1.0, benthic organisms are not protected and adverse effects may occur. See Section 3 for examples of these calculations and their interpretation.

Procedures for Determining Freely Dissolved Interstitial Water Concentrations

Table 2-1. Provisional partition coefficients for selected nonionic organic contaminants

Class	Contaminants	Log K _{OW} ^a	Log K _{BC} ^b	Log K _{PED} ^c	Log K _{PDMS} ^d	Log K _{POM} ^e
PAHs	Naphthalene	3.356	5.22	2.93	2.86	2.79
	C1-naphthalenes	3.8	5.46	3.40	3.22	3.24
	Acenaphthylene	3.223	5.15	2.79	2.75	2.66
	Acenaphthene	4.012	5.58	3.62	3.40	3.45
	C2-naphthalenes	4.3	5.73	3.93	3.64	3.74
	Fluorene	4.208	5.68	3.83	3.56	3.65
	C3-naphthalenes	4.8	6.00	4.45	4.05	4.25
	Anthracene	4.534	5.86	4.17	3.83	3.98
	Phenanthrene	4.571	5.88	4.21	3.86	4.02
	C1-fluorenes	4.72	5.96	4.37	3.99	4.17
	C4-naphthalenes	5.3	6.27	4.98	4.47	4.75
	C1-phenanthrene/anthracenes	5.04	6.13	4.70	4.25	4.49
	C2-fluorenes	5.2	6.22	4.87	4.39	4.65
	Pyrene	4.922	6.07	4.58	4.16	4.37
	Fluoranthene	5.084	6.16	4.75	4.29	4.53
	C2-Phenanthrene/anthracenes	5.46	6.36	5.14	4.60	4.91
	C3-fluorenes	5.7	6.49	5.40	4.80	5.16
	C1-pyrene/fluoranthenes	5.287	6.26	4.96	4.46	4.74
	C3-phenanthrene/anthracenes	5.92	6.61	5.63	4.98	5.38
	Benz(a)anthracene	5.673	6.47	5.37	4.78	5.13
	Chrysene	5.713	6.50	5.41	4.81	5.17
	C4-Phenanthrenes/anthracenes	6.32	6.82	6.05	5.32	5.78
	C1-Benzanthracene/chrysenes	6.14	6.73	5.86	5.17	5.60
	Benzo(a)pyrene	6.107	6.71	5.82	5.14	5.57
	Perylene	6.135	6.72	5.85	5.16	5.60
	Benzo(e)pyrene	6.135	6.72	5.85	5.16	5.60
	Benzo(b)fluoranthene	6.266	6.79	5.99	5.27	5.73
	Benzo(k)fluoranthene	6.291	6.81	6.02	5.29	5.75
	C2-benzanthracene/chrysenes	6.429	6.88	6.16	5.41	5.89
	Benzo(ghi)perylene	6.507	6.92	6.24	5.47	5.97
	C3-benzanthracene/chrysenes	6.94	7.16	6.70	5.83	6.41
	Indeno(1,2,3-cd)pyrene	6.722	7.04	6.47	5.65	6.19
	Dibenz(a,h)anthracene	6.713	7.04	6.46	5.64	6.18
C4-benzanthracene/chrysenes	7.36	7.38	7.14	6.18	6.83	

Equilibrium Partitioning Sediment Benchmarks (ESBs): Freely Dissolved Concentrations

Table 2-1. Continued

Class	Contaminants	Log K _{OW} ^a	Log K _{BC} ^b	Log K _{PED} ^c	Log K _{PDMS} ^d	Log K _{POM} ^e
Other Chemicals	Benzene	2.13	4.56	1.65	1.84	1.55
	Delta-BHC	3.78	-	3.38	3.21	3.22
	Gamma-BHC, Lindane	3.73	-	3.33	3.17	3.17
	Biphenyl	3.96	5.55	3.57	3.36	3.40
	4-Bromophenyl phenyl ether	5.00	-	4.66	4.22	4.45
	Butyl benzyl phthalate	4.84	-	4.49	4.09	4.29
	Chlorobenzene	2.86	4.95	2.41	2.44	2.29
	Diazinon	3.70	-	3.30	3.14	3.14
	Dibenzofuran	4.07	5.61	3.68	3.45	3.51
	1,2-Dichlorobenzene	3.43	5.26	3.01	2.92	2.86
	1,3-Dichlorobenzene	3.43	5.26	3.01	2.92	2.86
	1,4-Dichlorobenzene	3.42	5.26	3.00	2.91	2.85
	Di-n-butyl phthalate	4.61	-	4.25	3.90	4.06
	Dieldrin	5.37	-	5.05	4.53	4.82
	Diethyl phthalate	2.50	-	2.04	2.15	1.93
	Endosulfan mixed isomers	4.10	-	3.72	3.47	3.54
	Alpha-Endosulfan	3.83	-	3.43	3.25	3.27
	Beta-Endosulfan	4.52	-	4.16	3.82	3.97
	Endrin	5.06	-	4.72	4.27	4.51
	Ethylbenzene	3.14	5.11	2.71	2.68	2.57
	Hexachloroethane	4.00	-	3.61	3.39	3.44
	Malathion	2.89	-	2.44	2.47	2.32
	Methoxychlor	5.08	-	4.74	4.29	4.53
	Pentachlorobenzene	5.26	6.25	4.93	4.44	4.71
	1,1,2,2-Tetrachloroethane	2.39	-	1.92	2.05	1.81
	Tetrachloroethene	2.67	-	2.21	2.29	2.10
	Tetrachloromethane	2.73	-	2.28	2.34	2.16
	Toluene	2.75	4.90	2.30	2.35	2.18
	Toxaphene	5.50	-	5.19	4.64	4.96
	Tribromomethane (Bromoform)	2.35	-	1.88	2.02	1.77
	1, 2, 4-Trichlorobenzene	4.01	5.58	3.62	3.40	3.45
	1, 1, 1-Trichloroethane	2.48	-	2.01	2.13	1.90
	Trichloroethene	2.71	-	2.26	2.32	2.14
	m-Xylene	3.20	5.14	2.77	2.73	2.63

^a From corresponding ESB documents.

^b Derived using equation 2-4. K_{BC} values not derived for non-planar molecules.

^c Derived using equation 2-10.

^d Derived using equation 2-11.

^e Derived using equation 2-12.

Procedures for Determining Freely Dissolved Interstitial Water Concentrations

Table 2-2. Literature and calculated partition coefficients

Compound	Log K_{OW} ^a	Log K_{OC} ^{a,b}	Log K_{DOC} ^{a,c}
Endrin	5.06	4.97	4.13
Dieldrin	5.37	5.28	4.44

^a From corresponding ESB documents (U.S. EPA 2003b,c).

^b From corresponding ESB documents using: $\text{Log } K_{OC} = 0.00028 + 0.983 \times \text{Log } K_{OW}$ (U.S. EPA 2003b,c).

^c Derived using Equation 2-8.

Table 2-3. Solutions to Equation 2-7 using K_{DOC} values calculated from Equation 2-8

DOC (mg/L)	Endrin (% freely dissolved)	Dieldrin (% freely dissolved)
0	100	100
5	94	88
10	88	78
15	83	71
20	79	64
25	75	59
30	71	55
40	65	48
50	60	42
60	55	38
70	51	34

Equilibrium Partitioning Sediment Benchmarks (ESBs): Freely Dissolved Concentrations

Table 2-4. Advantages and disadvantages of selected approaches for determining freely dissolved interstitial water concentrations of nonionic organic contaminants

Approach	Advantages	Disadvantages
One-Carbon EqP Model	<ul style="list-style-type: none"> - Standard methods and guidance document available to commercial laboratories - Partition coefficients (e.g., K_{OW}, K_{OC}) and uncertainties available in the scientific literature 	<ul style="list-style-type: none"> - Simplistic model of NOC partitioning in sediments - May substantially over-estimate C_d
Two-Carbon EqP Model	<ul style="list-style-type: none"> - More complete and sophisticated model of NOC partitioning in sediment - Method for f_{BC} determination for commercial laboratories is available - Data available for PAHs 	<ul style="list-style-type: none"> - Limited information for partition coefficients (e.g., K_{BC}) and their uncertainties available in the scientific literature (especially for non-planar NOCs) - Uncertainty in the measurement of f_{BC} - May under-estimate C_d
Direct Measurement	<ul style="list-style-type: none"> - Direct determination of C_d - Partition coefficient (e.g., K_{DOC}) and related uncertainties available in the scientific literature 	<ul style="list-style-type: none"> - Large amounts of sediment required - Physical manipulation during centrifugation of sediment may result in artifacts that alter C_d - Methods are not standardized or available to commercial laboratories
Passive Samplers		
Passive Sampler: Polyethylene Devices (PED)	<ul style="list-style-type: none"> - Inexpensive and rugged sampling technology - Growing acceptance in scientific literature and in practical use - Laboratory and field deployments possible 	<ul style="list-style-type: none"> - Increasing but limited amount of information on partition coefficients (e.g., K_{PED}) and their uncertainties available in the scientific literature - Determination of sampler equilibrium is currently an area of research
Passive Sampler: Solid Phase Microextraction (SPME)	<ul style="list-style-type: none"> - Inexpensive sampling technology - Established acceptance in scientific literature and in practical use - Laboratory and field deployments possible 	<ul style="list-style-type: none"> - Increasing amount of information on partition coefficients (e.g., K_{PDMS}) and their uncertainties available in the scientific literature - Determination of sampler equilibrium is currently an area of research - Fibers are fragile and require protective covering when used
Passive Sampler: Polyoxymethylene (POM)	<ul style="list-style-type: none"> - Inexpensive and rugged sampling technology - Growing acceptance in scientific literature and in practical use - Laboratory and field deployments possible 	<ul style="list-style-type: none"> - Increasing but limited amount of information on partition coefficients (e.g., K_{POM}) and their uncertainties available in the scientific literature - Determination of sampler equilibrium is currently an area of research

Section 3

Example Calculations of $ESBTU_{FCV}$ and $IWTU_{FCV}$

3.1 Introduction

To assist users of this document, example calculations for deriving interstitial water toxic units are provided in Tables 3-1 and 3-2. Although the examples provided are for PAHs, they illustrate how chemical measurements can be used to evaluate the acceptability of a mixture of nonionic organic chemicals within the technical framework of the EqP approach (U.S. EPA, 2003a,d, 2008).

In these examples, the following values represent analytically measured concentrations: PAHs in sediment ($\mu\text{g/g}$ dry weight), PAHs in interstitial water that was generated by centrifugation ($\mu\text{g/L}$), PAHs absorbed to a passive sampler ($\mu\text{g/g}$), TOC (%) and BC (%) in sediment, and DOC in interstitial water (mg/L). All other values were calculated. The 34 PAHs presented in this example constitute what is defined as “total PAH” in U.S. EPA (2003d). Also listed are the FCVs expressed on an organic carbon normalized basis (C_{OC,PAH_i,FCV_i}) for each of the 34 PAHs from U.S. EPA (2003d). The sediment sample for Example A is from a manufactured gas plant site. The concentration of total (34) PAHs is $257 \mu\text{g/g}$ dry weight, the TOC content is 3.75%, the BC content is 1.2%, and the interstitial water DOC is 11 mg/L . The fraction OC (f_{OC}) and BC (f_{BC}) are calculated by dividing by 100 (i.e., % TOC/100 or %BC/100, respectively). The sediment sample for Example B is from a nearby location. The concentration of total PAHs is $39.4 \mu\text{g/g}$ dry weight, the TOC is 3.2 % ($f_{OC} = 0.032$), the BC is 0.3 % ($f_{BC} = 0.003$), and interstitial water DOC is 5 mg/L .

3.2 Estimates of Freely Dissolved Contaminants in Sediment Interstitial Water

As discussed in Section 2, two equilibrium partitioning models can be used to estimate the concentration of freely dissolved chemical in interstitial water based on the measured concentration of nonionic organic chemicals in bulk sediment. The first model, the one-carbon model, considers contaminant partitioning between interstitial water and TOC and generates the conventional ESB (i.e., U.S. EPA, 2003d, 2008). The second model, the two-carbon model, considers partitioning between interstitial water and two forms of carbon: NSOC and BC. Because partitioning to BC is greater than to NSOC, concentrations of freely dissolved chemical in interstitial water estimated using the two-carbon model are lower than estimates from the one-carbon model. Examples are provided for two sediments, one with relatively higher concentrations of BC in sediment and DOC in interstitial water.

3.2.1 One-Carbon Model

In the first step of this approach (see U.S. EPA, 2003d, 2008 for specifics), the dry weight concentration of each PAH was divided by the fraction of organic carbon to convert to the organic carbon normalized concentration (C_{OC} , $\mu\text{g PAH/g organic carbon}$). Second, the organic-carbon-normalized concentration of each PAH in the sediment was divided by its organic carbon normalized PAH-specific FCV (C_{OC,PAH_i,FCV_i}) to derive the conventional $ESBTU_{FCV_i}$ (U.S. EPA, 2003d). In both sediments, none of the measured C_{OC_i} exceed

Equilibrium Partitioning Sediment Benchmarks (ESBs): Freely Dissolved Concentrations

the corresponding $C_{OC, PAHi, Maxi}$, so solubility constraints did not affect the calculation of $ESBTU_{FCVi}$ (see solubility values for PAHs Table 3-4 in U.S. EPA, 2003d). Next, the $ESBTU_{FCVi}$ for the 34 PAHs were added to derive the $\sum ESBTU$ for the 34 PAHs ($\sum ESBTU_{FCV,34}$):

$$\sum ESBTU_{FCV,34} = \sum_i \frac{C_{OCi}}{C_{OC,PAHi,PCVi}} \quad (3-1)$$

The $\sum ESBTU_{FCV,34}$ is 9.3 for Sediment A (Table 3-1) and 1.7 for Sediment B (Table 3-2). A $\sum ESBTU_{FCV,34}$ value greater than 1.0 indicates that the concentration of PAHs may be non-protective to sensitive benthic organisms. Based on this one-carbon model assessment of toxic units, concentrations of PAHs in both sediments could be chronically toxic to sensitive benthic species. Note, chemicals which have others modes of toxicity that are more potent than narcosis (e.g., pesticides, phthalates) should be assessed on an individual basis, it is not appropriate to “sum” such chemicals unless there is evidence that they exhibit additive toxicity.

As noted above, the approach for using the one-carbon model followed the convention described in the earlier U.S. EPA ESB documents (U.S. EPA, 2003d; 2008) in which the dry weight PAH concentrations were converted to the organic carbon normalized concentrations (C_{OC}) and then divided by the organic carbon normalized PAH-specific FCV to derive the $ESBTU_{FCV}$. An alternative approach discussed in Section 2.1.1 and one more similar to the approach used in the two-carbon model discussed in the next section, is to calculate the C_d using Equation 2-2:

$$C_d = \frac{C_P}{f_{OC} K_{OC}}$$

this equation is equivalent to:

$$C_d = \frac{C_{OC}}{K_{OC}} \quad (3-2)$$

The C_d value calculated for each PAH would then be divided by the $C_{dPAHiFCVi}$ from Table 3-1 rather than the $C_{OC,PAHi,FCVi}$ to derive the $ESBTU_{FCVs}$. The two approaches will result in the same number of interstitial water toxic units for a given sediment but the approach using $C_{OC,PAHi,FCVi}$ is currently more commonly applied in assessing sediments when using the one-carbon model.

3.2.2 Two-Carbon Model

Like the conventional $\sum ESBTU_{FCV,34}$ calculated using the one-carbon model in Section 3.2.1, the sum of interstitial water toxic units ($\sum IW TU_{FCV}$) can also be calculated using a two-carbon model that accounts for association of PAHs with the fraction of BC (f_{BC}) and the fraction of NSOC (f_{NSOC}) in sediment. The elevated concentration of BC in Sediment A (1.2% of total dry weight) is within the range of levels observed at other manufactured gas plant sites (Driscoll et al., 2009). The concentration of BC in Sediment B (0.3% of total dry weight) is representative of levels observed near urban sources (~10% of TOC) (Gustaffson and Gschwend, 1998; Middelburg et al., 1999). As described in Section 2.2.1, the two-carbon model is used to calculate the freely dissolved concentration of each PAH ($C_{d,PAHi}$) in interstitial water using Equation 2-3:

$$C_d = \frac{C_P}{f_{NSOC} K_{OC} + f_{BC} K_{BC} C_d^{n-1}}$$

As discussed in Section 2, provisional values for K_{BC} used in this example were derived from the relationship developed by Driscoll et al. (2009).

Because C_d appears on both sides of Equation 2-3, an iterative approach must be used to solve for C_d . Statistical protocols such as the “Goal Seek” function in Excel[®] are available for this purpose. The estimated concentration of each PAH in interstitial water ($C_{d,PAHi}$) was divided by its PAH-specific FCV ($C_{d,PAHi,FCVi}$) to derive the IWTU_{FCVi} (Equation 2-10). Note that the $C_{d,PAHi,FCVi}$ is a different value than the $C_{OCPAHi,FCVi}$ used for calculating the one-carbon model based toxic units. The $C_{d,PAHi,FCVi}$ is a water-only based toxicity value and can be a FCV, SCV, or any other relevant water-only toxicity value, although toxic units are additive only for contaminants with similar modes of toxic action (e.g., narcosis for nonionic organic contaminants). For PAHs, $C_{d,PAHi,FCVi}$ values for the 34 compounds can be found in U.S. EPA (2003d). In these examples, none of the measured C_{di} exceed the corresponding $C_{d,PAHi,Maxi}$, so solubility constraints did not affect the derivation of IWTU_{FCVi} for these sediments (U.S. EPA, 2003d). Based on the two-carbon model, the total concentrations of dissolved PAHs in Sediment A and B were 19 and 5.51 $\mu\text{g/L}$, respectively. The IWTU_{FCVi} for the 34 PAHs were added to derive the $\sum\text{IWTU}$ for the 34 PAHs ($\sum\text{IWTU}_{FCV,34}$):

$$\sum IWTU_{FCV,34} = \sum_i \frac{C_d}{C_{d,PAHi,FCVi}} \quad (3-3)$$

The $\sum\text{IWTU}_{FCV,34}$ for Sediment A was 1.4 (Table 3-1) and 0.5 for Sediment B (Table 3-2). Although the $\sum\text{IWTU}_{FCV,34}$ for Sediment A (1.4) is less than the $\sum\text{IWTU}_{FCV,34}$ calculated using the one-carbon model (i.e., 9.3), the two-carbon model still predicts that this sediment could be chronically toxic to sensitive benthic species. For Sediment B, the $\sum\text{IWTU}_{FCV,34}$ of 0.5 indicates that the concentrations of PAHs in this sediment are acceptable for the protection of benthic organisms.

3.3 Measurement of Freely Dissolved Contaminants in Sediment Interstitial Water

This section presents two approaches that can be used to directly measure concentrations of nonionic organic contaminants in interstitial water. In the first approach, interstitial water produced by centrifugation is extracted with organic solvent and resulting concentrations are corrected for the fraction of total contaminants associated with DOC. The second approach uses a passive sampler placed in sediment to measure concentrations of freely dissolved contaminant in interstitial water.

3.3.1 Direct Measurement of Interstitial Water

In this approach, the $\sum\text{IWTU}$ is calculated from the total measured concentration of freely dissolved PAH in interstitial water (C_{IW}), after correction for the fraction of the total interstitial water concentration associated with DOC. Total measured concentrations of interstitial water PAHs were 6 and 8.8 $\mu\text{g/L}$ for Sediments A and B, respectively (Tables 3-1, 3-2). As described in Section 2.3, the percentage of the total interstitial water concentration for each PAH that is freely-dissolved (% C_d) is calculated using Equation 2-7:

$$\% C_d = \frac{1}{(DOC K_{DOC} + 1)} 100$$

Using the % C_d value derived for each PAH, the freely dissolved concentration of each PAH is calculated as:

$$C_d = C_{IW} \left(\frac{\% C_d}{100} \right) \quad (3-4)$$

Next, as shown in Section 3.2.2, the freely dissolved concentration of each PAH (C_{di}) is divided by its PAH-specific FCV ($C_{d,PAHi,FCVi}$) to derive the $IWTU_{FCVi}$. In these examples, none of the measured C_{di} exceed the corresponding $C_{d,PAHi,Maxi}$, so solubility constraints do not affect the calculation of $IWTU_{FCVi}$ for these sediments (U.S. EPA 2003d). The $IWTU_{FCVi}$ for the 34 PAHs were added to derive the $\sum IWTU$ for the 34 PAHs ($\sum IWTU_{FCV,34}$). The $IWTU_{FCVi}$ is 0.6 for Sediment A (Table 3-1) and 0.7 for Sediment B (Table 3-2). A $\sum IWTU_{FCV,34}$ value less than or equivalent to 1.0 indicates that concentrations of PAHs in these sediments are acceptable for the protection of benthic invertebrates (U.S. EPA, 2003d).

3.3.2 *Passive Sampling of Interstitial Water*

As discussed in Section 2.4, various passive samplers can be used to measure concentrations of freely dissolved contaminant in interstitial water. In the current examples, data for concentrations of PAHs associated with PED are used to determine the concentration of freely dissolved PAHs in interstitial water. For this example, the use of PRCs loaded in the PED demonstrated the target contaminants had achieved 100% equilibrium between the sampler and the freely dissolved phase. For actual deployments, it is critical to understand the equilibrium status of the samplers before performing the calculations below. First, the concentrations for each PAH associated with the PED ($\mu\text{g/g PED}$) is divided by its corresponding K_{PS-d} , to estimate the freely dissolved concentration in interstitial water ($\mu\text{g/L}$) (i.e., Equation 2-9):

$$C_d = \frac{C_{PS}}{K_{PS-d}}$$

The provisional K_{PS-d} or K_{PED} values used in these examples were derived from the relationship developed by Lohmann and Muir (2010) for polyethylene devices:

$$\text{Log } K_{PED} = -0.59 + 1.05 \text{ Log } K_{OW} \quad (3-5)$$

Second, the freely dissolved concentration of each PAH is divided by its PAH-specific FCV ($C_{d,PAHi,FCVi}$) to derive the $IWTU_{FCVi}$. In these sediments, none of the measured C_{di} exceed the corresponding $C_{d,PAHi,Maxi}$, so solubility constraints do not affect the calculation of $IWTU_{FCVi}$ (U.S. EPA, 2003d). The $IWTU_{FCVi}$ for the 34 PAHs were then added together to derive the $\sum IWTU$ for the 34 PAHs ($\sum IWTU_{FCV,34}$). The $\sum IWTU_{FCV,34}$ were 0.5 for Sediment A (Table 3-1) and 0.7 for Sediment B (Table 3-2). $\sum IWTU_{FCV,34}$ values less than or equivalent to 1.0 indicate that the concentrations of PAHs in these sediments are acceptable for the protection of benthic invertebrates (U.S. EPA, 2003d).

For both sediments, the direct measurement of interstitial water, as well as determinations of interstitial water concentrations based on concentrations in a polyethylene passive sampler, predicted a similar number of total toxic units: 0.6 and 0.5, respectively, for Sediment A, and 0.8 and 0.7, respectively, for Sediment B. For both approaches and sediments, concentrations of PAHs are protective and not predicted to be chronically toxic to sensitive benthic organisms.

3.4 **Considerations for Non-Planar Contaminants**

The two examples discussed above were performed using PAHs. As planar compounds, PAHs are expected to partition to black carbon to a substantially higher degree than non-planar compounds (Jonker and Koelmans, 2002; Cornelissen et al., 2005b). This is because planar compounds can better interact with the planar conformation of black carbon and form stronger intermolecular associations. This understanding is the basis for the two carbon model described in Section 2.2.1. The relationship between $\log K_{OW}$ and $\log K_{BC}$

(Equation 2-4) used to estimate K_{BC} was derived with PAHs. Consequently, at this time Equation 2-4 should not be used for non-planar nonionic organic chemicals; for example, DDTs and their degradation products, and ortho-substituted PCBs (also see Table 2-1). To this end, log K_{BC} values for non-planar compounds are not included in Table 2-1. If considering using the two-carbon model with non-planar compounds, it is recommended that compound-specific K_{BC} values be empirically determined.

3.5 Summary

These examples demonstrate the utility of the procedures for determining the freely dissolved concentrations of nonionic organic chemicals used for deriving interstitial water toxic units. The initial use of the one-carbon general model to predict the likelihood of

toxicity resulted in both sediments being designated as chronically toxic to benthic organisms. Use of the approaches described in this document results in a consistent reduction in expected chronic toxicity from both sediments. This downward trend in expected toxicity concluded with a designation that both sediments are protective of benthic organisms and neither would cause chronic toxicity. These examples also illustrate that deriving interstitial water toxic units can be a useful sediment assessment tool. However, $IWTU$ derivation is not inexpensive or particularly simple and, as noted earlier, require scientific expertise. In the next section of this document, a proposed strategy for implementing the use of $IWTUs$ is discussed that relates the benefits of using these approaches to the scientific robustness and financial costs.

Equilibrium Partitioning Sediment Benchmarks (ESBs): Freely Dissolved Concentrations

Table 3-1. Example calculations of $ESBTU_{FCV}$ and $IWTU_{FCV}$ for PAH mixtures: Sediment A

PAH _i	ESB-Final Chronic Values ^a			
	ESB-FCV $C_{OC, PAHi, FCVi}$ ($\mu\text{g/g}_{OC}$)	ESB-FCV $C_{d, PAHi, FCVi}$ ($\mu\text{g/L}$)	ESB-Maxi $C_{OC, PAHi, Maxi}$ ($\mu\text{g/g}_{OC}$)	ESB-Maxi $C_{d, PAHi, Maxi}$ ($\mu\text{g/L}$)
Naphthalene	385	193.55	61,700	30,995
C1-Naphthalenes	444	81.69	-	-
C2-Naphthalenes	510	30.24	-	-
C3-Naphthalenes	581	11.1	-	-
C4-Naphthalenes	657	4.048	-	-
Acenaphthylene	452	306.9	24,000	16,314
Acenaphthene	491	55.85	33,400	3,800
Fluorene	538	39.3	26,000	1,900
C1-Fluorenes	611	13.99	-	-
C2-Fluorenes	686	5.305	-	-
C3-Fluorenes	769	1.916	-	-
Phenanthrene	596	19.13	34,300	1,100
Anthracene	594	20.73	1,300	45
C1-Phenanthrenes/Anthracenes	670	7.436	-	-
C2-Phenanthrenes/Anthracenes	746	3.199	-	-
C3-Phenanthrenes/Anthracenes	829	1.256	-	-
C4-Phenanthrenes/Anthracenes	913	0.5594	-	-
Fluoranthene	707	7.109	23,870	239.9
Pyrene	697	10.11	9,090	131.9
C1-Fluoranthenes/Pyrenes	770	4.887	-	-
Benz[a]anthracene	841	2.227	4,153	11
Chrysene	844	2.042	826	2
C1-Benzanthracenes/Chrysenes	929	0.8557	-	-
C2- Benzanthracenes/Chrysenes	1,008	0.4827	-	-
C3- Benzanthracenes/Chrysenes	1,112	0.1675	-	-
C4- Benzanthracenes/Chrysenes	1,214	0.07062	-	-
Benzo[b]fluoranthene	979	0.6774	2,169	1.501
Benzo[k]fluoranthene	981	0.6415	1,220	0.7999
Benzo[a]pyrene	965	0.9573	3,840	3.810
Perylene	967	0.9008	431	0.4012
Benzo[e]pyrene	967	0.9008	4,300	4.012
Indeno[1,2,3-cd]pyrene	1,115	0.275	-	-
Dibenz[a,h]anthracene	1,123	0.2825	2,389	0.6012
Benzo[ghi]perylene	1,095	0.4391	648	0.2600
Total	-	-	-	-

Table 3-1. Continued

PAH _i	One-Carbon Model		
	C _{P,PAH_i} Measured Sediment Conc (µg/g dry wt)	C _{OC,PAH_i} Measured Sediment Conc (µg/g _{OC})	ESBTU _{FCV_i}
Naphthalene	5.0	133	0.3
C1-Naphthalenes	1.0	27	0.06
C2-Naphthalenes	1.6	43	0.08
C3-Naphthalenes	1.7	45	0.08
C4-Naphthalenes	1.1	29	0.04
Acenaphthylene	4.9	131	0.3
Acenaphthene	2.4	64	0.1
Fluorene	4.4	117	0.2
C1-Fluorenes	2.3	61	0.1
C2-Fluorenes	1.8	48	0.07
C3-Fluorenes	1.0	26	0.03
Phenanthrene	18.0	480	0.8
Anthracene	10.0	267	0.4
C1-Phenanthrenes/Anthracenes	16.0	427	0.6
C2-Phenanthrenes/Anthracenes	8.6	229	0.3
C3-Phenanthrenes/Anthracenes	2.6	69	0.08
C4-Phenanthrenes/Anthracenes	1.1	29	0.03
Fluoranthene	28.0	747	1.1
Pyrene	23.0	613	0.9
C1-Fluoranthenes/Pyrenes	23.0	613	0.8
Benz[a]anthracene	17.0	453	0.5
Chrysene	16.0	427	0.5
C1-Benzanthracenes/Chrysenes	7.7	205	0.2
C2- Benzanthracenes/Chrysenes	2.9	77	0.08
C3- Benzanthracenes/Chrysenes	1.1	29	0.03
C4- Benzanthracenes/Chrysenes	0.8	22	0.02
Benzo[b]fluoranthene	14.0	373	0.4
Benzo[k]fluoranthene	8.3	221	0.2
Benzo[a]pyrene	13.0	347	0.4
Perylene	2.8	75	0.08
Benzo[e]pyrene	7.9	211	0.2
Indeno[1,2,3-cd]pyrene	4.2	112	0.1
Dibenz[a,h]anthracene	1.4	37	0.03
Benzo[ghi]perylene	2.7	72	0.07
Total	257	-	9.3

Equilibrium Partitioning Sediment Benchmarks (ESBs): Freely Dissolved Concentrations

Table 3-1. Continued

PAH _i	Two Carbon Model			
	Log K _{OC} ^a (L/Kg NSOC)	Log K _{BC} ^b (L/Kg BC)	C _{d,PAHi} Estimated Freely Dissolved IW Conc (µg/L)	IWTU _{FCVi}
Naphthalene	3.299	5.24	4.07	0.02
C1-Naphthalenes	3.736	5.48	0.12	0.001
C2-Naphthalenes	4.227	5.75	0.09	0.003
C3-Naphthalenes	4.719	6.02	0.03	0.003
C4-Naphthalenes	5.21	6.29	0.01	0.001
Acenaphthylene	3.168	5.16	5.21	0.02
Acenaphthene	3.944	5.59	0.31	0.01
Fluorene	4.137	5.70	0.55	0.01
C1-Fluorenes	4.64	5.98	0.066	0.005
C2-Fluorenes	5.112	6.24	0.016	0.003
C3-Fluorenes	5.603	6.51	0.002	0.001
Phenanthrene	4.494	5.90	2.42	0.1
Anthracene	4.457	5.88	1.04	0.05
C1-Phenanthrenes/Anthracenes	4.955	6.15	0.75	0.1
C2-Phenanthrenes/Anthracenes	5.367	6.38	0.12	0.04
C3-Phenanthrenes/Anthracenes	5.82	6.63	0.006	0.01
C4-Phenanthrenes/Anthracenes	6.213	6.85	0.0007	0.001
Fluoranthene	4.998	6.18	1.61	0.2
Pyrene	4.839	6.09	1.68	0.2
C1-Fluoranthenes/Pyrenes	5.197	6.29	0.77	0.2
Benz[a]anthracene	5.577	6.50	0.215	0.1
Chrysene	5.616	6.52	0.180	0.09
C1-Benzanthracenes/Chrysenes	6.036	6.75	0.023	0.03
C2- Benzanthracenes/Chrysenes	6.32	6.91	0.0027	0.01
C3- Benzanthracenes/Chrysenes	6.822	7.19	0.00019	0.001
C4- Benzanthracenes/Chrysenes	7.235	7.41	0.00005	0.001
Benzo[b]fluoranthene	6.16	6.82	0.05	0.07
Benzo[k]fluoranthene	6.184	6.83	0.019	0.03
Benzo[a]pyrene	6.003	6.73	0.056	0.06
Perylene	6.031	6.75	0.0046	0.01
Benzo[e]pyrene	6.031	6.75	0.024	0.03
Indeno[1,2,3-cd]pyrene	6.608	7.07	0.0026	0.01
Dibenz[a,h]anthracene	6.599	7.06	0.0004	0.002
Benzo[ghi]perylene	6.397	6.95	0.0020	0.005
Total	-	-	19	1.4

Table 3-1. Continued

PAH _i	Directly Measured Interstitial Water				
	C _{IW, PAHi} Total Measured IW Conc (µg/L)	Log K _{DOC} ^c (L/Kg DOC)	Fraction Freely Dissolved	C _{d,PAHi} Estimated Freely Dissolved IW Conc (µg/L)	IWTU _{FCVi}
Naphthalene	0.25	2.44	0.997	0.249	0.001
C1-Naphthalenes	0.080	2.88	0.992	0.079	0.001
C2-Naphthalenes	0.270	3.38	0.974	0.263	0.009
C3-Naphthalenes	0.170	3.87	0.924	0.157	0.01
C4-Naphthalenes	0.099	4.37	0.796	0.079	0.02
Acenaphthylene	0.043	2.31	0.998	0.043	0.0001
Acenaphthene	1.300	3.09	0.987	1.283	0.02
Fluorene	1.100	3.29	0.979	1.077	0.03
C1-Fluorenes	0.120	3.79	0.936	0.112	0.008
C2-Fluorenes	0.073	4.27	0.831	0.061	0.01
C3-Fluorenes	0.065	4.76	0.611	0.040	0.02
Phenanthrene	0.790	3.65	0.954	0.753	0.04
Anthracene	0.180	3.61	0.957	0.172	0.008
C1-Phenanthrenes/Anthracenes	0.200	4.11	0.876	0.175	0.02
C2-Phenanthrenes/Anthracenes	0.140	4.53	0.731	0.102	0.03
C3-Phenanthrenes/Anthracenes	0.099	4.98	0.487	0.048	0.04
C4-Phenanthrenes/Anthracenes	0.081	5.38	0.276	0.022	0.04
Fluoranthene	0.370	4.15	0.865	0.320	0.05
Pyrene	0.300	3.99	0.902	0.271	0.03
C1-Fluoranthenes/Pyrenes	0.160	4.35	0.801	0.128	0.03
Benz[a]anthracene	0.110	4.74	0.625	0.069	0.03
Chrysene	0.093	4.78	0.604	0.056	0.03
C1-Benzanthracenes/Chrysenes	0.006	5.20	0.365	0.002	0.002
C2- Benzanthracenes/Chrysenes	0.006	5.48	0.229	0.001	0.003
C3- Benzanthracenes/Chrysenes	0.006	5.99	0.085	0.0005	0.003
C4- Benzanthracenes/Chrysenes	0.006	6.41	0.034	0.0002	0.003
Benzo[b]fluoranthene	0.063	5.32	0.302	0.019	0.03
Benzo[k]fluoranthene	0.031	5.35	0.290	0.009	0.01
Benzo[a]pyrene	0.056	5.17	0.383	0.021	0.02
Perylene	0.011	5.19	0.368	0.004	0.004
Benzo[e]pyrene	0.052	5.19	0.368	0.019	0.02
Indeno[1,2,3-cd]pyrene	0.020	5.77	0.132	0.003	0.01
Dibenz[a,h]anthracene	0.006	5.77	0.135	0.001	0.003
Benzo[ghi]perylene	0.021	5.56	0.200	0.004	0.01
Total	6	-	-	-	0.6

Equilibrium Partitioning Sediment Benchmarks (ESBs): Freely Dissolved Concentrations

Table 3-1. Continued

PAH _i	Passive Sampler			
	Passive Sampler Conc (µg/g PE)	Log K _{PED} ^d (L/Kg PE)	C _{d,PAH_i} Estimated Freely Dissolved IW Conc (µg/L)	IWTU _{FCV_i}
Naphthalene	0.16	2.93	0.19	0.001
C1-Naphthalenes	0.18	3.40	0.07	0.001
C2-Naphthalenes	2.02	3.93	0.24	0.008
C3-Naphthalenes	4.26	4.45	0.151	0.01
C4-Naphthalenes	5.95	4.98	0.063	0.02
Acenaphthylene	0.02	2.79	0.03	0.0001
Acenaphthene	4.66	3.62	1.11	0.02
Fluorene	6.87	3.83	1.02	0.03
C1-Fluorenes	2.09	4.37	0.09	0.006
C2-Fluorenes	4.08	4.87	0.055	0.01
C3-Fluorenes	8.94	5.40	0.036	0.02
Phenanthrene	11.02	4.21	0.68	0.04
Anthracene	2.07	4.17	0.14	0.007
C1-Phenanthrenes/Anthracenes	8.06	4.70	0.16	0.02
C2-Phenanthrenes/Anthracenes	12.51	5.14	0.09	0.03
C3-Phenanthrenes/Anthracenes	18.17	5.63	0.043	0.03
C4-Phenanthrenes/Anthracenes	29.68	6.05	0.0267	0.05
Fluoranthene	1.40	4.75	0.03	0.004
Pyrene	10.98	4.58	0.29	0.03
C1-Fluoranthenes/Pyrenes	17.38	4.96	0.19	0.04
Benz[a]anthracene	12.79	5.37	0.055	0.02
Chrysene	11.02	5.41	0.043	0.02
C1-Benzanthracenes/Chrysenes	1.22	5.86	0.002	0.002
C2- Benzanthracenes/Chrysenes	1.59	6.16	0.0011	0.002
C3- Benzanthracenes/Chrysenes	2.04	6.70	0.00041	0.002
C4- Benzanthracenes/Chrysenes	1.51	7.14	0.00011	0.002
Benzo[b]fluoranthene	13.66	5.99	0.01	0.02
Benzo[k]fluoranthene	17.62	6.02	0.017	0.03
Benzo[a]pyrene	8.64	5.82	0.013	0.01
Perylene	2.27	5.85	0.0032	0.004
Benzo[e]pyrene	7.82	5.85	0.011	0.01
Indeno[1,2,3-cd]pyrene	3.82	6.47	0.0013	0.005
Dibenz[a,h]anthracene	1.44	6.46	0.0005	0.002
Benzo[ghi]perylene	5.42	6.24	0.0031	0.007
Total	-	-	-	0.5

Note: Characteristics of the example sediment are: TOC (3.75%), DOC (11 mg/L), and BC (1.2%).

^a Values are from U.S. EPA (2003d).

^b Values are derived from relationship developed by Driscoll et al. (2009).

^c Values are derived from relationship developed by Burkhard (2000).

^d Values are derived from relationship developed by Lohmann and Muir (2010) (Equation 3-5).

Example Calculations of ESBTU_{FCV} and IWTU_{FCV}

Table 3-2. Example calculations of ESBTU_{FCV} and IWTU_{FCV} for PAH mixtures: Sediment B

PAH _i	ESB-Final Chronic Values ^a			
	ESB-FCV C _{OC, PAH_i, FCV_i} (µg/g _{OC})	ESB-FCV C _{d, PAH_i, FCV_i} (µg/L)	ESB-Maxi C _{OC, PAH_i, Maxi} (µg/g _{OC})	ESB-Maxi C _{d, PAH_i, Maxi} (µg/L)
Naphthalene	385	193.5	61,700	30,995
C1-Naphthalenes	444	81.69	-	-
C2-Naphthalenes	510	30.24	-	-
C3-Naphthalenes	581	11.1	-	-
C4-Naphthalenes	657	4.048	-	-
Acenaphthylene	452	306.9	24,000	16,314
Acenaphthene	491	55.85	33,400	3,800
Fluorene	538	39.3	26,000	1,900
C1-Fluorenes	611	13.99	-	-
C2-Fluorenes	686	5.305	-	-
C3-Fluorenes	769	1.916	-	-
Phenanthrene	596	19.13	34,300	1,100
Anthracene	594	20.73	1,300	45
C1-Phenanthrenes/Anthracenes	670	7.436	-	-
C2-Phenanthrenes/Anthracenes	746	3.199	-	-
C3-Phenanthrenes/Anthracenes	829	1.256	-	-
C4-Phenanthrenes/Anthracenes	913	0.5594	-	-
Fluoranthene	707	7.109	23,870	239.9
Pyrene	697	10.11	9,090	131.9
C1-Fluoranthenes/Pyrenes	770	4.887	-	-
Benz[a]anthracene	841	2.227	4,153	11
Chrysene	844	2.042	826	2
C1-Benzanthracenes/Chrysenes	929	0.8557	-	-
C2- Benzanthracenes/Chrysenes	1,008	0.4827	-	-
C3- Benzanthracenes/Chrysenes	1,112	0.1675	-	-
C4- Benzanthracenes/Chrysenes	1,214	0.07062	-	-
Benzo[b]fluoranthene	979	0.6774	2,169	1.501
Benzo[k]fluoranthene	981	0.6415	1,220	0.7999
Benzo[a]pyrene	965	0.9573	3,840	3.810
Perylene	967	0.9008	431	0.4012
Benzo[e]pyrene	967	0.9008	4,300	4.012
Indeno[1,2,3-cd]pyrene	1,115	0.275	-	-
Dibenz[a,h]anthracene	1,123	0.2825	2,389	0.6012
Benzo[ghi]perylene	1,095	0.4391	648	0.2600
Total	-	-	-	-

Equilibrium Partitioning Sediment Benchmarks (ESBs): Freely Dissolved Concentrations

Table 3-2. Continued

PAH _i	One-Carbon Model		
	C _{P,PAH_i} Measured Sediment Conc (µg/g dry wt)	C _{OC,PAH_i} Measured Sediment Conc (µg/g _{OC})	ESBTU _{FCV_i}
Naphthalene	0.2	7	0.02
C1-Naphthalenes	0.4	14	0.03
C2-Naphthalenes	0.8	24	0.05
C3-Naphthalenes	0.6	18	0.03
C4-Naphthalenes	0.2	7	0.01
Acenaphthylene	0.4	14	0.03
Acenaphthene	0.7	23	0.05
Fluorene	0.5	15	0.03
C1-Fluorenes	0.3	10	0.02
C2-Fluorenes	0.3	9	0.01
C3-Fluorenes	0.1	3	0.004
Phenanthrene	3.6	113	0.2
Anthracene	1.2	38	0.06
C1-Phenanthrenes/Anthracenes	2.3	72	0.1
C2-Phenanthrenes/Anthracenes	1.3	41	0.05
C3-Phenanthrenes/Anthracenes	0.4	11	0.01
C4-Phenanthrenes/Anthracenes	0.3	10	0.01
Fluoranthene	3.4	106	0.2
Pyrene	5.6	175	0.3
C1-Fluoranthenes/Pyrenes	3.5	109	0.1
Benz[a]anthracene	2.3	72	0.09
Chrysene	2.1	66	0.08
C1-Benzanthracenes/Chrysenes	1.0	30	0.03
C2- Benzanthracenes/Chrysenes	0.3	8	0.01
C3- Benzanthracenes/Chrysenes	0.1	4	0.003
C4- Benzanthracenes/Chrysenes	0.1	3	0.003
Benzo[b]fluoranthene	1.6	50	0.05
Benzo[k]fluoranthene	0.6	19	0.02
Benzo[a]pyrene	2.1	66	0.07
Perylene	0.5	15	0.02
Benzo[e]pyrene	1.1	34	0.04
Indeno[1,2,3-cd]pyrene	0.7	22	0.02
Dibenz[a,h]anthracene	0.2	7	0.01
Benzo[ghi]perylene	0.7	21	0.02
Total	39.4	-	1.7

Table 3-2. Continued

PAH _i	Two-Carbon Model			
	Log K _{OC} ^a (L/Kg NSOC)	Log K _{BC} ^b (L/Kg BC)	C _{d,PAH_i} Estimated Freely Dissolved PW Conc (µg/L)	IWTU _{FCV_i}
Naphthalene	3.299	5.24	0.22	0.001
C1-Naphthalenes	3.736	5.48	0.26	0.003
C2-Naphthalenes	4.227	5.75	0.21	0.007
C3-Naphthalenes	4.719	6.02	0.05	0.004
C4-Naphthalenes	5.21	6.29	0.00	0.001
Acenaphthylene	3.168	5.16	0.87	0.003
Acenaphthene	3.944	5.59	0.37	0.007
Fluorene	4.137	5.70	0.12	0.003
C1-Fluorenes	4.64	5.98	0.02	0.002
C2-Fluorenes	5.112	6.24	0.01	0.001
C3-Fluorenes	5.603	6.51	0.00	0.0002
Phenanthrene	4.494	5.90	1.14	0.06
Anthracene	4.457	5.88	0.25	0.01
C1-Phenanthrenes/Anthracenes	4.955	6.15	0.22	0.03
C2-Phenanthrenes/Anthracenes	5.367	6.38	0.04	0.01
C3-Phenanthrenes/Anthracenes	5.82	6.63	0.00	0.002
C4-Phenanthrenes/Anthracenes	6.213	6.85	0.00	0.001
Fluoranthene	4.998	6.18	0.35	0.05
Pyrene	4.839	6.09	0.98	0.1
C1-Fluoranthenes/Pyrenes	5.197	6.29	0.23	0.05
Benz[a]anthracene	5.577	6.50	0.06	0.03
Chrysene	5.616	6.52	0.05	0.02
C1-Benzanthracenes/Chrysenes	6.036	6.75	0.01	0.007
C2- Benzanthracenes/Chrysenes	6.32	6.91	0.00	0.001
C3- Benzanthracenes/Chrysenes	6.822	7.19	0.00	0.0003
C4- Benzanthracenes/Chrysenes	7.235	7.41	0.00	0.0002
Benzo[b]fluoranthene	6.16	6.82	0.01	0.01
Benzo[k]fluoranthene	6.184	6.83	0.00	0.003
Benzo[a]pyrene	6.003	6.73	0.02	0.02
Perylene	6.031	6.75	0.00	0.002
Benzo[e]pyrene	6.031	6.75	0.01	0.008
Indeno[1,2,3-cd]pyrene	6.608	7.07	0.00	0.004
Dibenz[a,h]anthracene	6.599	7.06	0.00	0.001
Benzo[ghi]perylene	6.397	6.95	0.00	0.004
Total	-	-	5.51	0.5

Equilibrium Partitioning Sediment Benchmarks (ESBs): Freely Dissolved Concentrations

Table 3-2. Continued

PAH _i	Directly Measured Interstitial Water				
	C _{IW, PAH_i} Measured Total IW Conc (µg/L)	Log K _{DOC} ^c (L/Kg DOC)	Fraction Freely Dissolved	C _{d, PAH_i} Estimated Freely Dissolved IW Conc (µg/L)	IWTU _{FCVi}
Naphthalene	0.92	2.44	0.999	0.919	0.005
C1-Naphthalenes	1.30	2.88	0.996	1.297	0.02
C2-Naphthalenes	1.10	3.38	0.988	1.091	0.04
C3-Naphthalenes	0.48	3.87	0.964	0.468	0.04
C4-Naphthalenes	0.15	4.37	0.896	0.139	0.03
Acenaphthylene	0.02	2.31	0.999	0.018	0.0001
Acenaphthene	1.90	3.09	0.994	1.892	0.03
Fluorene	0.46	3.29	0.990	0.457	0.01
C1-Fluorenes	0.20	3.79	0.970	0.196	0.01
C2-Fluorenes	0.11	4.27	0.915	0.103	0.02
C3-Fluorenes	0.01	4.76	0.775	0.005	0.002
Phenanthrene	0.44	3.65	0.978	0.434	0.02
Anthracene	0.18	3.61	0.980	0.178	0.009
C1-Phenanthrenes/Anthracenes	0.16	4.11	0.940	0.153	0.02
C2-Phenanthrenes/Anthracenes	0.14	4.53	0.856	0.126	0.04
C3-Phenanthrenes/Anthracenes	0.06	4.98	0.676	0.041	0.03
C4-Phenanthrenes/Anthracenes	0.04	5.38	0.456	0.020	0.04
Fluoranthene	0.19	4.15	0.934	0.177	0.02
Pyrene	0.36	3.99	0.953	0.343	0.03
C1-Fluoranthenes/Pyrenes	0.16	4.35	0.898	0.144	0.03
Benz[a]anthracene	0.05	4.74	0.786	0.037	0.02
Chrysene	0.06	4.78	0.770	0.045	0.02
C1-Benzanthracenes/Chrysenes	0.03	5.20	0.559	0.017	0.02
C2- Benzanthracenes/Chrysenes	0.01	5.48	0.396	0.002	0.005
C3- Benzanthracenes/Chrysenes	0.01	5.99	0.170	0.001	0.006
C4- Benzanthracenes/Chrysenes	0.01	6.41	0.073	0.004	0.006
Benzo[b]fluoranthene	0.04	5.32	0.487	0.018	0.03
Benzo[k]fluoranthene	0.02	5.35	0.473	0.007	0.01
Benzo[a]pyrene	0.03	5.17	0.577	0.018	0.02
Perylene	0.07	5.19	0.561	0.039	0.04
Benzo[e]pyrene	0.03	5.19	0.561	0.021	0.02
Indeno[1,2,3-cd]pyrene	0.02	5.77	0.251	0.005	0.02
Dibenz[a,h]anthracene	0.01	5.77	0.255	0.001	0.005
Benzo[ghi]perylene	0.03	5.56	0.354	0.009	0.02
Total	8.8	-	-	-	0.7

Table 3-2. Continued

PAH _i	Passive Sampler			
	Passive Sampler Conc (µg/g PE)	Log K _{PED} ^d (L/Kg PE)	C _{d,PAH_i} Estimated Freely Dissolved IW Conc (µg/L)	IWTU _{FCV_i}
Naphthalene	0.66	2.93	0.767	0.004
C1-Naphthalenes	2.50	3.40	0.997	0.01
C2-Naphthalenes	8.58	3.93	1.020	0.03
C3-Naphthalenes	14.37	4.45	0.510	0.05
C4-Naphthalenes	10.29	4.98	0.109	0.03
Acenaphthylene	0.03	2.79	0.045	0.0001
Acenaphthene	7.21	3.62	1.720	0.03
Fluorene	2.16	3.83	0.320	0.008
C1-Fluorenes	2.81	4.37	0.121	0.009
C2-Fluorenes	7.49	4.87	0.101	0.02
C3-Fluorenes	2.23	5.40	0.009	0.005
Phenanthrene	6.43	4.21	0.397	0.02
Anthracene	2.31	4.17	0.156	0.008
C1-Phenanthrenes/Anthracenes	7.40	4.70	0.147	0.02
C2-Phenanthrenes/Anthracenes	15.43	5.14	0.111	0.03
C3-Phenanthrenes/Anthracenes	28.74	5.63	0.068	0.05
C4-Phenanthrenes/Anthracenes	34.46	6.05	0.031	0.06
Fluoranthene	9.35	4.75	0.167	0.02
Pyrene	15.18	4.58	0.401	0.04
C1-Fluoranthenes/Pyrenes	18.39	4.96	0.201	0.04
Benz[a]anthracene	5.35	5.37	0.023	0.01
Chrysene	30.24	5.41	0.118	0.06
C1-Benzanthracenes/Chrysenes	11.51	5.86	0.016	0.02
C2- Benzanthracenes/Chrysenes	8.68	6.16	0.006	0.01
C3- Benzanthracenes/Chrysenes	4.98	6.70	0.001	0.006
C4- Benzanthracenes/Chrysenes	13.74	7.14	0.001	0.01
Benzo[b]fluoranthene	6.73	5.99	0.007	0.01
Benzo[k]fluoranthene	9.33	6.02	0.009	0.01
Benzo[a]pyrene	19.93	5.82	0.030	0.03
Perylene	20.61	5.85	0.029	0.03
Benzo[e]pyrene	4.98	5.85	0.007	0.008
Indeno[1,2,3-cd]pyrene	2.94	6.47	0.001	0.004
Dibenz[a,h]anthracene	2.88	6.46	0.001	0.004
Benzo[ghi]perylene	27.96	6.24	0.016	0.04
Total	-	-	-	0.7

Note: Characteristics of the example sediment are: TOC (3.2%), DOC (5 mg/L), and BC (0.3%).

^a Values are from U.S. EPA (2003d).

^b Values are derived from relationship developed by Driscoll et al. (2009).

^c Values are derived from relationship developed by Burkhard (2000).

^d Values are derived from relationship developed by Lohmann and Muir (2010) (Equation 3-5).

Section 4

Implementation of Freely Dissolved Interstitial Water Concentrations

4.1 Introduction

A typical component of assessing contaminated sediment sites is the collection of sediment samples for chemical analysis to determine the likelihood that sediment contamination will result in adverse toxicological effects to the benthos. For several years, the use of sediment quality guidelines, like the ESBs (U.S. EPA, 2003b,c,d, 2008), have been one line of evidence for performing these assessments. Depending upon whether toxic effects are suspected or demonstrated based on a sediment assessment, the site may need to be remediated via dredging, natural monitored recovery or capping (U.S. EPA, 2005). As discussed previously in this document, because of technological advances, the use of the freely dissolved concentrations of contaminants in the interstitial water may result in a more accurate assessment of toxic effects than the one-carbon general model used to derive ESBs for nonionic organic chemicals.

As discussed in Table 2-4, currently, the use of ESBs based on the one-carbon model may over-predict C_d and be more environmentally conservative (i.e., protective) and less expensive than using toxic units derived based on the freely dissolved concentrations in sediment interstitial water discussed in this document. The two carbon EqP model discussed in this document may result in less environmentally conservative assessments and requires the measurement of sedimentary black carbon. At this time, black carbon measurements are not commonly

performed by most commercial environmental chemistry laboratories limiting their practicality. Further, the two carbon model is applicable for all classes of nonionic organic chemicals only if the appropriate K_{BC} values are available for the model calculations. Currently, many K_{BC} values are derived using linear free energy relationships between K_{BC} and K_{OW} for planar chemicals like PAHs but not non-planar compounds. As noted earlier, these K_{BC} s may not be appropriate for use with non-planar compounds and may result in elevated uncertainties in estimates of freely dissolved concentrations. Similarly, the collection of sufficient sediment interstitial water for direct measurement of contaminants continues to include significant artifacts and requires additional chemical analyses that may not always be cost effective (e.g., DOC, interstitial water). Currently, the analysis of whole or bulk contaminated sediments for a suite of nonionic organic chemicals is less expensive than performing a similar chemical analysis for passive samplers, such as SPME, PEDs or POM. However, the difference in cost is rapidly decreasing. Further, the number of laboratories capable of performing the analysis on passive samplers is currently limited but is also growing as the methods become more established. Considering these advantages and disadvantages, implementing the use of the approaches for determining the freely dissolved concentrations of sediment interstitial water chemicals discussed in this document requires the scientifically-informed balancing of environmental protection and cost. However, the

additional costs incurred in improved sediment characterization may be offset by the reduced costs for risk management and remediation. Further, an implementation framework for performing sediment assessments should seriously consider a weight of evidence approach.

4.2 Implementation of Freely Dissolved Concentrations

Figure 4-1 illustrates a potential tiered approach for implementing the use of freely dissolved interstitial water concentrations while balancing environmental protection, risk management and cost. The first tier involves using the one-carbon EqP-based ESB to assess the likelihood of toxicity to the benthos. Sediments in which the ESB is not exceeded are considered environmentally unimpacted and require no further consideration based on the ESB line of evidence. However, this is a very important conclusion with the potential to carry significant implications for the entire site assessment. Consequently, it is critical that every scientific effort (e.g., high data quality, robust analytical chemistry) should be taken to insure this conclusion is accurate. Sediments in which the ESB is exceeded using the one-carbon EqP model are considered as representing a possible risk to the benthos and may require remediation. However, the second tier of this implementation approach may be performed on sediments which exceed the conventional EqP-based ESB. In the second tier, a passive sampler may be used to generate interstitial water toxic units (Section 2.4). If for a given contaminant, the interstitial water toxic units are greater than one, the sediments are considered as representing a possible risk to the benthos and may require remediation. Like the first tier, if the interstitial water toxic units in Tier 2 are not greater than one, the sediment is considered environmentally unimpacted and requires no further consideration based on the ESB line of evidence. Again, like the decision made in Tier 1, this is a very important conclusion with the potential to carry

significant implications for the entire site assessment. It is critical that every scientific effort (e.g., high data quality, robust analytical chemistry) is taken to insure this conclusion is accurate.

In the second tier, the two carbon model can also be used to generate interstitial water toxic units (Section 2.2). However, given the uncertainty around the K_{BC} values currently available in the scientific literature as well as the measurement of f_{BC} , the use of passive samplers in Tier 2 is recommended over the two carbon model. In addition, as discussed above, because of the continued difficulties and costs associated with collecting interstitial water, a similar recommendation is made for using a passive sampler based measure to generate interstitial water toxic units rather than a direct measurement of interstitial water (Section 2.3). Using the passive sampler approach, if the IWTUs exceed 1.0, sediment toxicity testing can be conducted in the third tier to verify the findings of the first two tiers. The cost of testing and analysis in the third tier is likely to be the greatest compared to the others and may require collection and chemical analysis of more sediment (and possibly interstitial water). However, the performance of sediment toxicity testing with sensitive organisms is one of the most data rich and accurate lines of evidence to assess for the adverse effects of sediment contaminants on the benthos. It should be recognized that if a whole sediment toxicity test finds significant toxicity, the cause or causes may be toxic chemicals other than those measured in Tiers 1 and 2. Finally, in a recommended weight of evidence sediment assessment, toxicity testing should not be used in exclusion of other lines of evidence including chemistry, bioaccumulation, TIE, and benthic community analyses. It is highly recommended that the data generated in Tier 3, as well as Tiers 1 and 2, of the proposed tiered approach be informed by lines of evidence in addition to acute and chronic toxicity testing. This

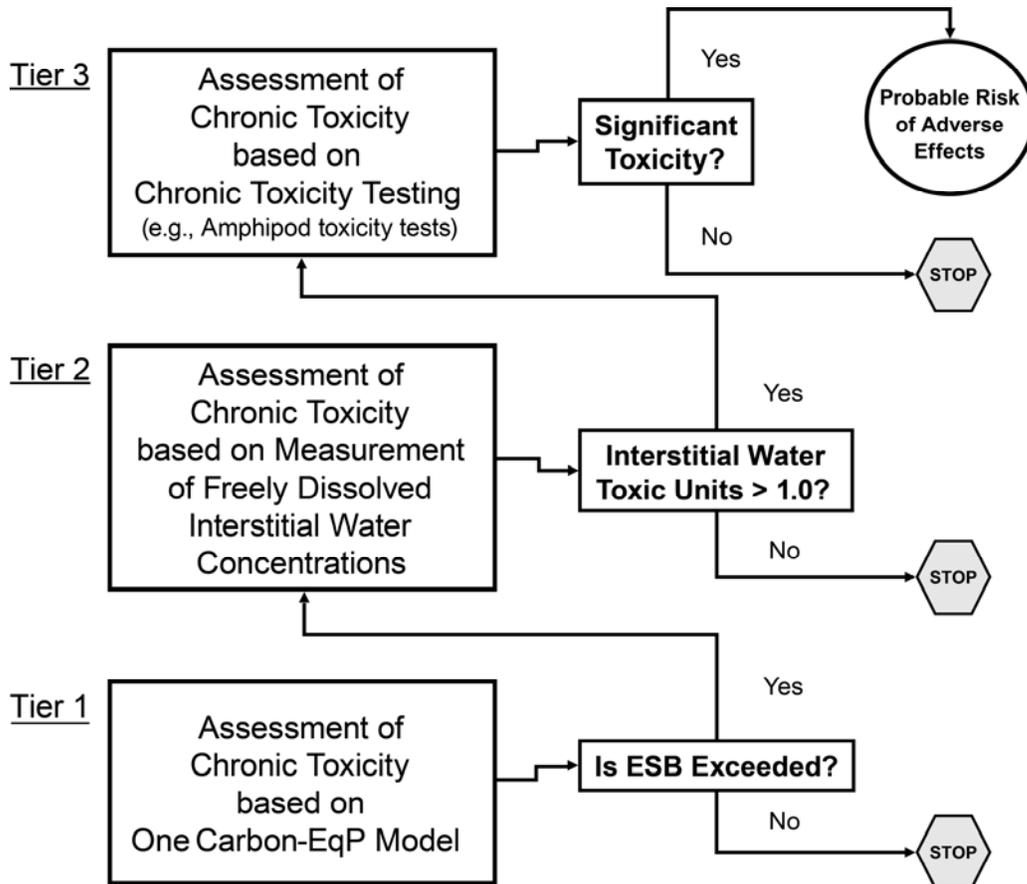
consideration emphasizes the merits of a weight of evidence approach when performing contaminated sediment assessments.

4.3 Research Needs

As discussed in Section 1.5, there remain several areas of research and development for the approaches for determining interstitial water concentrations discussed in this document. Most of these areas involve making a better measure of (i.e., standardizing) or reducing the uncertainty associated with the array of partition

coefficients used in these approaches (e.g., K_{BC} , K_{PED} , K_{PDMS} , K_{POM}). A second area is improving the measurement of black carbon in sediments. Currently, the commonly used version of this measurement involving the removal of inorganic and NSOC (Gustafsson et al., 1997) has been shown to be highly variable in inter-laboratory comparisons (Gustafsson et al., 2001). In addition, for the passive samplers, it is critical to develop improvements in the methods for the determination of when equilibrium between chemicals in the interstitial water and the passive sampler has been established.

Figure 4-1. Schematic of proposed tiered approach for implementing the use of the freely dissolved interstitial water concentrations of nonionic organic chemicals (based on Burgess, 2009).



Section 5

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