EPA/600/R-06/162F
ERASC-011F
October 2009

EVALUATING ECOLOGICAL RISK TO INVERTEBRATE RECEPTORS FROM PAHS IN SEDIMENTS AT HAZARDOUS WASTE SITES

by

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This is contribution AED-05-030 of the Office of Research and Development National Health and Environmental Effects Research Laboratory's Atlantic Ecology Division.

This report should be cited as Burgess, R.M. 2009. Evaluating Ecological Risk to Invertebrate Receptors from PAHs in Sediments at Hazardous Waste Sites. U.S. Environmental Protection Agency, Ecological Risk Assessment Support Center, Cincinnati, OH. EPA/600/R-06/162.

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ACKNOWLEDGMENTS

The first draft of this document was internally (within EPA) reviewed by Robert Ozretich and Walter Berry (EPA Office of Research and Development, National Health and Environmental Effects Research Laboratory (ORD/NHEERL). Programmatic review was conducted by Venessa Madden of EPA Region 7, a Trichair of EPA's Ecological Risk Assessment Forum.

PURPOSE OF THIS DOCUMENT

In March 2004, ORD's Ecological Risk Assessment Support Center (ERASC) received a request from the Ecological Risk Assessment Forum relating to the evaluation of ecological risk to vertebrate and benthic invertebrate receptors from polycyclic aromatic hydrocarbon compounds (PAHs) in sediment at hazardous waste sites. This paper only addresses risks to benthic invertebrates because reaching a consensus scientific position on vertebrate risk issues is a longer-term prospect. Benthic invertebrates are an important component of the biotic integrity of the nation's waters.

Like the U.S. EPA Equilibrium Partitioning Sediment Benchmark (ESB) for PAH mixtures document (U.S. EPA, 2003a) that this white paper is based on, this report is meant as technical information. To cite selected text from the recently released ESB for Tier 2 nonionic organic chemicals (U.S. EPA, 2008):

> 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 equilibrium partitioning (EqP) approach is appropriate to that program and, if so, how best to incorporate this technical information into that program's risk assessment process. At the same time, the ESBs do not substitute for the Clean Water Act 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 risk management decisions.

In other words, the approach described in this white paper is simply a tool to be applied to the greater problem of assessing risk, in this case, risk associated with PAHs in sediments at hazardous waste sites. As discussed below, the use of the EqP approach discussed here as part of a tiered risk assessment is one way that an assessment could be performed. At sites where the assumptions of EqP are violated because of site-specific conditions, approaches like solid phase microextraction (SPME) may be necessary to attain accurate measures of PAH exposure concentrations. Furthermore, as discussed below, risk assessors may choose to formulate a risk assessment strategy using EqP for screening purposes to be followed in a secondary tier with the

measurement of PAH bioavailability using SPME and/or toxicity testing. It is from this perspective with the objective of describing one tool in the risk assessment tool box that the following technical information is provided.

INTRODUCTION

In principal, there are many ways to attempt to address the risk to invertebrates associated with PAHs in sediments and whenever possible the use of multiple lines of evidence to conduct a risk assessment is recommended (Adams et al., 2005). For example, Table 1 lists several approaches for quantifying exposure and effects of PAHs, as well as other organic contaminants, in sediments. These include the use of analytical chemistry on whole sediments and interstitial waters to derive protective guidelines (e.g., U.S. EPA, 2003a, 2005, 2008; Long et al., 1995; Swartz, 1999; Fairey et al., 2001; Field et al., 2002), application of recently developed passive sampler technologies to measure bioavailable concentrations (e.g., Hawthorne et al., 2005), conducting acute and chronic sediment and interstitial water toxicity tests (ASTM, 1998a,b,c; U.S. EPA, 1994, 2000, 2001a) and performance of bioaccumulation studies (U.S. EPA, 1993, 2000) to demonstrate contaminant bioavailability and biological effects. How these approaches are used is also a topic of debate; for example, Figure 1 presents a conceptual model using the methods listed above to address the question of whether a sediment is likely to cause adverse effects. The approach discussed in this white paper uses data resulting from the chemical analysis of whole sediments, mechanistic partitioning, and additive narcosis mode of action models to predict adverse toxicological effects. In Figure 1, this approach is used in the first tier of the assessment to screen for the likelihood of adverse effects. In other conceptual models, for example, the approach discussed here could be applied in a diagnostic mode later in the assessment process to determine if adverse effects are likely to be due to PAHs. The *PAHs* addressed in this paper are composed of carbon and hydrogen and do not include any heterocyclic atoms like oxygen, sulfur or nitrogen, or functional groups such as nitro or hydroxyl.

Due to the use of fossil fuels in industrialized societies as well as biomass fuels in developing countries (including forest fires) and subsequent transport via atmospheric and aquatic pathways, PAHs are among the most widely distributed organic pollutants. Furthermore, because of their presence in hydrocarbon-based substances ranging from petroleum to creosote,

TABLE 1. Examples of Approaches for Determining Exposures and Effects of PAHs

Approach	Specific Method or Technique	Examples	References
Analytical Chemistry	Mechanistic Guidelines	Equilibrium Partitioning Sediment Benchmarks (ESBs)	U.S. EPA, 2003a,b,c, 2005, 2008
	Empirical Guidelines	Effects-Range Limit (ERL) and Effects-Range Median (ERM) Sediment Quality Guideline Quotient (SQGQ1) Logistic Regression Models (LRM) Consensus	Long et al., 1995, 2000 Fairey et al., 2001 Field et al., 2002 Swartz, 1999; MacDonald et al., 2000
	Passive Samplers	Solid Phase Microextraction (SPME)	Hawthorne et al., 2005
Toxicity Testing	Acute and Chronic	-	ASTM, 1998a,b,c; U.S. EPA, 1994, 2000, 2001a
Bioaccumulation Studies	Standard 28-day	-	U.S. EPA, 1993, 2000

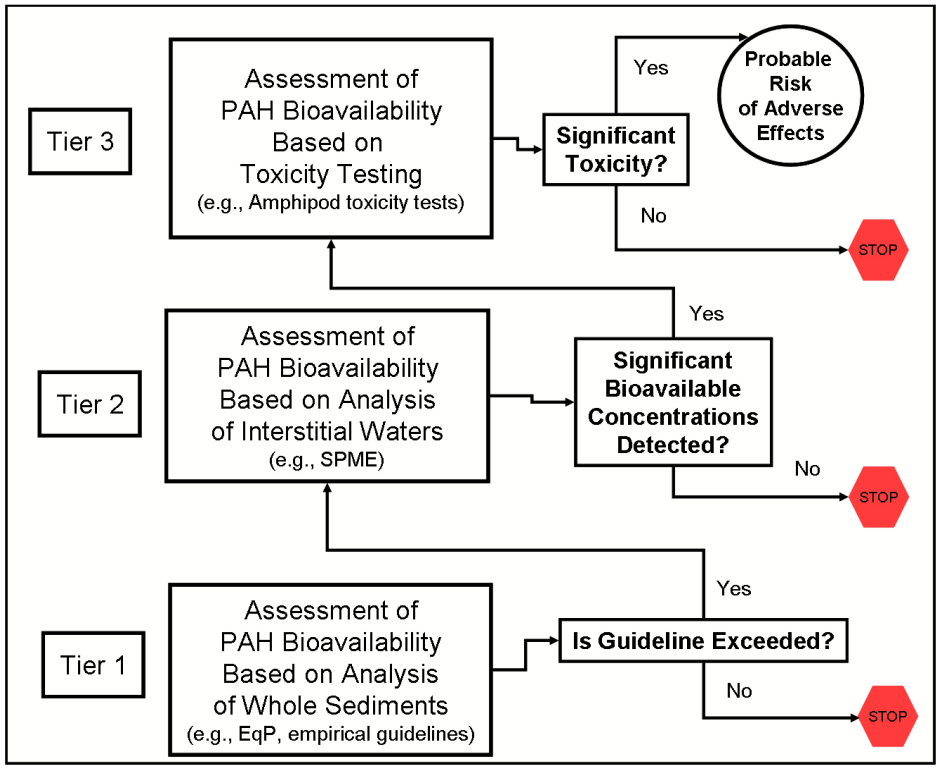

FIGURE 1. Conceptual Model for Applying Various Sediment Assessment Approaches in a Tiered System to Determine the Risk of Adverse Effects Due to PAHs in Sediments.

they are found in concentrations of parts per million (mg/kg) in heavily industrialized sites, while in areas remote from human activity they occur in parts per trillion (ng/kg).

PAHs in the environment are known to originate primarily from two sources: petrogenic and pyrogenic (biogenic PAHs make a very small contribution). Petrogenic PAHs originate from petroleum sources including different types of oils, coals and organic shales. Their introduction to the environment varies from industrial production, refining and transport, to spills and waste site releases, and natural seeps and outcrops. Pyrogenic PAHs are produced when fossil fuels are incompletely oxidized during combustion. They are, therefore, frequently released into the environment via the atmosphere, often associated with different forms of soot or black carbon. Eventually, these PAHs are removed from the air phase through association with aerosols which then settle into terrestrial and aquatic environments. Pyrogenic PAHs can also be associated with specific industrial sources (e.g., manufactured gas plants).

There are two basic types of PAHs: parent and alkylated. These classifications involve the chemical structure of PAHs. Parent PAHs consist primarily of benzene rings fused together. Conversely, alkylated PAHs have various levels of alkyl substitutions added to the fused ring structure. Because of the different sources and types of PAHs, determining the specific sources of PAHs in the environment is often complex; for example, combustion-related pyrogenic parent PAHs are frequently ubiquitous while alkylated PAHs from both pyrogenic and petrogenic sources may be more localized.

The prevalent mechanism of PAH toxicity to invertebrates is narcosis, which results in the alteration of cell membrane function. This alteration can result in mild toxic effects or mortality depending upon the exposure. Some PAHs also demonstrate photoactivated toxicity. This form of toxicity can cause mortality at very low concentrations of PAHs but requires direct exposure of organisms to ultraviolet (UV) radiation in sunlight. Further, water strongly attenuates UV radiation; thus, relatively shallow overlying water will protect benthic organisms from adverse effects. However, it is possible that benthic organisms with a pelagic life stage which includes swimming to the air-water interface may be exposed to elevated UV levels. The magnitude of risk associated with this sort of exposure in combination with the bioaccumulation of PAHs has not been studied extensively. The UV radiation causes the chemical bonds in the PAHs to excite and form high energy radicals, which, for a very brief time period, oxidize the tissue of exposed organisms. Carcinogenicity and teratogenicity have also been reported to occur

in vertebrates (e.g., fish) (Hawkins et al., 1988) due to exposure to certain PAHs (e.g., benzo(a)pyrene), but there are limited data with regard to benthic invertebrates. In general, unless conditions result in elevated UV levels, narcosis is the most common mode of action of concern with PAHs in sediments.

Each of the above characteristics results in factors contributing to the nature of the PAH exposure and kinds of PAH toxic effects. In this white paper, EqP is recommended for use in predicting PAH exposure concentrations, and additive narcosis theory is applied to determine whether or not sufficient PAHs are present to cause adverse effects. A selection of PAHs defined as "total PAH" is also provided as well as an analytical method for measuring PAHs. This white paper summarizes an approach for evaluating ecological risk to benthic invertebrate receptors from PAHs in sediments at hazardous waste sites. This approach is based upon the ESB for PAH mixtures document prepared by the U.S. EPA (2003a). Consequently, this white paper should be used in conjunction with U.S. EPA (2003a). More recently, others have demonstrated the usefulness of the EqP approach for understanding the bioavailability of PAHs in sediments (e.g., Landrum et al., 2003; Barata et al., 2005; McGrath et al., 2005; Neff et al., 2005; Hawthorne et al., 2006). This white paper does not address bioaccumulation or trophic transfer of PAHs from contaminated sediments by aquatic organisms. Also, under site-specific conditions it is possible for the assumptions used to predict risk associated with PAHs using EqP to be violated (e.g., presence of black carbon or unusual carbon) (see U.S. EPA [2003a] for more discussion). Under such conditions, site-specific predictions of the risk associated with PAHs may be necessary using methods that directly measure interstitial water PAH concentrations (e.g., Hawthorne et al., 2005) or toxicity (U.S. EPA, 1994, 2000).

STATE OF PRACTICE

Invertebrate Risk Assessment

A brief and limited survey of project managers, scientists and risk assessors at sites around the country, including the Pine Street Bridge Canal, Hocomonco, and Baird and McGuire sites in Massachusetts (Region 1), the Ashland site in Wisconsin (Region 5), and Lower Duwamish in Washington State (Region 10), indicated several characteristics of how PAH risk to invertebrates is assessed currently at contaminated sediment sites. First, there is no "standard state of practice" per se, rather, assessments are performed differently at each site using

site-specific information. Secondly, because of the metabolism of PAHs by many organisms at various levels of the food web, in general, there is no clear relationship between body burdens of PAHs and effects, and hence tissue residues are seldom used as measures of exposure. Thirdly, as a consequence of PAH metabolism, exposure and effects measurements are most often assessed in the benthos, where acute and sublethal toxicity may be observed. Specifically, sediment or interstitial (pore) water measures of PAHs are used to quantify exposure while toxicity to benthic organisms is applied as a measure of effects. In some instances, benthic community composition and condition are used to assess effects. Sediment quality guidelines including empirical (Long et al., 1995; Field et al., 2002) and consensus (Swartz, 1999; MacDonald et al., 2000) approaches as well as the mechanistic ESBs (U.S. EPA, 2003a,b,c, 2005, 2008) are also used as complementary and predictive tools for assigning risk. In a few rare cases, photo-enhanced toxicity caused by PAHs has also been used to assess risk.

OVERVIEW OF PAH EXPOSURE TO INVERTEBRATES

Use of Equilibrium Partitioning (EqP) to Predict Exposure

To determine the exposure invertebrates experience in contaminated sediments it is necessary to measure or predict the concentrations of bioavailable PAHs. For hydrophobic organic contaminants like PAHs, under equilibrium conditions, the interstitial water concentration of PAH is the most accurate indicator of the bioavailable exposure concentration. The interstitial water concentration can be measured empirically using several methods (U.S. EPA, 2001b). However, the results may be affected by manipulation of the sediment and interstitial water, and the methods may be logistically impractical and expensive. Measurement of the interstitial water concentration of PAHs has the additional challenge of assessing the effect of dissolved organic carbon (DOC) on bioavailability. The presence of DOC has been shown to reduce PAH bioavailability (e.g., McCarthy and Jimenez, 1985; Landrum et al., 1987). Recently, new promising analytical techniques have been applied to directly measure interstitial water concentrations of PAHs including SPME (Hawthorne et al., 2005). These methods also consider the effects of DOC on PAH bioavailability.

An alternative approach for determining exposure is to *predict* PAH interstitial water concentrations. The use of EqP is recommended for making such predictions. In a sediment system, the predominant phases involved in EqP include the sediment organic carbon and

dissolved phase (i.e., interstitial water) (see Figure 2). Based on EqP, if the sediment concentration of PAH and concentration of sediment organic carbon are known, the interstitial water concentration of PAH can be predicted. As discussed above, because the interstitial water concentration of PAH is the most accurate indicator of the bioavailable concentration, knowing this concentration allows for an assessment of potential risk to benthic invertebrates.

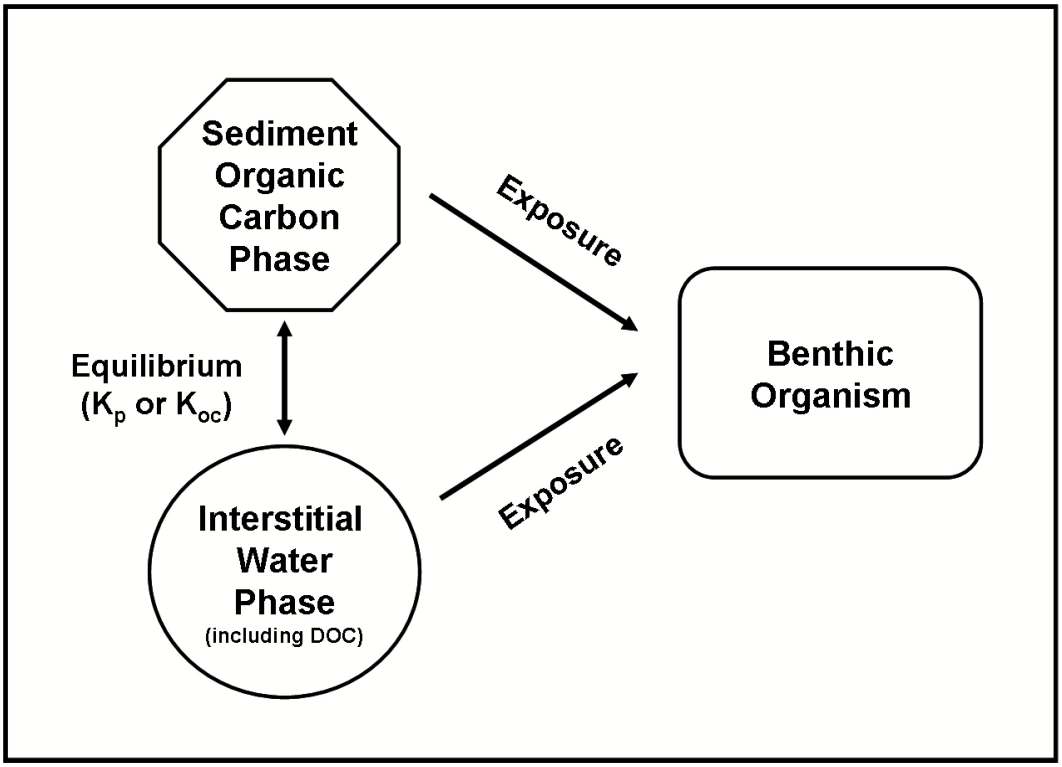

FIGURE 2. Diagram of Important Sediment Phases Affecting the Bioavailability of PAHs in Sediments Dominated by Organic Carbon

Equilibrium Partitioning (EqP) Model Assumptions

Use of EqP to predict exposure concentrations comes with several assumptions: (1) the environmental system and phases therein are at or approximating equilibrium, (2) interstitial water is a good measure of bioavailable contaminant, and (3) the sediment organic carbon is the primary partitioning phase for the contaminant. Quantitatively, we can represent the EqP approach as follows:

$$K_{P1} = f_{OC} \cdot K_{OC} \qquad [1]$$

where, K_{P1} is a one particulate phase partition coefficient (L/kg sediment [dry]), f_{OC} the fraction organic carbon of the sediment (g organic carbon/g sediment [dry]), and K_{OC} the organic carbon normalized partition coefficient (L/kg organic carbon). Recent studies demonstrate that PAHs can very strongly associate with other forms of carbon, specifically black carbon present in soots, fly ash and chars, and alter their geochemical behavior as compared to partitioning to "regular" organic carbon (e.g., Accardi-Dey and Gschwend, 2002). The influence of black carbon can be shown as follows:

$$K_{P2} = f_{OC} \cdot K_{OC} + f_{BC} \cdot K_{BC} \cdot C_D^{n-1} \qquad [2]$$

where, K_{P2} is the two particulate phase partition coefficient (L/kg sediment [dry]), f_{BC} the fraction black carbon (g black carbon/g sediment [dry]), K_{BC} is the black carbon normalized partition coefficient (L/kg black carbon), C_D the dissolved phase concentration (µg/L) of the contaminant of interest, and n a Freundlich coefficient used to consider non-linear sorption by the black carbon. If black carbon is measured or suspected to be present in the sediments of interest, a site-specific prediction using Equation 2 or measure of bioavailable PAHs may be necessary (Section 6.8 of U.S. EPA, 2003a discusses black carbon in detail).

Definition of Total PAHs and Analytical Methods

The term *total*, when discussing PAHs is misleading. There are tens of thousands of possible PAH structures ranging from the smallest PAH naphthalene to the largest forms like coronene. Alkylation, especially in petrogenic PAHs, contributes several thousand or more varying structures of PAHs. Current technology does not allow for the direct analytical measurement of all these PAHs. Early methods for measuring PAHs focused on the 13 priority pollutant PAHs identified by the U.S. EPA. Since the mid-1980s, for NOAA's National Status and Trends Program, 23 PAHs are routinely analyzed. Currently, the U.S. EPA's Ecological Monitoring and Assessment Program (EMAP) measures up to 34 PAHs. Also, the U.S. EPA PAH mixtures benchmark document (U.S. EPA, 2003a) recommends these 34 PAHs be analyzed when assessing the risk represented by PAHs in contaminated sediments. For the purposes of this white paper, these 34 PAHs are recommended for analysis in order to capture PAHs constituting an operational definition of "total PAHs."

The 34 PAHs are listed in Table 2. Although this list is far from comprehensive, it does incorporate many of the most common parent PAHs and many alkylated PAHs frequently found in PAH mixtures. Often, a major limitation in the analysis of PAHs is the availability of standards, especially for the alkylated PAHs. As analytical methods improve for measuring PAHs and standards become more readily available, the list presented in Table 2 may expand to include more PAH molecules. For example, recent work by Hawthorne et al. (2005, 2006) discusses approaches using alkylated standards to more effectively quantify PAH concentrations. Further, as the list of PAHs increases in number of analytes, uncertainty in method predictions will decrease. The level of uncertainty is likely to never be negligible but will decline as the most common PAHs are included in the analysis. For example, predictions made using the list of 34 PAHs will have less uncertainty than estimates using only 13 PAHs. Examples of analytical methods for the analysis of the 34 PAHs are provided in Lauenstein and Cantillo (1998) and Hawthorne et al. (2005). For the analysis of total organic carbon, methods discussed in U.S. EPA (2001b) and Ryba and Burgess (2002) are recommended. Black carbon analysis using a thermal oxidation method is described in Gustafsson et al. (1997) and Acardi-Dey and Gschwend (2002).

OVERVIEW OF PAH EFFECTS TO INVERTEBRATES

Use of Narcosis Model to Predict Effects

As discussed above, the principal form of toxicity elicited by PAHs to benthic invertebrates is narcosis. Narcotic toxicants frequently demonstrate additive toxicity; that is, the effects of narcotic toxicants can be added together to summarize the total amount of toxicity present in a mixture of such chemicals (as occurs in sediments). It has been observed that this additivity can occasionally over-estimate toxicity (i.e., result in a conservative and overly-protective estimate of risk). Figure 3 illustrates the approach used in U.S. EPA (2003a) and discussed in Di Toro and McGrath (2000), Di Toro et al. (2000) and Mount et al. (2003) for predicting toxicity to benthic organisms caused by PAHs.

Using contaminated site sediment data, including PAH concentrations and sediment organic carbon content, EqP is used to predict the bioavailable concentrations of the 34 PAHs. As discussed in U.S. EPA (2003a), the bioavailable concentration of each PAH is then converted to toxic units based on narcosis theory. The effects endpoints used to calculate toxic units in

TABLE 2. List of PAHs Recommended for Analytical Measurement to Quantify "Total PAHs" (from U.S. EPA, 2003a)

PAH	CAS*	Molecular Weight (µg/mol)
Naphthalene	91203	128.17
C1-Naphthalenes	-	142.20
Acenaphthylene	208968	152.2
Acenaphthene	83329	154.21
C2-Naphthalenes	-	156.23
Fluorene	86737	166.22
C3-Naphthalenes	-	170.25
Anthracene	120127	178.12
Phenanthrene	85018	178.23
C1-Fluorenes	-	180.25
C4-Naphthalenes	-	184.28
C1-Phenanthrene/anthracenes	-	192.26
C2-Fluorenes	-	194.27
Pyrene	129000	202.26
Fluoranthene	206440	202.26
C2-Phenanthrene/anthracenes	-	206.29
C3-Fluorenes	-	208.30
C1-Pyrene/fluoranthenes	-	216.29
C3-Phenanthrene/anthracenes	-	220.32
Benz(a)anthracene	56553	228.29
Chrysene	218019	228.29
C4-Phenanthrenes/anthracenes	-	234.23
C1-Benzanthracene/chrysenes	-	242.32
Benzo(a)pyrene	50328	252.31
Perylene	198550	252.31
Benzo(e)pyrene	192972	252.32
Benzo(b)fluoranthene	205992	252.32
Benzo(k)fluoranthene	207089	252.32
C2-Benzanthracene/chrysenes	-	256.23
Benzo(ghi)perylene	191242	276.23
C3-Benzanthracene/chrysenes	-	270.36
Indeno(1,2,3-cd)pyrene	193395	276.23
Dibenz(a,h)anthracene	53703	278.35
C4-Benzanthracene/chrysenes	-	284.38

* For C# PAHs CAS is not available.

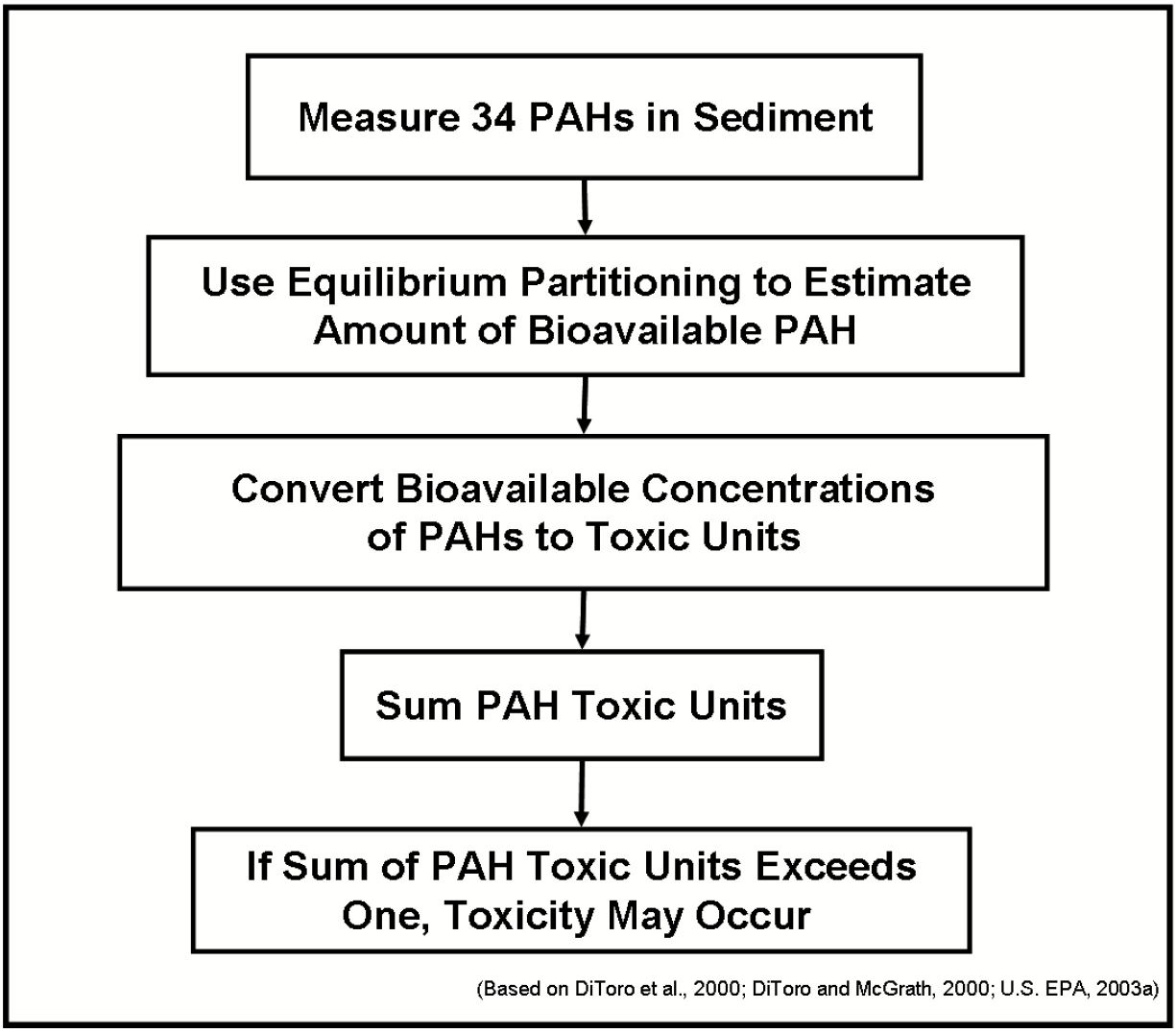

FIGURE 3. Simplified Flowchart of Approach for Predicting Toxicity of PAHs to Benthic Organisms

U.S. EPA (2003a) are the PAH final chronic values (FCVs). The FCVs for over 60 PAHs, including the 34 PAHs discussed above in Table 2, are reported in Table 3-4 of U.S. EPA (2003a). Because toxicity caused by narcotic chemicals has been demonstrated to be additive, these toxic units are summed together and an estimate of whether or not toxicity may occur can be derived. For example, if the sum of the toxic units exceeds a value of 1.0, toxicity to benthic invertebrates may occur. It should be noted that estimates of the bioavailable amounts of PAHs in the interstitial water can not exceed PAH solubility. If PAH solubility is exceeded, a non-aqueous phase liquid may form and observed toxicity maybe due to other mechanisms including smothering. The

organic carbon normalized maximum sediment concentration of a PAH ($C_{OC,PAHi,MAXi}$) can be calculated by multiplying the PAH solubility by the PAH K_{OC} value (see U.S. EPA, 2003a). If the organic carbon normalized sediment concentration, $C_{OC,PAHi}$, exceeds the maximum sediment concentration, the $C_{OC,PAHi,MAXi}$ should be used for calculating actual toxic units in place of $C_{OC,PAHi}$ (the subscript *i* indicates the identity of a given PAH; for example, anthracene or pyrene).

Examples of Equilibrium Partitioning (EqP) Approach in Use

A simple example of this approach is provided below. For simplicity, three PAHs are addressed in this example rather than the recommended 34. All the information needed to work with this example, except sediment concentrations and sediment organic carbon (i.e., site data), is available in U.S. EPA (2003a). As shown in Table 3, concentrations of the PAHs anthracene, fluoranthene and chrysene range from 3328 to 51896 µg/kg in a sediment with an organic carbon content of 0.0202 g_{OC}/g. Dividing the PAH concentration by the sediment organic carbon (and again dividing by 1000 to account for differences in units) results in the organic carbon normalized PAH concentration ($C_{OC,PAHi}$) (the subscript *i* indicates the identity of a given PAH; for example, anthracene or pyrene). This value is a more realistic indicator of the concentration of bioavailable PAHs. Dividing the $C_{OC,PAHi}$ by an organic carbon normalized toxicity value ($C_{OC,PAHi,FCVi}$) generates toxic units for each PAH. For this example, and as used in U.S. EPA (2003a), PAH FCVs are applied to generate sediment toxicity values. These values, $C_{OC,PAHi,FCVi}$ (in $\mu g/g_{OC}$), for individual PAHs are calculated by multiplying the PAH specific FCV (in µg/L) by the K_{oc} for that PAH (and again dividing by 1000 to account for differences in units); they are also reported in Table 3-4 of U.S. EPA (2003a). As noted above, if the sum of the toxic units exceeds 1.0, there is an elevated likelihood that toxicity to benthic organisms may occur. In the example above, because of the high concentrations of fluoranthene and chrysene in the sediments, the sum of the toxic units easily exceeds 1.0 with a value of 5.17. These sediments are predicted to exhibit chronic toxicity from PAHs. The same basic process is used when considering all the other PAHs.

More complex examples of the use of this type of approach can be found in the scientific literature (e.g., Swartz et al., 1995; Di Toro and McGrath, 2000; Di Toro et al., 2000; Ozretich et al., 2000). In their study, Swartz et al., (1995) evaluated an early version of the EqP approach, in which toxic units of 13 PAHs based on sediment concentrations were used to successfully predict

TABLE 3. Example Calculation of Toxic Units Associated with a Sediment Contaminated with Three PAHs

PAH	Concentration (µg/kg)	Sediment Organic Carbon (g_{OC}/g)	$C_{OC,PAHi}$ ($\mu g/g_{OC}$)	$C_{OC,PAHi,FCVi}$ ($\mu g/g_{OC}$)	Toxic Units
Anthracene	3328	0.0202	164.8	594	0.28
Fluoranthene	51896	0.0202	2569	707	3.63
Chrysene	21453	0.0202	1062	844	1.26
					$\sum = 5.17$

observed sediment toxicity. In an extension of Swartz et al. (1995), Ozretich et al. (2000) included 33 PAHs in his evaluation of this type of approach using contaminated sediments from Elliot Bay, Washington. In that evaluation, the approach was generally successful in predicting observed sediment toxicity (Ozretich et al., 2000). In their review of these data sets, Di Toro and McGrath (2000) reported the EqP-based approach accurately predicted toxic or non-toxic effects in over 90% of sediments evaluated. Further, Di Toro and McGrath (2000), Di Toro et al. (2000) and Mount et al. (2003), describe in great detail the technical basis for the EqP approach, discussing its performance in comparison to the results of toxicity testing and EMAP benthic analyses (Di Toro and McGrath, 2000).

Finally, in U.S. EPA (2003a) three 'real-life'-like examples are provided and discussed in detail in Section 6.3. To enhance the realism of the examples, the authors include scenarios where only 13 PAHs were measured as well as cases in which all 34 PAHs were quantified.

PAH Datasets

Frequently, especially in the case of older data sets, fewer than the 34 recommended PAHs were measured. Under some conditions, the toxic units contribution of PAHs not measured can be predicted using uncertainty factors (Section 6 in U.S. EPA, 2003a). In principle, the uncertainty factor serves as a multiplier to convert the toxic units associated with 13 or 23 measured PAHs to the toxic units of the desired 34 PAHs based on a selected confidence level (e.g., 95%). However, due to the unique distribution of PAHs in contaminated sediments resulting from their original source(s), uncertainty factors tend to be very site-specific. Consequently, the uncertainty factors in

U.S. EPA (2003a) should only be used to provide a very general estimate of the toxic units associated with 34 PAHs. Further, if only 13 or 23 PAHs have been measured in the contaminated sediments of interest, the development of site-specific uncertainty factors using a subset of sediments from the site is highly recommended. Site-specific uncertainty factors would provide a cost-effective way to reduce the variability around the predicted toxic units at the contaminated site (see U.S. EPA [2003a] and Mount et al. [2003] for a discussion of how to calculate site-specific uncertainty factors). However, it is very strongly encouraged that whenever possible all 34 PAHs are measured in sediment samples to avoid the need for generic or site-specific uncertainty factors.

Model Assumptions and Uncertainties

The approach described above for predicting risk to benthic invertebrates from sediment PAHs also requires several assumptions including the following: (1) benthic invertebrates do not appreciably metabolize PAHs, (2) the PAHs used to make predictions of toxicity are composed of carbon and hydrogen and do not include any heterocyclic atoms like oxygen, sulfur or nitrogen, or functional groups such as nitro or hydroxyl, and (3) the invertebrates for which risk is being predicted are coupled to the benthic environment; that is, they are exposed to toxic chemicals primarily via the sediment. See Di Toro and McGrath (2000), Di Toro et al. (2000), Mount et al. (2003) and U.S. EPA (2003a) for further discussion of these assumptions.

It is worth noting that a sum of toxic units greater than 1.0 can occur without the occurrence of significant benthic organism toxicity. This may happen if another sediment phase, like the black carbon discussed earlier, is reducing PAH bioavailability. Further, sediment toxicity to benthic organisms can occur if the sum of toxic units is less than 1.0, but this will most likely be due to the presence of other toxicants including, possibly, unanalyzed PAHs.

Primary uncertainties associated with this approach include (1) analytical uncertainties, including under-estimating the concentration of alkylated PAHs, which limits the accurate measurement of all toxic PAHs contributing to toxicity, (2) uncertainties in the equilibrium partitioning models resulting in over- and under-predictions of bioavailable PAH concentrations, and (3) uncertainties in the narcosis model causing under- and over-predictions of toxicity. Some of these uncertainties have been discussed already. Further, Sections 6 and 7 of U.S. EPA (2003a) go into detail on the uncertainties with this approach, and it is recommended that the users of this white paper refer to that document for more information.

SUMMARY

This white paper provides an overview of an approach for assessing risk to invertebrate receptors resulting from exposure to PAHs in contaminated sediments at hazardous waste sites. PAHs are possibly the most widely distributed of anthropogenic organic pollutants. The approach is based on the procedures described in U.S. EPA (2003a) and involves the use of EqP to determine exposure/bioavailability and additive narcosis theory to estimate sublethal toxicity of PAHs to benthic invertebrates. In an evaluation of over 30 sediments, this approach made accurate predictions over 90% of the time. The white paper also provides examples of how to use this approach with analytical data resulting from the analysis of contaminated sediments. The approach, particularly when used with other contaminated sediment assessment methods, offers risk assessors a useful tool for assessing the risk of PAHs to benthic invertebrates at hazardous waste sites. As noted earlier, assessments of sediments are improved when multiple lines of evidence are used (Adams et al., 2005). Finally, development of new technologies for measuring bioavailable concentrations of PAHs in sediments, as well as advances in analytical methods for PAH quantification, offer promising ways to supplement the EqP tool discussed in this white paper.

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