Use of Equilibrium Partitioning Sediment Benchmarks (ESBs) to Predict Toxicity of PAH Contaminated Sediments

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ABSTRACT

Recent studies by the Electric Power Research Institute (EPRI) and others have shown that the toxicity of polycyclic aromatic hydrocarbons (PAHs) to aquatic invertebrates in sediments at manufactured gas plant (MGP) sites is considerably lower than predicted by traditional sediment benchmarks. The binding of PAHs to black carbon is one mechanism that may explain this reduced toxicity. Another possible explanation is that the mixture of PAHs typically present at MGP sites has lower concentrations of certain toxic PAHs, as compared to the sediments used to derive the traditional benchmarks. The major implication of the present work is that assessments that compare PAH levels at MGP sites to traditional benchmarks may overestimate risks and areas of a site that require further assessment and remediation. A primary benefit of the present research is that it provides a means of conducting site-specific assessments that more accurately characterize the potential toxicity and need for additional action. The new methodology used in the present work uses two simple analyses: the measurement of black carbon, which can be conducted by commercial laboratories, and the measurement of a suite of 34 PAHs in sediment. EPRI research has demonstrated that the measurement on this larger suite of PAHs and the use of The U.S. Environmental Protection Agency (EPA) Equilibrium Partitioning Sediment Benchmarks (ESBs) results in a more accurate prediction of toxicity. Regulatory agencies are open to accepting this approach, but additional work is needed to demonstrate its validity. The method offers a cost-effective tool that can be used with other approaches to focus areas that may require assessment and action.

CONTENTS

1
INTRODUCTION

From the early 1800s Manufactured Gas Plants (MGP) produced byproducts including commodities such as coal tars that contain high concentrations of polycyclic aromatic hydrocarbons (PAHs) (Hayes et al., 1996). MGPs were often located close to water bodies, and contamination of sediment with PAHs is common at these sites. The distribution of PAHs in the aquatic environment is of concern because of their toxicity, carcinogenicity and persistence (Neff, 1979). Many state regulatory authorities use empirical Sediment Quality Guidelines (SQGs), such as the Effects Range Low and Median (ER-L and ER-M, Long and Morgan, 1990, Long et al, 1995), Ontario Lowest and Severe Effect Levels (LEL and SEL, Persaud et al., 1993), and Consensus Threshold and Probable Effect Concentrations (TEC and PEC, MacDonald et al., 2000), for predicting toxicity or as remediation goals for sediments. However, one of the greatest sources of uncertainty associated with use of empirical SQGs is that they do not take into account site-specific bioavailability of sediment-associated contaminants. Although the National Research Council (NRC, 2001) stated that sediment cleanup goals should be based upon site-specific risk considerations, sediment remediation goals at MGP sites typically do not consider the bioavailability of the specific forms of PAHs that are present at these sites. The presence of weathered non-aqueous phase liquid (NAPL), oil pockets, coal tar, coke, or other forms of PAHs that do not partition freely in the environment (Ghosh et al., 2003) may trigger expensive clean-up actions that are not based on site-specific risks.

The US Environmental Protection Agency (US EPA) recently published Equilibrium Partitioning Sediment Benchmarks (ESBs) for PAH mixtures (US EPA, 2003) that can be used to estimate the bioavailability and toxicity of sediment-associated PAHs to benthic (bottom-dwelling) organisms. The ESB approach calculates an "Equilibrium Partitioning Sediment Benchmark Toxic Unit" (ESB TU) for each PAH as the concentration of the PAH in the site sediment (or pore water) divided by the Final Chronic Value (FCV) for that PAH. Concentrations of PAHs below the FCV are not expected to be toxic. If the sum of the ESB Toxic Units (TUs) for "total PAHs" in the sediment or pore water (ESB Sum-TU$_{TOT}$) is less than or equal to 1.0, the concentration of PAHs in the sediment is acceptable for the protection of benthic organisms from chronic effects. A few recent studies have demonstrated that ESBs are useful in identifying sediment samples at MGP sites that are not likely to be toxic (EPRI, 2003 and 2004, Kane Driscoll et al., In prep. Kreitinger et al., 2004).

US EPA (2003) defines "total PAHs" as comprising, at a minimum, the 34 PAHs that were measured in the US EPA Environmental Monitoring and Assessment Program (US EPA EMAP, 1996). This definition is used because few databases are available that have measured a greater number of PAHs, and because the use of fewer PAHs would underestimate the total toxicity of the PAH mixture. US EPA recognizes that most historical data consist of either the 13 PAHs that were identified by the US EPA as compounds of concern, or the 23 PAHs that are typically monitored by the National Oceanic and Atmospheric Administration (NOAA). If data on only 13

PAHs are available, US EPA recommends that an uncertainty factor (UF) be applied to the Sum-TU_{13} to estimate the Sum-TU_{34} for the full suite of PAHs, including both unsubstituted (e.g., non-alkylated) PAHs, as well as PAHs that contain alkyl groups (e.g., 1-methylnaphthalene). Data collected for this report are used to develop an MGP-specific UF that is likely to be more accurate predictor of chronic toxicity to benthic invertebrates than the US EPA UF, which may tend to overestimate the concentration of alkylated PAHs in MGP sediments.

US EPA recognizes that a comparison of concentrations of PAHs in bulk sediment to FCVs as described above may be overprotective at some sites if the characteristics of the sediment or of the PAHs reduce the partitioning of PAHs into pore water and associated toxicity. For example, several studies have demonstrated that partitioning of PAHs cannot always be explained by standard models of equilibrium partitioning to sediment organic carbon (e.g., McGroddy and Farrington, 1995, Maruya et al., 1996, Ghosh et al., 2003). Additional studies suggest that PAHs that are occluded in or partitioned to soot carbon or soot-like particles are not available for partitioning (Gustaffsson et al., 1997, et al., 2000a, Buchelli and Gustaffson, 2000, and Accardi-Dey and Gschwend, 2002). The presence soot-like carbonaceous particles in sediment (collectively termed "black carbon") has been shown to limit bioaccumulation of PAHs in sediment by benthic invertebrates (Vinturella et al., 2004, Rust et al., 2004), which is likely to result in reduced toxicity. The draft US EPA Bioavailability Procedure (US EPA, 2000), which assumes that the bioavailable concentration of PAHs in sediment can be reasonably measured or estimated from the "freely-dissolved" chemical in pore water, can be used to develop site-specific ESBs. A site-specific approach that is based on the bioavailable fraction of PAHs has the potential to inform MGP site managers when negotiating cleanup values that are appropriately based on actual bioavailability and toxicity.

The research presented in this Technical Update demonstrates that ESBs can be used for assessing the toxicity of PAHs in sediments at MGP sites. In a preliminary study, existing data from MGP sites were used to examine the ability of the ESB approach to predict acute toxicity to benthic invertebrates (EPRI, 2003). Additional samples were collected to test the ability of the ESBs to accurately predict chronic toxicity of PAH-contaminated sediments from MGP sites (EPRI, 2004). Specific objectives of the present work include:

- Examine whether the general, non site-specific ESB approach (US EPA, 2003) can be used as a conservative predictor of toxicity (or lack of toxicity) of sediment-associated PAHs at MGP sites.

- Validate the use of the draft US EPA Bioavailability Procedure (US EPA 2000) to develop site-specific ESBs that take into account the bioavailability of PAHs at MGP sites.

- Calculate an MGP-specific UF that can be used to predict toxicity associated with the specific suite of PAHs that are likely to be present at MGP sites.

2
MATERIALS AND METHODS

This section provides an overview of the methods that were used to test the ability of the ESBs to predict the chronic toxicity of PAH-contaminated sediments from MGP sites. Additional details are provided in EPRI (2004).

2.1 Field Collection

Sediment samples were collected from a former coking plant in New Jersey that also produced coke oven gas for distribution and from two freshwater sites in central New York that are former MGP sites (EPRI 2004). Samples of surficial sediment (0-15 cm) were collected from freshwater intertidal and subtidal sediments to represent a range of PAH concentrations from approximately 10 mg/kg to 1000 mg/kg total PAHs. Subsamples were taken for sediment chemistry, sediment characteristics, generation of pore water, and toxicity testing.

2.2 Sediment Analyses

Sediment samples were analyzed for 34 PAHs listed in Table A.1, total organic carbon (TOC) and "black carbon", which is procedurally defined as carbon remaining after furnace drying and acid treatment of sediments to remove other forms of carbon (Gustaffson *et al.,* 1997 and Accardi-Dey and Gschwend, 2003). The difference between the concentrations of TOC and "black carbon" is assumed to represent non-pyrogenic organic carbon (NPOC) that is derived from plant material and other non-MGP sources.

2.3 Pore water Analyses

Pore water was generated by a series of sediment centrifugations and decanting or siphoning the supernatant. Samples of pore water were analyzed of total organic carbon (TOC) and dissolved organic carbon (DOC), phases which can bind PAHs and reduce bioavailability.

2.4 Sediment Toxicity Tests

A 28-day sediment toxicity test with the freshwater amphipod, *Hyalella azteca,* was conducted on sediment from every sample location. Endpoints examined included survival and growth. A ten-day sediment bioaccumulation test with the freshwater oligochaete, *Lumbriculus variegatus*, was also conducted on a subset of three sediment samples. Bioaccumulation test results are not presented in this report because this test was not run on all samples.

2.5 Calculation of the Sum of ESB Toxic Units

The Sum of ESB Toxic Units (ESB-TU) was calculated in three ways. For the non site-specific approach, measured concentrations of PAHs and the fraction organic carbon (fOC) in sediment are used to estimate the Sum of Toxic Units (termed Sum-TU, Sed fOC, see Section A.1 for details). Site-specific values, which are expected to more accurately reflect the reduced bioavailability of PAHs at MGP sites, are calculated in two ways. Site-specific Sum TU values are calculated from measured concentrations of PAHs and dissolved organic carbon (DOC) in porewater (termed Sum-TU, PW DOC, see Section A.2 for details). Site-specific Sum TU are also calculated from measured concentrations of PAHs, non-pyrogenic organic carbon and black carbon in sediment (termed Sum-TU, Sed fNPOC, fBC, see Section A.3 for details).

2.6 Calculation of Uncertainty Factors

Data from the recent EPRI study (EPRI 2004) as well as from an earlier study (EPRI 2003) were used to calculate MGP-specific UFs for estimating the ESB Sum-TU for the full suite of 34 PAHs (ESB Sum-TU$_{34}$) from the ESB Sum-TU calculated for 13 PAHs (ESB Sum-TU$_{13)}$. For each sample, the ESB Sum-TU$_{34}$ is divided by the Sum-TU$_{13}$ to calculate an UF. The data are used to estimate the 50th percentile and 95th percentile MGP-specific UF, which are contrasted with the US EPA 50th percentile and 95th percentile UF.

3
RESULTS AND DISCUSSION

This section compares the actual results of the sediment toxicity tests with three approaches for predicting the toxicity of sediments: non site-specific ESB that are based on measurements of PAHs in sediment, site-specific ESB prediction that account for the presence of black carbon in sediment and site-specific predictions that are based on measurements of PAHs in porewater.

3.1 Sediment Toxicity

Only one sediment sample (5,130 mg PAH/kg) showed significantly reduced survival (64%) of *H. azteca* in comparison to laboratory controls (Fig 1). None of the samples had significantly reduced growth (Fig 2). One sample (325 mg total PAHs/kg) showed no adverse effects on growth and survival in the sediment toxicity test (Fig 1 and 2), but resulted in complete mortality of test organisms in a ten-day bioaccumulation test (data not shown). The other samples that were tested in the bioaccumulation test, containing 9 or 44 mg total PAHs/kg, did not exhibit reduced survival in the bioaccumulation test.

Figure 1. Relationship of ESB Sum-Toxic Units to Survival in Sediment Toxicity Tests
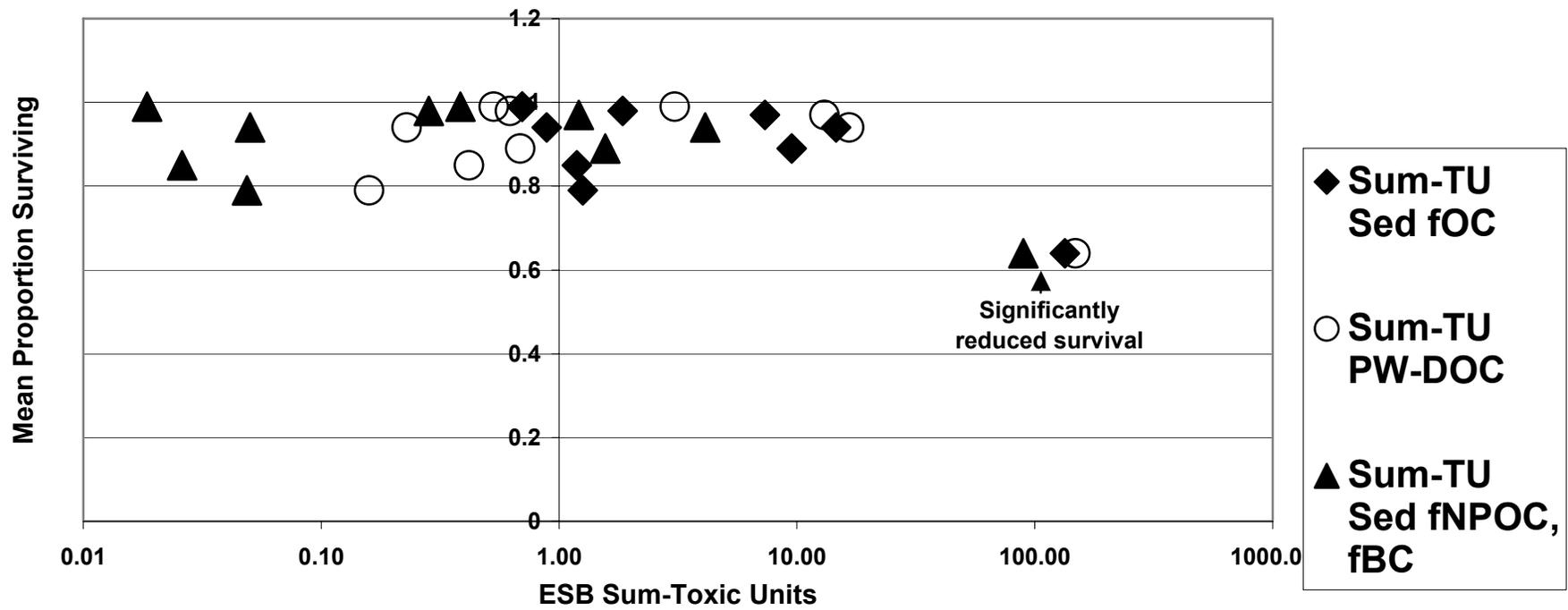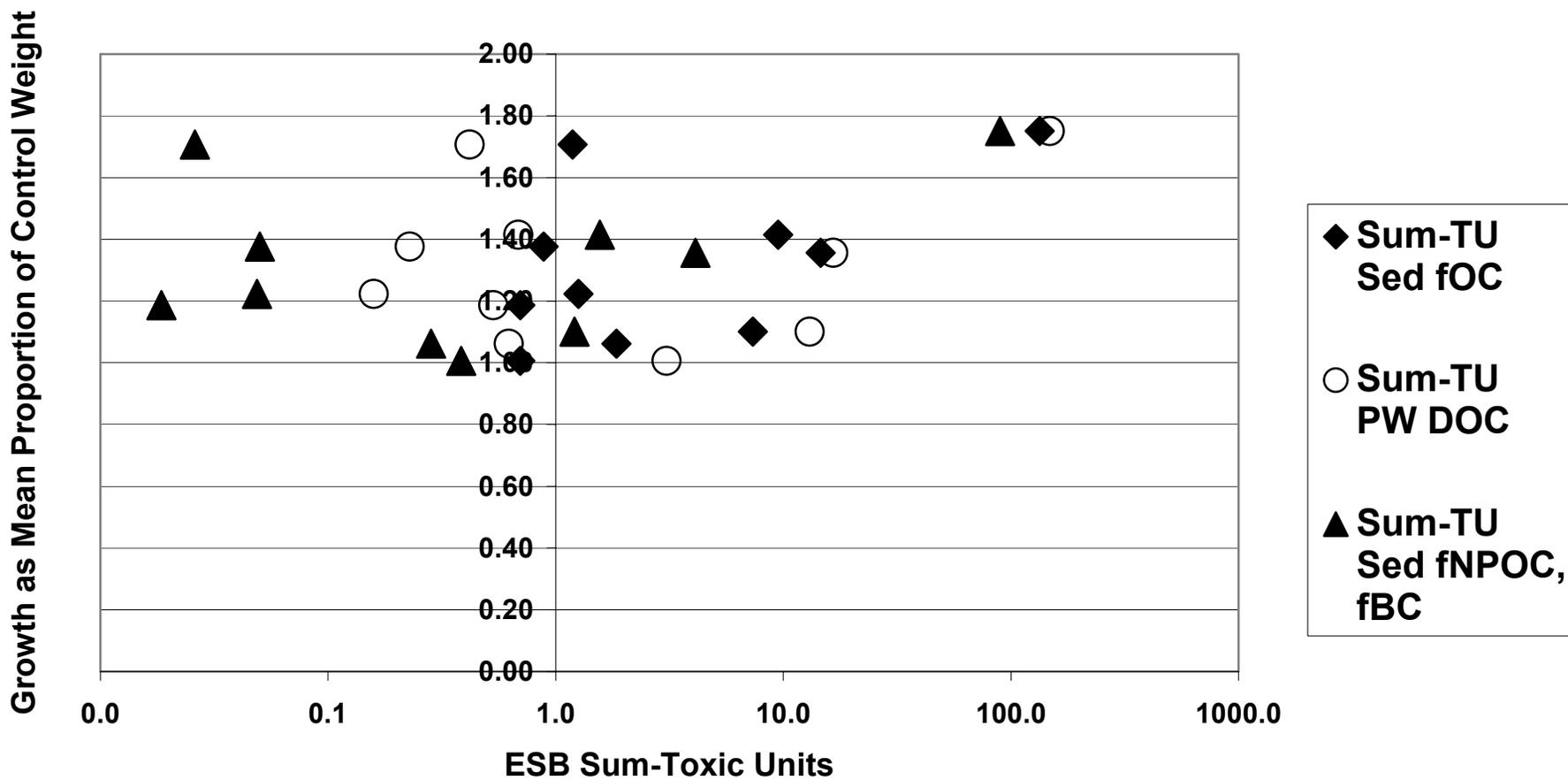
Figure 2. Relationship of Sum ESB-Toxic Units to Growth in Sediment Toxicity Tests

3.2 Comparison of Predictions Based on Non Site-Specific Sum Toxic Units to Results of Sediment Toxicity Tests

Results indicate that the Sum of Toxic Unit values that are based on measured concentrations of PAHs and fOC in sediment (Sum-TU, Sed fOC), overestimated toxicity in two sediment samples with concentrations 257 and 272 mg PAHs/kg. For these samples, this non site-specific approach calculated Sum-TU of 7 and 9.5, suggesting that the samples should be toxic. However, these samples were not toxic in the sediment toxicity test. Sum-TU, Sed fOC:

- Correctly predicted lack of toxicity (Sum-TU < 1.0) in samples with concentrations of total PAHs ranging from 9 to 21 mg/kg (Fig 3);

- Correctly predicted lack of toxicity (Sum-TU close to 1.0, ranging between 1.0 and 2.0) in samples with concentrations of total PAHs ranging from 37 to 44 mg/kg (Fig 3);

- Over-predicted toxicity (Sum-TU substantially above 1.0, ranging from 7 to 9.5 TU) in two samples with concentrations of total PAHs ranging from 257 to 272 mg/kg (Fig 3), that were not toxic in the sediment toxicity test;

- Correctly predicted toxicity (Sum-TU = 15) in one sample with a concentration of 325 mg/kg (Fig 3), that was not toxic in the sediment toxicity test, but was toxic in the sediment bioaccumulation test. (Although the sediment bioaccumulation test is not typically used to assess sediment toxicity, mortality of the bioaccumulation test organisms is considered an indication of toxicity for this sample.); and

- Correctly predicted toxicity (Sum-TU = 89.5) in one sample with a high concentration of PAHs in sediment (5,160 mg/kg, Fig 3), which was toxic in the sediment toxicity test.

3.3 Comparison of Site-Specific Sum-Toxic Units that Incorporate Black Carbon to Results of Sediment Toxicity Tests

Results indicate that site-specific Sum of Toxic Unit values that incorporate measurements of black carbon (Sum-TU, Sed fNPOC, fBC) are in closest agreement with results of sediment toxicity tests. Sum-TU, Sed fNPOC, fBC:

- Correctly predicted lack of toxicity (Sum-TU < 1.0) in samples with concentrations of PAHs in sediment ranging from 9 to 44 mg/kg (Fig 3);

- Correctly predicted lack of toxicity (Sum-TU close to 1.0, ranging between 1.0 and 2.0) in samples with concentrations of PAHs in sediment ranging from 257 to 272 mg/kg (Fig 3);

- Correctly predicted toxicity (Sum-TU = 4.1) in one sample (325 mg/kg) that was not toxic in the sediment toxicity test, but that was toxic to worms in the bioaccumulation test (Fig 3); and,

- Correctly predicted toxicity (Sum-TU = 89.5) in one sample (Fig 3) with a high concentration of PAHs in sediment (5,160 mg/kg).

3.4 Comparison of Site-Specific Sum-Toxic Units for Porewater to Results of Sediment Toxicity Tests

Results indicate that the Sum of Toxic Unit values that were based on measured pore water concentrations (Sum-TU, PW DOC) were somewhat variable, and in some cases measured concentrations of PAHs in pore water were higher than would be predicted from concentrations in bulk sediment (Fig 3). Sum of Toxic Units for pore water:

- Correctly predicted lack of toxicity (Sum-TU < 1.0) in samples with concentrations of PAHs in sediment ranging from 20 to 257 mg/kg (Fig 3);

- Over-predicted toxicity (Sum-TU = 3.1) in one sample with a low concentration of PAHs (9 mg/kg) that was not toxic (Fig 3);

- Over-predicted toxicity (Sum-TU =13.1) in one sample with a higher concentration of PAHs (272 mg/kg) that was not toxic (Fig 3);

- Correctly predicted toxicity in two samples (Sum-TU = 16.6 and 148) with high concentrations of PAHs (325 and 5,160 mg/kg, respectively) that were toxic in the sediment bioaccumulation test (325 mg/kg, Fig. 3) or the sediment toxicity test (5,160 mg/kg, Fig. 3).

3.5 Uncertainty Factors

Data for ten MGP samples were used to calculate 50th and 95th percentile $UF_{TOT,13}$ values of 1.60 and 1.85, respectively. These MGP-specific values are close to 50th and 95th percentile values of 1.59 and 1.85 that were previously reported for 4 MGP site samples (EPRI, 2003), but smaller than the US EPA 50th and 95th percentile $UF_{TOT,13}$ values of 2.75 and 11.5. Another study (Hawthorne *et al.*, In press) of 45 samples from six MGP impacted sites reported a mean $UF_{TOT,13}$ of 2.9, which is comparable to the US EPA 50th percentile value of 2.75, and a 95th percentile of 4.2, which is lower that the US EPA value of 11.5, but higher than the MGP-specific of 1.85 from the present study (EPRI 2004). Collectively, these studies demonstrate that the application of the US EPA UF 95th percentile $UF_{TOT,13}$ overestimates the Sum-TU for these samples.

$UF_{TOT,13}$ may differ among sites if the proportion of alkylated to unsubstituted PAHs varies. For example, PAHs from petrogenic sources (*e.g.*, oils and gas) tend to have higher proportions of alkylated PAHs than PAHs from pyrogenic sources (*e.g.*, MGP coal tars) because the high temperatures that produce pyrogenic PAHs tend to destroy the more reactive alkylated PAHs. Data that were used to develop the US EPA UF were obtained from the U.S. EPA Environmental Monitoring and Assessment Program (EMAP, US EPA, 2003) that were conducted in the Louisianan and Carolinian provinces. In the development of the UF, the ESB Sum-TU for the Louisiana data set was found to be more impacted than the Carolinian data set by the presence of alkylated PAHs. This suggests that some of the Louisiana sediment samples were influenced by PAHs from petrogenic, rather than pyrogenic sources (J. McGrath, Pers. communication). Since pyrogenic PAHs at MGP sites tend to have low proportions of alkylated PAHs, the US EPA UF may overestimate the contribution of alklyated PAHs in these MGP samples.

Figure 3. ESB Sum-TU for MGP Sediments
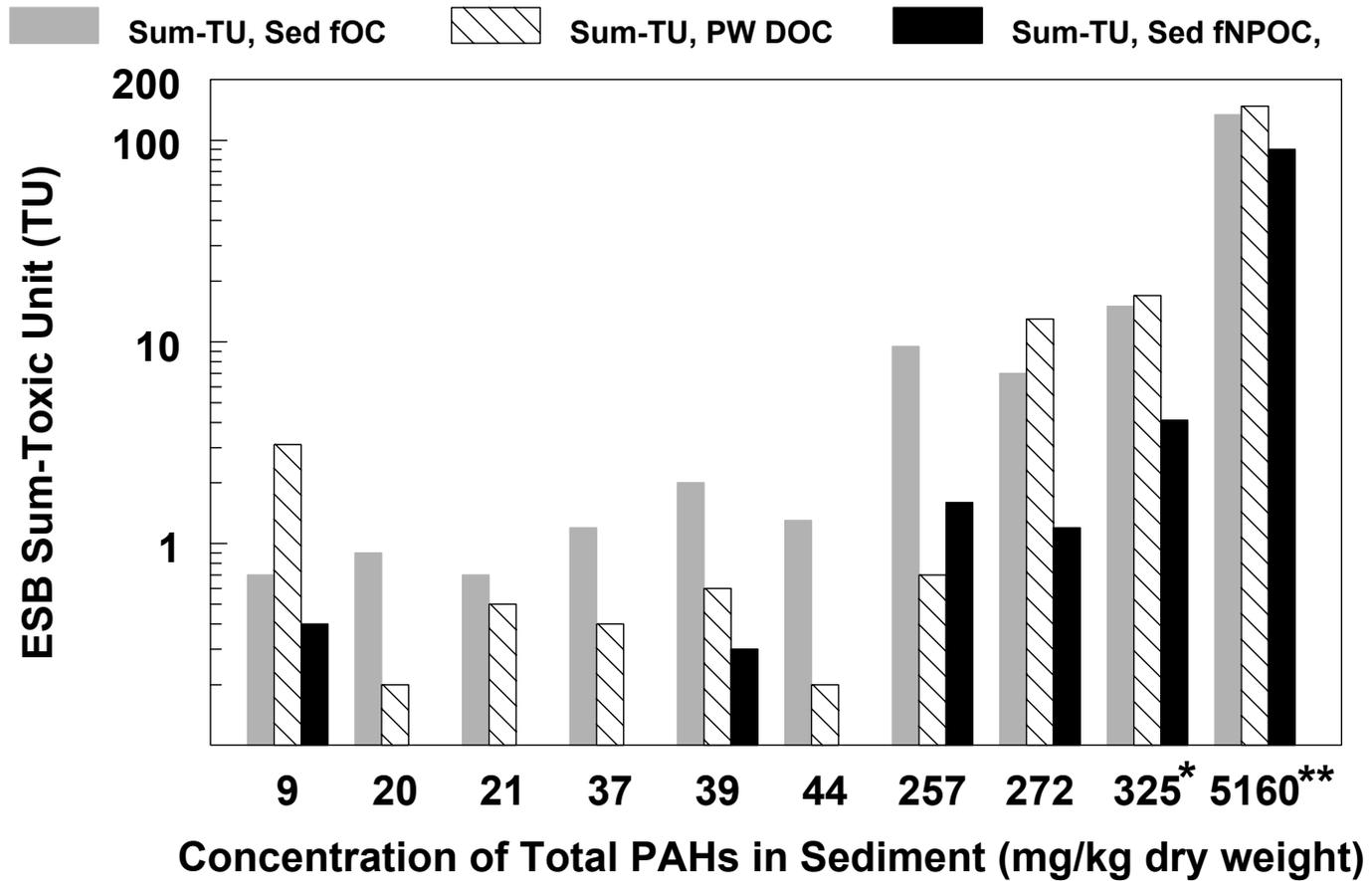
*Survival significantly reduced in bioaccumulation test
**Survival significantly reduced in toxicity test

4

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

The data clearly demonstrate that site-specific ESB that account for the presence of black carbon are useful for the identification of concentrations of PAHs that are not toxic to benthic invertebrates. Measurements based on bulk sediment overestimated toxicity by incorrectly predicting that samples with concentrations of PAHs in the range of 200-300 mg/kg would be toxic. Site-specific ESB that accounted for the presence of black carbon correctly predicted that samples with concentrations of PAHs as high as 200-300 mg/kg would not be toxic These results are in agreement with those of Kreitinger et al., (2004) that reported that Sum-TU based on concentrations of PAHs in bulk sediment overestimated toxicity of MGP sediments, whereas Sum-TU based on concentrations of bioavailable PAHs in pore water or sediment were able to differentiate toxic and non-toxic samples. These data demonstrate that methods that account for the presence of black carbon may be used to demonstrate that MGP samples with elevated concentrations of PAHs (as high as 200-300 mg/kg in this study) are not toxic to sediment-dwelling invertebrates. Assessments of MGP sites should consider using measurements of black carbon to estimate the bioavailability of PAHs in sediment. Future assessments of PAH contaminated sites should also analyze sediment samples for the full suite of 34 PAHs so that overly conservative uncertainty factors need not be applied in the calculation of the ESB Sum-TU. This is particularly important at MGP sites since PAHs at MGP sites tend to have low proportions of alkylated PAHs in comparison to other industrial sites. This study and others demonstrate that the application of the US EPA UF overestimates the concentration of alkylated PAHs in sediments at MGP sites and their contribution to toxicity.

The presence of NAPL in one of the samples (5,160 mg total PAHs/kg) indicates that PAHs in that sample are likely partitioning to the NAPL phase. For such samples, estimates of equilibrium concentrations of PAHs in pore water that do not take into account partitioning to NAPL are likely to overestimate the ESB Sum-TU and likelihood of toxicity (McGrath et al., 2001). Additional research into the ability of the ESB approach to predict toxicity of sediments that contain NAPL should be conducted.

Predictions based on measured concentrations of PAHs in pore water, which is a potentially useful promising analytical technique, overestimated toxicity in fewer samples than estimates based on bulk sediment but in more samples than estimates that incorporate black carbon. In some samples, measured concentrations of PAHs in pore water were higher than would be predicted from concentrations in bulk sediment (Fig 3). Additional studies should be conducted to examine the accuracy and precision of the analytical methods that are used to measure freely dissolved PAHs in pore water. The centrifugation and decanting method that was used in the present study (EPRI 2004) to isolate porewater may be subject to artifacts if particulate material is resuspended during the process of decanting the porewater. Alternative methods, such as

flocculation of particulates in centrifuged supernatant with alum (Ghosh et al., 2000b, Hong et al., 2003, Kreitinger et al., 2004), should also be considered for use in measuring freely dissolved PAHs in porewater.

Additional research that collects synoptic measurements of bioavailability and toxicity using various analytical techniques will most effectively demonstrate the validity of the site-specific ESB approach. For example, various techniques, such as low-density polyethylene device samplers (Vinturella et al., 2004), polyoxymethylene extraction (Jonker and Koelmans, 2001) and desporption to XAD resin (Lamoreaux and Brownawell, 1999, Rust et al., 2004) have been used to measure the bioavailable fraction of PAHs in sediments, and supercritical fluid extraction (Kreitinger et al., 2004) has been used to demonstrate the relationship between bioavailable PAHs in sediments and toxicity to benthic invertebrates. However, the measurement of black carbon in sediment will likely continue to be used to assess risk in the near future, since this analysis is readily available from commercial laboratories.

Concordance among various lines of evidence, which should include bioaccumulation tests, sediment toxicity tests with various test organisms, along with validation and standardization of analytical techniques for measuring freely dissolved concentrations in pore water and black carbon in sediment, will increase confidence in the reliability of the site-specific ESB approach for use in environmental risk assessments at MGP sites and other PAH contaminated sites.

5
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A
ATTACHMENT A

This section describes the three methods that were used to calculate ESB Sum-TU. As described below (Section A.1), non-site specific ESB Sum-TU were calculated from the concentrations of PAHs and fraction organic carbon in bulk sediment. Site-specific ESB Sum-TU were calculated in two ways: from the concentration of PAHs and dissolved organic carbon in porewater (Section A.2) and from the concentration PAHs, non-pyrogenic organic carbon, and black carbon in sediment (Section A.3).

A.1 Calculation of Non Site-Specific Sum-TU, based on measured concentrations of PAHs in sediment

For the non site-specific approach, measured concentrations of PAHs and fraction organic carbon (fOC) in bulk sediment are used to estimate the concentrations of PAHs that are freely dissolved in pore water (C_w) using the following relationship:

$$Kd = fOC * K_{OC}$$

where:

K_d is the observed sediment-pore water partition coefficient (l/kg) = C_{SED}/C_W

C_{SED} = the concentration of PAH in sediment (ug/kg dry wt)

C_W = the concentration of truly dissolved PAH in pore water (ug/l)

fOC is the weight fraction of sediment total organic carbon (kg organic carbon/kg dry wt)

K_{OC} is the organic carbon-water partition coefficient (l/kg)

For each PAH, C_w is divided by its corresponding FCV to calculate a TU. The corresponding Sum-TU for 34 PAHs, which is based on measured concentrations of PAHs and fOC in bulk sediment, is termed and discussed below as Sum-TU, Sed fOC.

A.2 Site-Specific Sum-TU based on measured concentrations of PAHs in Pore water

The freely dissolved concentration of each PAH in pore water, Cw, is estimated from the total measured concentration in pore water and the concentration of DOC. The percent of the total measured PAH in pore water that is freely dissolved is calculated as:

$$C_W = (\% \text{ of total that is freely dissolved}) * C_{TOT}$$

where:

C_W = the concentration of truly dissolved PAH in pore water (ug/l)

C_{TOT} = the total measured concentration of PAH in pore water (ug/l)

% of total that is freely dissolved = $1/(DOC * K_{DOC} + 1) * 100$

DOC = the concentration of dissolved organic carbon in pore water (kg/L)

K_{DOC} = the DOC-water partition coefficient (l/kg) = 0.08 K_{OW} (Burkhard, 2000)

K_{OW} = the octanol-water partition coefficient (l/kg)

For each PAH, C_W is divided by its corresponding FCV to calculate a TU. The corresponding Sum-TU for 34 PAHs, which is based on the measured concentrations of PAH and DOC in pore water, is termed and discussed below as the Sum-TU, PW DOC.

A.3 Site-Specific Sum-TU based on measured concentrations of PAHs and black carbon in sediment

The freely dissolved concentration of each PAH in pore water, C_W, is estimated from the measured concentration in sediment (C_{SED}), the fraction of non-pyrogenic organic carbon in sediment (f_{NPOC}), and the fraction of black carbon in sediment (f_{BC}) according to the following relationship:

$$K_d = f_{NPOC} * K_{OC} + f_{BC} * K_{BC} C_W^{n-1}$$

where:

K_d = the solid to pore water distribution coefficient (l/kg) = C_{SED}/C_W

C_{SED} = the concentration of PAH in sediment (ug/kg dry wt)

C_W = the concentration of truly dissolved PAH in pore water (ug/l)

f_{NPOC} is the weight fraction of non-pyrogenic organic carbon in sediment (kg non-pyrogenic organic carbon/kg dry wt, calculated from the difference between total organic carbon and black carbon)

K_{OC} = the organic carbon to pore water distribution coefficient (l/kg)

f_{BC} is the weight fraction of black carbon in sediment (kg black carbon/kg dry wt)

K_{BC} is the black carbon to pore water partition coefficient (l/kg)

n is the Freundlich exponent, which accounts for nonlinear sorption behavior (n=0.6, Accardi-Dey and Gschwend, 2002).

An iterative approach is used to solve for C_W. For each PAH, C_W is divided by its corresponding FCV to calculate a TU. The corresponding Sum-TU for 34 PAHs, which is based on the measured concentrations of PAHs, fNPOC and fBC in sediment, is termed and discussed below as Sum-TU, Sed fNPOC, fBC.

Since black carbon distribution coefficients, K_{BC}, were not available for all 34 PAHs used in the ESB approach, a regression relationship was used to develop these values. The relationship between K_{BC} values for 17 PAHs that were determined experimentally (Accardi-Dey and Gschwend, 2003) and K_{OW} is presented in Fig A.1. Estimated K_{BC} values are presented in Table A.1.

Table A.1. Partition Coefficients for 34-PAHs (US EPA, 2003)

Alkylated PAH	Limit of Water Solubility (mg/L)	Molecular Weight	Log K_{OW}	Log K_{OC}	Log K_{BC}
Naphthalene	3.10E+01	128.19	3.36	3.30	5.10
C1-Naphthalenes		142.20	3.80	3.74	5.24
C2-Naphthalenes		156.23	4.30	4.23	5.48
C3-Naphthalenes		170.25	4.80	4.72	5.75
C4-Naphthalenes		184.28	5.30	5.21	6.02
Acenaphthylene	1.63E+01	152.20	3.22	3.17	4.80
Acenaphthene	3.80E+00	154.21	4.01	3.94	5.40
Fluorene	1.90E+00	166.20	4.21	4.14	6.00
C1-Fluorenes		180.25	4.72	4.64	5.70
C2-Fluorenes		194.27	5.20	5.11	5.98
C3-Fluorenes		208.30	5.70	5.60	6.24
Phenanthrene	1.10E+00	178.20	4.57	4.49	6.30
Anthracene	4.50E-02	178.20	4.53	4.46	6.10
C1-Phenanthrenes/Anthracenes		192.26	5.04	4.96	5.88
C2-Phenanthrenes/Anthracenes		206.29	5.46	5.37	6.15
C3-Phenanthrenes/Anthracenes		220.32	5.92	5.82	6.38
C4-Phenanthrenes/Anthracenes		234.23	6.32	6.21	6.63
Fluoranthene	2.40E-01	202.26	5.08	5.00	6.70
Pyrene	1.32E-01	202.26	4.92	4.84	6.20
C1-Fluoranthenes/Pyrenes		216.29	5.29	5.20	6.09
Benz[a]anthracene	1.10E-02	228.29	5.67	5.58	6.90
Chrysene	2.00E-03	228.29	5.71	5.62	6.80
C1-Chrysenes		242.32	6.14	6.04	6.52
C2-Chrysenes		256.23	6.43	6.32	6.75
C3-Chrysenes		270.36	6.94	6.82	6.91
C4-Chrysenes		284.38	7.36	7.24	7.19
Benzo[b]fluoranthene	1.50E-03	252.32	6.27	6.16	6.00
Benzo[k]fluoranthene	8.00E-04	252.32	6.29	6.18	6.80
Benzo[a]pyrene	3.81E-03	252.31	6.11	6.00	6.90
Perylene	4.01E-04	252.31	6.14	6.03	6.73
Benzo[e]pyrene	4.01E-03	252.32	6.14	6.03	6.90
Indeno[1,2,3-cd]pyrene		276.23	6.72	6.61	6.75
Dibenz[a,h]anthracene	6.01E-04	276.23	6.71	6.60	6.80
Benzo[g,h,i]perylene	2.60E-04	278.35	6.51	6.40	7.06

Figure A1. Relationship between log octanol-water partition coefficent (K_{ow}) and log black carbon-water partition coefficent (K_{BC})

$y = 0.5437x + 3.4144$

$R^2 = 0.6645$

log K_{OW}
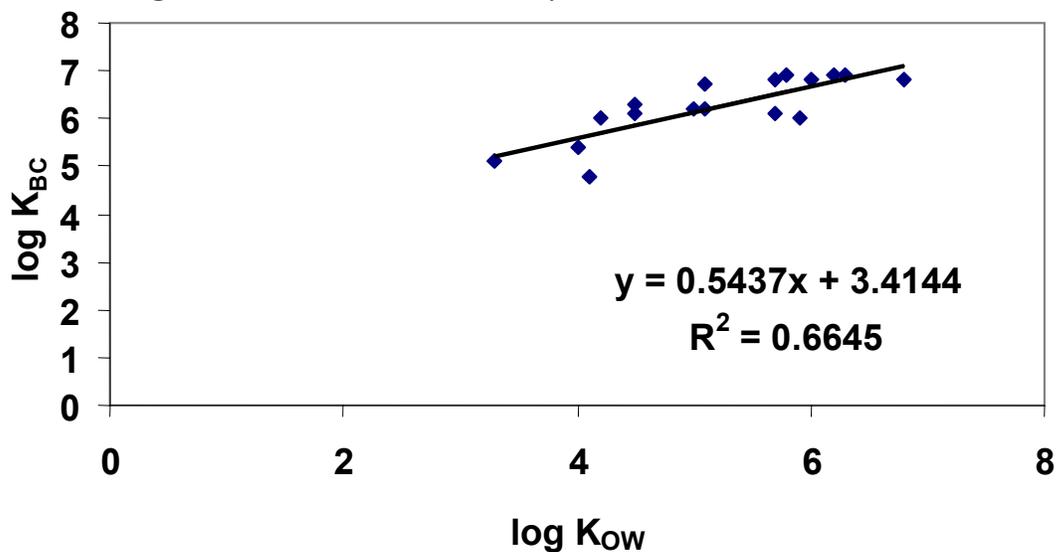
Data from Accardi-Dey and Gschwend, 2003,

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