

MEASUREMENT OF TOTAL POLYCYCLIC AROMATIC HYDROCARBON CONCENTRATIONS IN SEDIMENTS AND TOXIC UNITS USED FOR ESTIMATING RISK TO BENTHIC INVERTEBRATES AT MANUFACTURED GAS PLANT SITES

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Abstract—The U.S. Environmental Protection Agency's (U.S. EPA) narcosis model requires the measurement of 18 parent and 16 groups of alkyl polycyclic aromatic hydrocarbons (PAHs) (so-called 34 PAHs) in sediments to calculate the number of PAH toxic units (TU) available to benthic organisms. If data for the 34 PAHs are not available, the U.S. EPA proposes estimating the risk by multiplying the TU for 13 parent PAHs by 11.5 (95% confidence interval) based on data from 488 sediments. This estimate is overly conservative for PAHs from pyrogenic manufactured gas plant (MGP) processes based on the analysis of 45 sediments from six sites. Parent PAHs contributed approximately 40% of the total concentrations and TU for MGP sediments. In contrast, parent PAHs from diesel fuel and petroleum crude oil contributed only 2 and 1%, respectively, of the PAH concentrations and TU, compared to approximately 98 to 99% contributed by the alkyl PAHs. Statistical comparison of the TU based on the measured 34 alkyl and parent PAHs and those based on only 13 parent PAHs demonstrated that a factor of 4.2 (rather than 11.5) is sufficient to estimate total TU within a 95% confidence level for MGP sites. Similarly, measurement of parent PAHs is sufficient to accurately estimate the total 34 alkyl and parent PAH concentrations for MGP-impacted sediments.

Keywords—Manufactured gas plant Polycyclic aromatic hydrocarbons Sediment Hydrocarbon narcosis Toxic units

INTRODUCTION

The U.S. Environmental Protection Agency's (U.S. EPA) guidelines for protecting benthic organisms in polycyclic aromatic hydrocarbon (PAH)-contaminated sediments are based on the calculation of benchmark values for complex mixtures of PAHs that estimate risk using the hydrocarbon narcosis and equilibrium partitioning models [1–5]. The hydrocarbon narcosis risk model requires the measurement on sediment of 18 parent PAHs and 16 groups of prominent C1 to C4 alkyl PAH derivatives (so-called 34 PAHs) rather than the historically measured 16 priority pollutant parent PAHs determined using U.S. EPA Method 8310 (<http://www.epa.gov/SW-846/pdfs/8310.pdf>) or the 13 (or 23) PAHs reported in the majority of sediment monitoring programs in the United States [2]. Sediment concentrations of the 34 PAHs are used along with their expected sediment/water/lipid partitioning behavior to calculate a hazard quotient, referred to as a toxic unit (TU), that is used as a benchmark for predicting the toxicity of PAHs to benthic invertebrates. Because the typical sample contains hundreds of alkyl PAH isomers and because few alkyl PAH standards are available, accurately determining the total 34 PAH concentrations can be difficult and expensive. In addition, nearly all previous investigations have relied only on parent PAH measurements to determine total PAH concentrations, which makes the use of historical data problematic.

In an effort to address these problems, the U.S. EPA protocol suggests the estimation of TUs based on the sediment concentrations of 13 parent PAHs multiplied by a factor of 11.5 (95% confidence interval) [2]. However, the use of this correlation is discouraged since petrogenic (petroleum-de-

rived) and pyrogenic PAHs (e.g., produced under pyrolysis conditions such as those used for manufactured gas plant [MGP] processes) have dramatically different relative proportions of parent versus alkyl PAHs. Petrogenic PAHs are dominated by alkyl PAH derivatives, while pyrogenic MGP PAHs have much lower proportions of alkyl derivatives [6–8]. Thus, any correlations used to estimate total 34 parent and alkyl PAH concentrations based on parent PAH concentrations will be more accurate if they are based on the specific industrial process or site-specific PAH distributions that occur at the sites in question.

The goal of the present study was to evaluate and improve the accuracy of the proposed methods to determine the 34 PAHs on sediment samples and to investigate the effects of common analytical approaches for both pyrogenic and petrogenic PAHs on the TU predicted using the proposed U.S. EPA narcosis risk model. The total 34 alkyl and parent PAH concentrations are reported for 45 sediment samples collected at six different sites impacted by MGP processes. The number of alkyl PAH standards is increased over those in the proposed 34 PAH method [2,9] in an effort to more accurately determine alkyl isomer concentrations. The relative proportions of parent and alkyl PAHs from these pyrogenic sources are compared to those from petrogenic sources (diesel fuel from a local supplier and petroleum crude oil from the National Institute of Standards and Technology [NIST], Gaithersburg, MD, USA, SRM 1582). Manufactured gas plant site-specific factors for estimating the total 34 PAH concentrations and PAH TU based on parent PAH concentrations are presented.

EXPERIMENTAL

Sediment samples

More than 100 sediment samples were collected using a Ponar grab sampler (Forestry Suppliers, Jackson, MS, USA)

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at six different sites thought to be impacted by former MGP activities. Approximately 15 L each of sediment/water slurry were immediately transferred to a 20-L bucket, sieved through a 2-mm screen to remove debris, and briefly mixed before subsampling into new glass jars. Samples (~200 g) were then cooled on ice in the dark and shipped to the laboratory by overnight air delivery. (The bulk of each sample was stored separately for subsequent biological testing.) Storage was at 4°C in the dark. The sediment samples typically had approximately 50 wt % water as stored. Sediment collection and storage procedures were based on previous recommendations [10,11].

A preliminary estimate of PAH concentrations on each sediment was performed by mixing 2 g of the wet sediment with 2 g of sodium sulfate and extracting with 20 ml of 1:1 acetone/methylene chloride for 18 h in a bath sonicator and analyzing the extracts as described here for the Soxhlet extracts. Based on these initial estimates of PAH concentrations, 45 sediments were selected for additional study to represent the range of PAH concentrations (from background to highly contaminated) found at the six MGP sites.

Sediment preparation and analysis

All sediment analyses were performed within 28 d of sample collection. Sediment samples were prepared fresh daily as suggested by the U.S. EPA [10] by transferring approximately 40 ml of the sediment/water slurry to a certified clean 40-ml glass VOA vial and centrifuging for 30 min at 1,000 g. (Higher speed caused the glass vials to break.) This typically resulted in 10 to 20 ml of pore water that could be removed with a pipette. The remaining wet sediment was recovered, quadruplicate 2-g samples of the sediment were mixed with an equal weight of sodium sulfate, and each replicate was extracted for 18 h in a Soxhlet apparatus with 150 ml of 1:1 acetone:methylene chloride. Each extract was then spiked with 5 µl of a mixture of two- to six-ring perdeuterated PAHs (*d*-PAHs) as internal standards and analyzed as described here. More dilute extracts were concentrated under a gentle stream of clean nitrogen before gas chromatography/mass spectrometry (GC/MS) analysis. No samples were air-dried before extraction in order to avoid any losses of the more volatile PAHs. However, replicate portions of each sediment were dried overnight at 80°C to allow their moisture content to be determined and to allow presentation of the concentration data on a dry-weight basis.

The 34 parent and alkyl PAH sediment concentrations were determined in a manner analogous to the method proposed by the U.S. EPA, based on the previous work by Denoux et al. [2,9]. However, the method was modified to increase the number of *d*-PAH internal standards and the number of alkyl PAH calibration standards (Table 1). The *d*-PAH internal standards included naphthalene-*d*₈ (0.97 mg/ml), acenaphthene-*d*₁₀ (0.95 mg/ml), fluorene-*d*₁₀ (1.00 mg/ml), phenanthrene-*d*₁₀ (0.90 mg/ml), fluoranthene-*d*₁₀ (1.00 mg/ml), pyrene-*d*₁₀ (0.89 mg/ml), benz[*a*]anthracene-*d*₁₂ (0.73 mg/ml), chrysene-*d*₁₂ (0.73 mg/ml), benzo[*a*]pyrene-*d*₁₂ (0.24 mg/ml), perylene-*d*₁₂ (0.54 mg/ml), and benzo[*ghi*]perylene-*d*₁₂ (0.91 mg/ml). When no deuterated analog of a PAH was available, the *d*-PAH with the closest molecular structure was used (e.g., benzo[*a*]pyrene-*d*₁₂ was used as the internal standard for benzo[*e*]pyrene, the parent *d*-PAH was used as the internal standard for the related alkyl PAHs).

While most parent PAHs (and many of their perdeuterated

analogs) are available as pure standards, few alkyl PAHs are available, so their response must be estimated rather than measured in many cases. The calibration and quantitation of the more highly alkylated PAHs is increasingly complicated by the fact that a single group can have multiple (even hundreds for C₃- and C₄-alkyl PAHs) of alkylated isomers that are listed as a single PAH in the total 34 PAH list. Finally, the MS response of different isomers will vary. In an effort to best determine and estimate the alkyl PAH response factors, we determined the GC/MS response (vs the appropriate parent *d*-PAH) of every alkyl PAH available as pure standards from commercial sources (Table 1). This attempt was complicated by the fact that stated purities of several of the alkyl PAHs were not accurate. Therefore, each of the alkyl PAHs we obtained from commercial sources was analyzed by GC with flame ionization detection to determine its purity and by GC/MS to determine if its mass spectrum was consistent with its reported identity. The chemical purity of the 22 alkyl PAHs tested ranged from approximately 70 to 98%, and these purities were used to correct their response factors. When no standard was available for a particular group of alkyl isomers, the response factor was estimated on the basis of the closest analogous isomers (Table 1).

All GC/MS quantitations of the sediment PAH concentrations were based on daily three-point calibration curves containing the parent and alkyl PAH standard compounds. All analyses were performed with an Agilent model 5973 GC/MS (Agilent Technologies, Wilmington, DE, USA) operated in the selected ion mode for the molecular ions of the target PAHs and *d*-PAHs and equipped with a 60-m Agilent HP-5 MS column (0.25-µm film thickness, 250-µm i.d.). The oven temperature was held at 100°C during the injection, then programmed at 6°C per min to 320°C (hold for 10 min). The possible presence of petroleum contaminants was routinely evaluated by monitoring an ion (*m/z* = 85) that is characteristic for petroleum alkanes.

Toxic unit calculations

According to the U.S. EPA protocol [1,2], risk from sediment PAHs to benthic organisms is based on the number of PAH TU freely dissolved in the sediment pore water. All PAHs are assumed to have the same toxicity (on a molar basis) in this model and differ only in their tendency to partition from sediment to pore water and from pore water to the organism. For sediment PAHs, K_{oc} and K_{lipid} partitioning coefficients (estimated from K_{ow} values as described by Di Toro et al. [2–4]) can be used to calculate the concentration of each PAH that represents one toxic unit (details are given in U.S. EPA [2]). The sediment concentrations (on a sediment organic carbon basis) of each PAH that represents one toxic unit are given in the Appendix and are fairly similar for all the PAHs. Toxic units are calculated simply by dividing each sediment PAH concentration by the related concentration that represents one toxic unit (Appendix) and by the organic carbon content of the sediment.

For the sediment samples, the concentrations of individual PAHs that represent one toxic unit are quite similar and range only from approximately 400 µg/g for lower-molecular-weight PAHs to approximately 1,100 µg/g for higher-molecular-weight PAHs (Appendix). Also, little change exists in the values for alkyl PAHs versus their parent PAH. In essence, the values for sediment PAHs are similar since the K_{oc} and K_{ow} values used to estimate the partitioning behavior of a particular

Table 1. Relative contributions of parent and alkyl polycyclic aromatic hydrocarbons (PAHs) from petroleum crude oil, diesel fuel, and manufactured gas plant (MGP)-contaminated sediments to total PAH concentrations

| | PAH concn. ($\mu\text{g/g}$) | | | | | GC/MS RRF ^b vs parent |
|--|--------------------------------|-----------------------------|-------------------------------|-------|-------|--|
| | Crude oil ^a | Diesel fuel ^a | MGP-contaminated sediments | | | |
| | | | HD-5 | HD-10 | HD-22 | |
| Naphthalene | 3.52 | 6.04 | 135 | 8.1 | 0.24 | 1.00 |
| 2-Methylnaphthalene | 27.18 | 20.75 | 86 | 7.6 | 0.14 | 0.55 |
| 1-Methylnaphthalene | 10.29 | 16.90 | 50 | 4.4 | 0.07 | 0.54 |
| C2 Naphthalenes | 96.94 | 154.64 | 134 | 10.0 | 0.56 | 0.34 |
| C3 Naphthalenes | 100.21 | 222.40 | 61 | 4.6 | 0.46 | 0.31 |
| C4 Naphthalenes | 100.23 | 160.59 | 23 | 2.2 | 0.37 | 0.25 |
| Acenaphthylene | 0.48 | 0.32 | 16 | 2.4 | 0.28 | 1.00 |
| Acenaphthene | 0.43 | 0.22 | 63 | 5.8 | 0.07 | 1.00 |
| Fluorene | 1.04 | 4.29 | 37 | 4.1 | 0.09 | 1.00 |
| C1 Fluorenes | 8.47 | 21.23 | 42 | 4.3 | 0.44 | 0.49 |
| C2 Fluorenes | 23.79 | 33.45 | 40 | 3.2 | 0.45 | 0.40 |
| C3 Fluorenes | ND ^d | ND | ND | ND | ND | 0.25 |
| Phenanthrene | 2.65 | 9.81 | 119 | 12.6 | 0.56 | 1.00 |
| Anthracene | ND | 0.49 | 65 | 4.4 | 0.38 | 1.00 |
| C1 Phenanthrenes/anthracenes | 32.96 | 42.31 | 155 | 14.8 | 1.03 | 0.40 |
| C2 Phenanthrenes/anthracenes | 134.72 | 147.36 | 180 | 23.0 | 3.31 | 0.16 |
| C3 Phenanthrenes/anthracenes | 148.31 | 99.93 | 72 | 10.6 | 1.95 | 0.15 |
| C4 Phenanthrenes/anthracenes | 99.40 | 46.92 | 13 | ND | ND | 0.14 |
| Fluoranthene | 0.07 | 0.01 | 75 | 9.9 | 1.07 | 1.00 |
| Pyrene | 0.27 | 0.24 | 77 | 10.1 | 1.00 | 1.00 |
| C1 Fluoranthenes/pyrenes | 4.38 | 2.07 | 130 | 16.8 | 1.46 | 0.45 |
| Benz[<i>a</i>]anthracene | 0.12 | 0.01 | 35 | 4.5 | 0.50 | 1.00 |
| Chrysene | 0.50 | 0.07 | 33 | 4.8 | 0.71 | 1.00 |
| C1 Benz[<i>a</i>]anthracenes/chrysenes | 4.25 | 4.89 | 65 | 13.4 | 1.27 | 0.47 |
| C2 Benz[<i>a</i>]anthracenes/chrysenes | 83.34 | 5.01 | 107 | 21.4 | 2.32 | 0.25 |
| C3 Benz[<i>a</i>]anthracenes/chrysenes | 82.58 | ND | 128 | ND | ND | 0.20 |
| C4 Benz[<i>a</i>]anthracenes/chrysenes | 32.71 | ND | 121 | ND | ND | 0.15 |
| Benzo[<i>b+k</i>]fluoranthene ^c | 0.11 | 0.01 | 23 | 4.0 | 0.69 | 1.00 |
| Benzo[<i>e</i>]pyrene | 0.04 | 0.02 | 11 | 2.4 | 0.36 | 1.00 |
| Benzo[<i>a</i>]pyrene | 0.06 | ND | 34 | 4.0 | 0.54 | 1.00 |
| Perylene | 0.85 | ND | 7 | 1.3 | 0.72 | 1.00 |
| Indeno[1,2,3- <i>cd</i>]pyrene | 0.03 | ND | 41 | 10.9 | 1.05 | 1.00 |
| Dibenz[<i>a,h</i>]anthracene | 0.03 | ND | 9 | 2.0 | 0.18 | 1.00 |
| Benzo[<i>ghi</i>]perylene | 0.04 | ND | 17 | 4.1 | 0.46 | 1.00 |

^a Crude oil and diesel fuel PAH concentrations were normalized to a total sediment concentration of 1,000 $\mu\text{g/g}$ to allow comparison with PAH concentrations on the MGP-contaminated sediments. A sediment organic carbon content of 1% was assumed to calculate the toxic units for sediment contaminated with the crude oil at a total PAH concentration of 1,000 $\mu\text{g/g}$.

^b All relative response factors (RRFs) are based on the gas chromatography/mass spectrometry (GC/MS) peak area per ng of the alkyl PAH in a standard solution compared to that of its parent PAH as determined by GC/MS. The relative response factors of alkyl PAHs for which no standards were available were estimated on the basis of the closest analogous alkyl PAH. Alkyl PAHs used to determine the GC/MS relative response factors included alkyl naphthalenes (1-methyl-, 2-methyl-, 1, 2-dimethyl-, 1,3-dimethyl-, 1, 8-dimethyl-, 2,7-dimethyl- and 1-ethyl-, 2-ethyl-, 1,4,5-trimethyl-, 2, 3, 5-trimethyl-, and 2-isopropyl-); 1-methylfluorene; 2-methyl- and 9-methylanthracene, 1-methyl-, 2-methyl-, and 3-methylphenanthrene, 9,10-dimethylanthracene; 2-ethylanthracene; 2-tertbutylanthracene; 1-methyl-7-isopropylphenanthrene; 1-methylpyrene; 7-methylbenz[*a*]anthracene; and 7,12-dimethylbenz[*a*]anthracene. Relative response factors for alkyl phenanthrenes/anthracenes, alkyl fluoranthenes/pyrenes, and alkyl benz[*a*]anthracenes/chrysenes are compared to phenanthrene.

^c Benzo[*b*]fluoranthene and benzo[*k*]fluoranthene are reported as their sum because of insufficient chromatographic resolution.

^d ND = not detected.

PAH from sediment to water and then from water to the organism increase in a similar manner with PAH size and thus tend to cancel each other out for determining the sediment concentration that represents one toxic unit [2].

Analysis of variance

The variance in the TU uncertainty factor was evaluated using an unconditional hierarchical random effects model [12]. Both sample location and site were treated as random variables,

and the 95 and 99% confidence intervals were estimated using the unconditional mean model [13].

RESULTS AND DISCUSSION

Determining alkyl PAH and total PAH concentrations

The determination of total PAHs has largely been defined by the analysis method used to measure individual PAHs. Frequently, the total PAH concentration reported for a sample has been based on the sum of the 16 individual priority pollutant

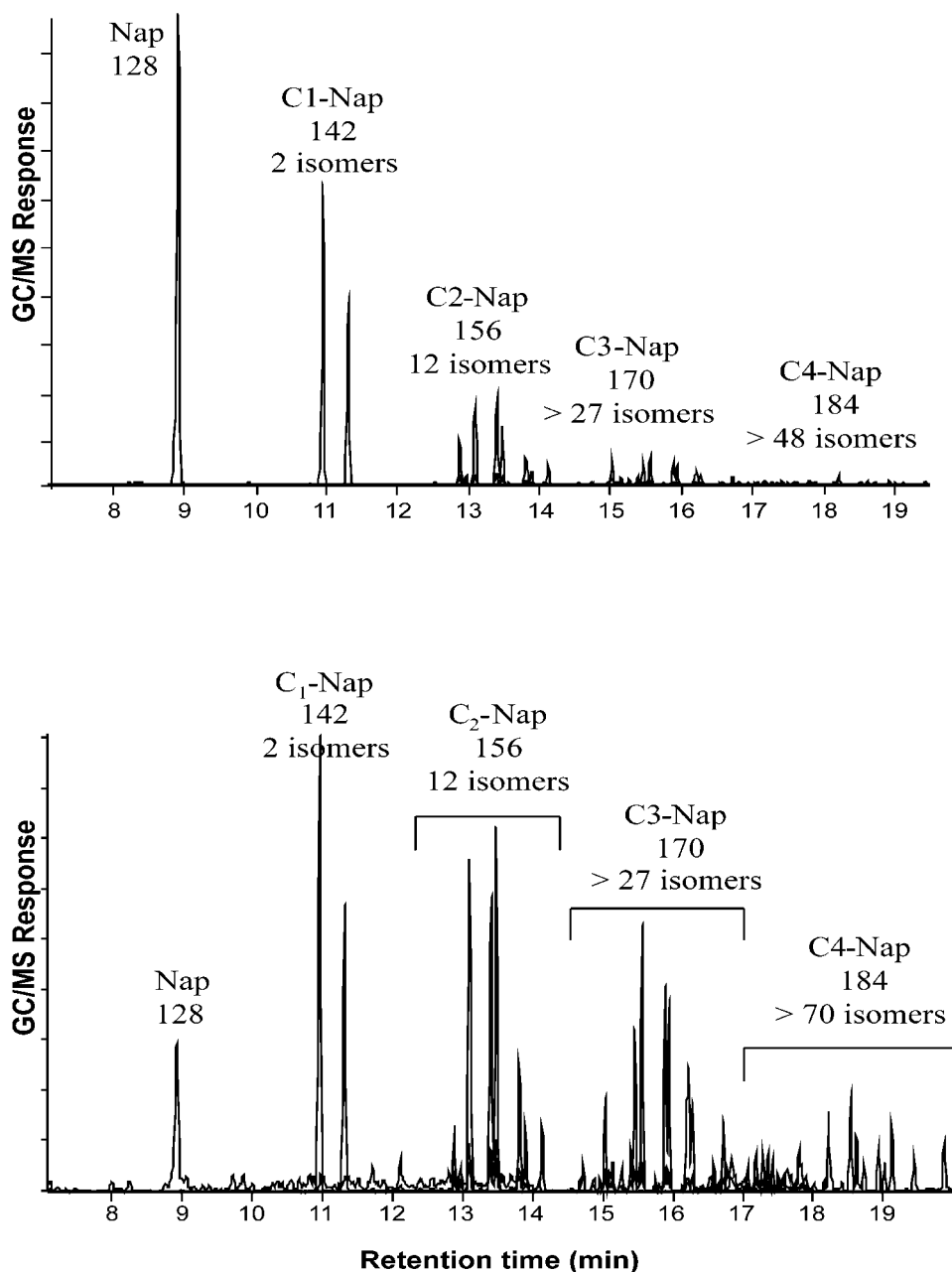


Fig. 1. Naphthalene and alkyl naphthalene distributions in pyrogenic polycyclic aromatic hydrocarbons (PAHs) from manufactured gas plant tar (top) and petrogenic PAHs from petroleum crude oil (bottom). GC/MS = gas chromatography/mass spectrometry.

PAHs determined by U.S. EPA Method 8310. For pyrogenic sources of PAHs (e.g., MGP processes), the parent PAHs are the predominant species, and the sum of the 16 U.S. EPA PAHs has been reported to represent about one-third to two-thirds of the actual total PAH concentrations [14]. In contrast, PAHs from petrogenic sources (e.g., petroleum) are dominated by alkyl derivatives [6–8], as shown by a comparison of MGP tar and petroleum crude oil (NIST Standard Reference Material 1582) in Figure 1 for the simplest case: naphthalene and its alkyl derivatives.

Two features are notable in Figure 1. First, the parent naphthalene dominates the pyrogenic MGP tar profile, while the alkyl derivatives of naphthalene dominate the petrogenic crude oil profile. In addition, the complicated nature of determining the concentration of one group of alkyl isomers is made apparent by the large number of individual compounds that con-

stitute a single PAH group. For example, the petrogenic C4-naphthalene group contains more than 70 individual PAHs yet is reported only as a single compound in the total 34 PAH method. It should be noted that the alkyl naphthalenes represent the least number of possible isomers compared to the higher-molecular-weight PAHs. Therefore, the PAH concentrations reported for the 34 PAH method actually represent several hundred individual PAH compounds.

Additional care must also be taken to avoid including non-target compounds in the integration of a group of alkyl PAHs. For example, dibenzothiophene elutes at the end of the C4-naphthalene cluster and frequently has a higher concentration than the total C4-naphthalene group. Since both dibenzothiophene and C4-naphthalenes have m/z 184 as their molecular ion, care must be taken not to include the peak area of dibenzothiophene in the C4-naphthalene peak area. Similarly, the

Table 2. Relative contributions of parent and alkyl polycyclic aromatic hydrocarbons (PAHs) in petroleum crude oil, diesel fuel, and manufactured gas plant (MGP)-contaminated sediments by PAH ring number

| | Relative PAH concn. (% of total) | | | | | Relative PAH toxic units (% of total) | | | | |
|-------------------------------------|----------------------------------|--------------------------|----------------------------|-------|-------|---------------------------------------|-------------|----------------------------|-------|-------|
| | NIST crude oil | Diesel fuel | MGP-contaminated sediments | | | NIST crude oil | Diesel fuel | MGP-contaminated sediments | | |
| | | | HD-5 | HD-10 | HD-22 | | | HD-5 | HD-10 | HD-22 |
| 2-Ring | | | | | | | | | | |
| Parent | 0.4 | 0.6 | 6.1 | 3.5 | 1.1 | 0.7 | 1.0 | 10.5 | 6.3 | 2.1 |
| C1 to C4 alkyl | 33.5 | 57.5 | 15.9 | 12.4 | 7.0 | 43.4 | 64.0 | 21.3 | 17.3 | 9.9 |
| 3-Ring | | | | | | | | | | |
| Parent | 0.5 | 1.5 | 13.4 | 12.6 | 6.1 | 0.6 | 1.7 | 16.2 | 15.9 | 8.5 |
| C1 to C4 alkyl | 44.8 | 39.1 | 23.7 | 24.1 | 31.6 | 41.0 | 32.5 | 22.1 | 23.2 | 32.8 |
| 4-Ring | | | | | | | | | | |
| Parent | 0.1 | 0.0 | 9.8 | 12.6 | 14.4 | 0.1 | 0.0 | 8.9 | 11.8 | 14.8 |
| C1 to C4 alkyl | 20.7 | 1.2 | 24.7 | 22.3 | 22.2 | 14.1 | 0.8 | 16.8 | 17.2 | 18.8 |
| 5+6-Ring | | | | | | | | | | |
| Parent | 0.1 | 0.0 | 6.4 | 12.4 | 17.6 | 0.1 | 0.0 | 4.1 | 8.2 | 13.2 |
| | PAH concn. ($\mu\text{g/g}$) | | | | | PAH toxic units | | | | |
| | NIST crude oil ^a | Diesel fuel ^a | MGP-contaminated sediments | | | NIST crude oil | Diesel fuel | MGP-contaminated sediments | | |
| | | | HD-5 | HD-10 | HD-22 | | | HD-5 | HD-10 | HD-22 |
| Total U.S. EPA 34 PAHs ^b | 1,000 | 1,000 | 2,232 | 232 | 22.7 | 138 | 159 | 333 | 33.4 | 2.96 |
| Total U.S. EPA 13 PAHs | 9.4 | 21.5 | 711 | 75 | 6.1 | 1.9 | 4.3 | 125 | 12.2 | 0.88 |
| Total U.S. EPA 16 PAHs | 9.3 | 21.5 | 779 | 92 | 7.8 | 2 | 4.3 | 131 | 13.7 | 1.03 |
| Total parent PAHs | 10.2 | 21.5 | 797 | 95 | 8.9 | 2 | 4.3 | 133 | 14.1 | 1.14 |
| % Parent vs total | 1.0% | 2.2% | 35.7% | 41.2% | 39.2% | 1.4% | 2.7% | 39.8% | 42.3% | 38.6% |

^a Crude oil and diesel fuel concentrations and toxic units were based on assuming a sediment concentration of 1,000 $\mu\text{g/g}$ (total 34 PAHs) and a sediment organic concentration of 1 wt % . NIST = National Institute of Standards and Technology (Gaithersburg, MD, USA).

^b Total 34 PAHs is the sum of the 18 parent PAHs and the 16 groups of alkyl PAHs listed in U.S. EPA [2], total 13 PAHs is the sum of the 13 parent PAHs used for sediment surveys as described in U.S. EPA [2], total 16 PAHs is the sum of the 16 U.S. EPA priority pollutant PAHs, and the total parent PAHs is the sum of the 18 parent PAHs determined in the total 34 PAH method.

deuterated internal standard, fluorene- d_{10} , elutes in the middle of the C3-alkylnaphthalene cluster and has an approximately 15% ion at m/z 170, which is the same mass as monitored to determine the C3-alkylnaphthalene compounds. For the majority of the samples in the present study, this interfering peak from fluorene- d_{10} was substantially larger than the total C3-alkylnaphthalene peaks, and therefore, care was needed to remove its peak area to avoid grossly overestimating the C3-alkyl naphthalene concentrations. Careful monitoring of secondary confirmatory ions can help avoid such misidentifications [9]. In addition, we routinely analyzed representative extracts in the full MS scan mode and confirmed individual peak identities on the basis of their full mass spectra.

Calibration for alkyl PAHs

The method for determining the 34 PAHs includes a calibration standard for only five out of the 16 groups of alkyl PAHs measured by the method. For the remaining alkyl PAHs, the GC/MS response factor for the parent PAH is used; that is, the response factor of the alkyl PAH compared to the parent is assumed to be 1.0 [2,9]. Unfortunately, this approach can yield substantial errors in the concentrations of the more highly alkylated PAHs. As shown in Table 1, the C3 and C4 alkyl PAHs have GC/MS responses of only approximately 15 to 25% of their related parent PAH. Thus, using the response factor of the parent PAH for an alkyl PAH will underestimate the concentration of C3 and C4 alkyl PAHs by a factor of four to seven. Since the pyrogenic PAHs have very low concentrations of highly alkylated PAHs, this inaccuracy does not

greatly affect the total concentrations or TU reported. However, for petrogenic PAHs, the use of appropriate response factors for alkylated PAHs is necessary to obtain reasonable total PAH concentrations and TU values as discussed here. In the absence of appropriate alkyl PAH calibration compounds, the values in Table 1 could be used to improve the estimate of alkyl PAH concentrations.

Alkyl PAHs from petrogenic and pyrogenic sources

A quantitative comparison of petrogenic and pyrogenic PAH distributions is given in Tables 1 and 2 for the petroleum crude oil, diesel fuel, and three representative MGP sediments that are contaminated with low, medium, and high levels of pyrogenic PAHs. All samples were analyzed to determine the total PAHs based on the 34 alkyl and parent PAH list, the 18 parent PAHs in the 34 list, and the 16 U.S. EPA priority pollutant PAHs. The number of TU (as calculated by the U.S. EPA's narcosis model [2]) was also determined for each sample.

For the crude oil, only 1% of the total 34 PAH concentration and 1.4% of the total TU are contributed by the 18 parent PAHs on that list, while the 16 groups of alkyl isomers account for approximately 99% of the total 34 PAH concentrations and TU. (Note that the 34 PAH method does not include any alkyl derivatives of five- and six-ring PAHs.) Similarly, the parent PAHs accounted for only 2.2% of the total 34 PAH concentrations and 2.7% of the total TU in diesel fuel (Table 2). In contrast, the parent PAHs in the pyrogenic MGP samples account for 35 to 42% of the total PAH concentrations and TU.

Table 3. Underestimation of alkyl polycyclic aromatic hydrocarbons alkyl PAH concentrations and toxic units using parent PAH response factors for alkyl PAH calibration. MGP = manufactured gas plant; NIST = National Institute of Standards and Technology (Gaithersburg, MD, USA)

| | NIST crude oil | Diesel fuel | MGP-contaminated sediments | | |
|---|-------------------|----------------|----------------------------|-------|-------|
| | | | HD-5 | HD-10 | HD-22 |
| Total 34 PAH concn. ($\mu\text{g/g}$) | | | | | |
| Based on measured RRFs ^a | 1,000 | 1,000 | 2,232 | 232 | 22.7 |
| Based on assumed RRFs ^b | 250 | 293 | 1,240 | 141 | 13 |
| Ratio assumed vs measured RRFs | 25% | 29% | 56% | 61% | 57% |
| Total 34 PAH toxic units | | | | | |
| Based on measured RRFs ^a | 138 | 159 | 333 | 33.4 | 2.96 |
| Based on assumed RRFs ^b | 38 | 49 | 61 | 7.2 | 0.59 |
| Ratio assumed vs measured RRFs | 27% | 31% | 61% | 63% | 57% |

^a Alkyl PAH concentrations are based on relative response factors (RRFs) from Table 1.

^b Alkyl PAH concentrations are based on parent PAH relative response factors as suggested in reference [9].

It should be noted that different crude oil sources and the degree of weathering will affect the fraction of alkyl PAHs, and the alkyl fraction of 99% for NIST crude oil is only a representative value. However, it remains true that petrogenic PAHs are still highly dominated by alkyl PAHs regardless of the petroleum source or degree of weathering [15,16]. Clearly, any error in measuring alkyl PAH concentrations more profoundly affects the calculation of TU for the petrogenic crude oil than for the sediments contaminated with the pyrogenic MGP PAHs.

As described previously, the alkyl PAH concentrations were based on determining the GC/MS response factors using 22 standard alkyl isomers. However, the National Oceanic and Atmospheric Administration method [9] that is the basis for the 34 PAH determinations states, "The response factor of the alkyl homologues was assumed to be equal to that of respective unsubstituted parent compounds." In order to determine the effect of this assumption on alkyl PAH concentrations and TU compared to the concentrations based on our experimentally determined response factors, we redetermined the total concentrations and TU for the same four samples by using the National Oceanic and Atmospheric Administration suggested assumption. As shown in Table 3, using the assumption that the alkyl PAH response factors are the same as the parent PAH underestimated the actual total PAH concentrations and TU by a factor of four for the crude oil and by a factor of three for the diesel fuel. For the MGP sediments, the error is not so great, but the concentrations and TU are underestimated by about 40% by using the parent response factors to calibrate for the alkyl PAHs. These discrepancies lead to substantial underestimation of the alkyl PAH concentrations and related

TU and will certainly lead to incompatible data among different laboratories, particularly for petrogenic PAHs.

These results also demonstrate the need to carefully evaluate historical total PAH data in the context of the analytical method used and the source of PAHs (whether pyrogenic or petrogenic). For example, the determination of the so-called total PAHs in the United States has often been based on the sum of the 16 priority pollutant PAHs listed by the U.S. EPA. If two sediments were contaminated at an actual total PAH concentration of 1,000 mg/kg with a petrogenic source such as the petroleum crude oil and a pyrogenic source of PAHs such as MGP processes, the total PAH concentrations reported based on the 16 priority pollutant PAHs would be very different. Based on the results in Table 2, the total concentration reported based on the U.S. EPA's priority pollutant PAH method would be fairly reasonable for the MGP-contaminated sample, that is, approximately 350 mg/kg versus the true value of 1,000 mg/kg. However, the value reported for crude oil and diesel-contaminated samples would be only 10 and 20 mg/kg, respectively, rather than the true value of 1,000 mg/kg. These results support the recent report that the ecological risks of PAHs at petroleum-contaminated sites are underestimated because of the reliance on PAH data based only on the U.S. EPA's 16 priority pollutant PAHs [7].

Correlation of parent and alkyl PAH concentrations for MGP site sediments

The PAH concentrations of the 45 sediments are summarized in Table 4. The sediments used in this study ranged from coarse sand to soft organic muck having total organic carbon values from 0.6 to 11 wt %. Total 34 PAH concentrations

Table 4. Summary of 45 sediment characteristics; TOC = total organic carbon

| Sample location (all USA) | No. of sediments | Total 34 PAH concn. ($\mu\text{g/g}$) | | Total 34 PAH toxic units | | Range in TOC, (wt %) |
|------------------------------|---------------------|--|--------|-----------------------------|--------|-------------------------|
| | | Range | Median | Range | Median | |
| Hudson River | 13 | 23–11,400 | 232 | 0.9–512 | 4.2 | 1.8–10.3 |
| Lower Hudson River | 5 | 197–1,010 | 307 | 10.–49 | 15 | 2.7–3.4 |
| Oneonta, NY | 4 | 107–1,040 | 530 | 3.5–24 | 9 | 3.1–11.0 |
| Boston, MA | 5 | 76–515 | 130 | 1.9–7.7 | 2.9 | 5.1–9.3 |
| Plattsburgh, NY | 8 | 16–3,430 | 235 | 0.5–137 | 22 | 0.7–6.5 |
| Troy, NY | 10 | 10–2,290 | 323 | 0.7–122 | 20 | 0.6–4.8 |

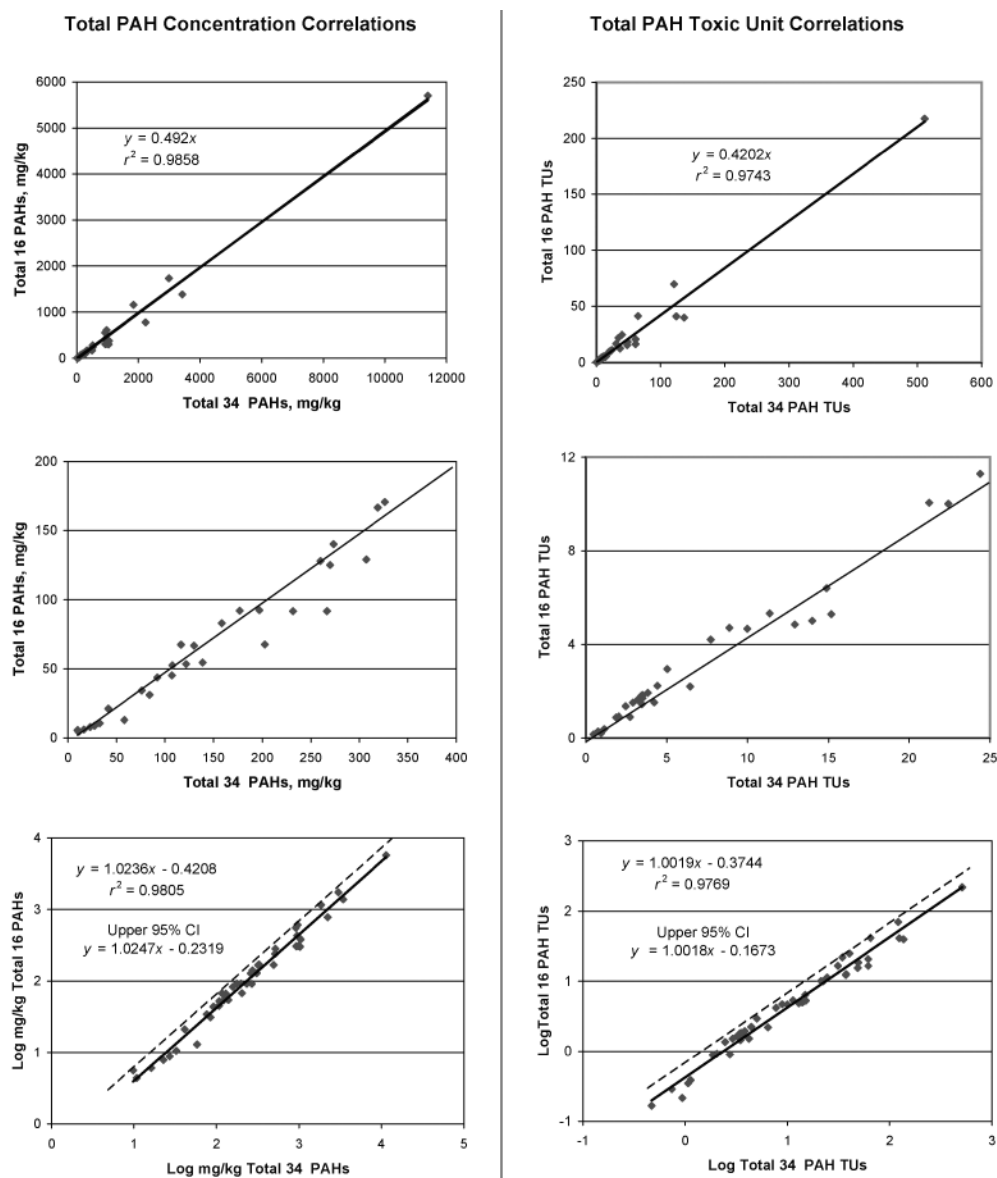


Fig. 2. Comparison of polycyclic aromatic hydrocarbon (PAH) concentrations (left side) and toxic units (right side) based on total 34 (alkyl and parent) PAHs and total 16 parent PAHs in 45 sediment samples from manufactured gas plant sites. The top two plots show linear correlations, with the center two plots showing an expanded scale of the top two plots. The bottom two plots show log-log correlations and the 95% upper confidence intervals (CI). TU = toxic units.

ranged from 10 to 11,400 $\mu\text{g/g}$, representing the range of near-ambient background concentrations to highly impacted. The individual PAH concentration reproducibility for replicate extractions and analyses of the sediments showed relative standard deviations typically 10 to 30% for quadruplicate samples. Several of the sediments had particles of pitch, bricks, and other residuals of the historic MGP industrial processes that contributed to the sediment heterogeneity.

As noted previously, the list of parent PAHs reported by various methods are not the same. The 34 PAH method includes the 18 parent PAHs listed in Table 1. The U.S. EPA's 16 priority pollutant PAHs include the same parent PAHs, with the exclusion of benzo[*e*]pyrene and perylene. Similarly, the 13 PAHs historically reported in sediment surveys [2] exclude those same two PAHs as well as indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene, and benzo[*ghi*]perylene. Fortunately, the concentrations of these excluded PAHs is typically low com-

pared to the remaining parent PAHs, and their exclusion has little effect on either the total PAH concentrations or TU for either pore water or sediment as shown in Table 2. Therefore, the following discussions, unless otherwise noted, will be based on the 16 parent PAHs that are reported by the U.S. EPA's priority pollutant method. However, the same discussions apply whether the 18 or 13 parent PAHs are considered.

Even though the PAH concentrations found in the 45 sediments ranged over three orders of magnitude, the relative concentrations of alkyl versus parent PAHs remained quite constant for the sediment samples, as shown in the left side of Figure 2. The correlation coefficient (r^2) of the total 34 PAH concentrations with the sum of the 16 priority pollutant PAHs was 0.99 on a linear basis and 0.98 on a log basis. Similarly, the correlation of the TU calculated from the total 34 PAHs with the TU calculated only from the 16 parent PAHs is very high ($r^2 = 0.97$ on a linear basis and 0.98 on a log basis), as

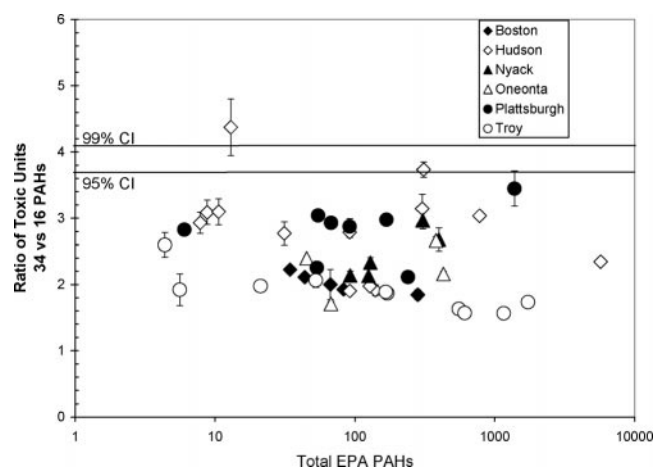


Fig. 3. Ratio of total toxic units based on the total 34 parent and alkyl polycyclic aromatic hydrocarbons (PAHs) compared to the total 16 parent PAHs for 45 sediments from manufactured gas plant sites, USA. CI = confidence intervals.

shown on the right side of Figure 2. (Note that the center plots on Fig. 2 use the same regression line as the top plots but only expand the axes so that the less contaminated samples can be observed.) Based on the strong correlations shown in Figure 2, a reasonable estimate of the total 34 PAH concentrations can be made for these 45 sediments by simply dividing the sum of the 16 parent PAH concentrations by the slope of the linear regression line (0.49).

Estimating toxic units from parent PAH concentrations

As shown in Figure 2, strong correlations exist between the sediment and pore-water TU calculated from the 34 alkyl and parent PAHs and those calculated from the 16 priority pollutant parent PAHs, indicating that predictions of total TU from only parent PAH data may be valid. In order to determine the accuracy of using parent PAHs to estimate the TU based on the 34 alkyl and parent PAHs, uncertainty factors were calculated for the total 34 PAH TU and for those based on the 16 parent PAHs for sediments from each sample site and sample location. As shown in Figure 3, the ratio of the TU from the 34 PAHs and the 16 PAHs were fairly similar for all 45 sediments from the six sites regardless of the level of contamination. A few samples exhibited higher ratios resulting from a greater con-

tribution of alkylated PAHs associated with petroleum products used at the site. The presence of some petroleum contamination in these sediments was confirmed by GC/MS identification of petroleum alkanes in their extracts.

To further understand the sources of variability in the ratio of TU measured using 34 PAHs and 16 PAHs, an analysis of variance was conducted. This analysis demonstrated that both the sample location within a site and the location of the MGP site contributed significantly to the variability of the ratio. Approximately 36, 60, and 4%, respectively, of the variance was attributed to the MGP site location, sample location within the MGP site, and the replicate analysis of individual sediment samples.

As discussed earlier, data from 488 sediments was used by the U.S. EPA to determine that the number of total TU can be estimated within the 95% confidence interval by multiplying the number of TU calculated from the measurement of 13 parent PAHs (Table 1) by 11.5 [2]. However, the uncertainty factors calculated for the sites in the present study were considerably lower than that determined in the assessment of 488 samples by the U.S. EPA (Table 5), and the overall mean for the ratio of TU calculated from the measurement of 34 PAHs and 13 PAHs calculated in our study (2.9) compared favorably to that estimated in the study referenced by the U.S. EPA (2.8) [2]. The variability in the ratio was much smaller for MGP sites as evidenced by the lower values of upper 95 and 99% confidence intervals (4.2 and 4.6, respectively) compared to those reported by the U.S. EPA (11.5 and 16.9). The variability for total PAH concentrations is essentially the same as those shown in Table 5 for total TU; that is, the upper 95 and 99% confidence intervals for estimating the total 34 PAH concentrations were 3.5 and 3.9 for the 16 parent PAHs and 4.2 and 4.7 for the 13 parent PAHs. Based on these results and those shown in Figures 2 and 3, it seems reasonable to estimate total PAH concentrations and TU from the measurement of parent PAHs for sediments at sites known to be contaminated from MGP processes. However, it should be noted that any significant petroleum contamination could invalidate these estimates by increasing the proportion of alkyl PAHs relative to parent PAHs. As noted in the *Experimental* section, we routinely monitored petroleum alkanes in these samples, and no significant petroleum contamination was found at these MGP sites.

Table 5. Uncertainty factors for toxic units based on total 34 polycyclic aromatic hydrocarbons (PAHs) compared to 16 parent PAHs and 13 parent PAHs; CL = confidence limit

| | <i>n</i> ^c | 34 PAHs vs 16 parent PAHs ^a | | | 34 PAHs vs 13 parent PAHs ^b | | |
|--------------------|-----------------------|--|--------------|--------------|--|--------------|--------------|
| | | Mean | 95% upper CL | 99% upper CL | Mean | 95% upper CL | 99% upper CL |
| All sites (USA) | 45 | 2.5 | 3.6 | 4.0 | 2.9 | 4.2 | 4.6 |
| Hudson River | 13 | 2.9 | 4.2 | 4.7 | 3.5 | 4.9 | 5.4 |
| Lower Hudson River | 5 | 2.5 | 3.2 | 3.4 | 2.9 | 3.4 | 3.6 |
| Oneonta, NY | 4 | 2.2 | 3.0 | 3.3 | 2.5 | 3.3 | 3.5 |
| Boston, MA | 5 | 2.0 | 2.3 | 2.4 | 2.5 | 2.9 | 3.0 |
| Plattsburgh, NY | 8 | 2.7 | 3.6 | 3.9 | 3.1 | 6.3 | 4.2 |
| Troy, NY | 10 | 1.9 | 2.5 | 2.6 | 2.2 | 3.0 | 3.2 |

^a Toxic units based on the determination of 34 alkyl and parent PAHs versus the U.S. Environmental Protection Agency's 16 priority pollutants; PAHs determined by Method 8310 (<http://www.epa.gov/SW-846/pdfs/8310.pdf>).

^b Toxic units based on the determination of 34 alkyl and parent PAHs versus the 13 parent PAHs used for correlation in U.S. EPA [2].

^c Number of individual sediments from each site. Each sediment was analyzed in quadruplicate.

CONCLUSION

The accurate measurement of alkyl PAHs necessary to determine the total 34 PAH TU required for the U.S. EPA's narcosis risk model is hampered by the complex nature of the alkyl PAH distributions and by the lack of suitable standard alkyl PAH compounds. Assumptions made by different laboratories for alkyl PAH response factors will affect the reported concentrations (and associated TU), and the assumption that alkyl PAHs have the same GC/MS response factor as their parent PAH can result in an underestimation of total PAH concentrations and TU by as much as 75% for PAHs from petrogenic sources. The current approach of using the related parent PAH as a calibration standard results in artificially low values for the more highly alkylated PAHs, especially for petrogenic PAHs, since they are dominated by alkyl PAHs much more than pyrogenic PAHs. Since most historical sediment data includes only parent PAHs, predictive correlations are needed to estimate total TU from existing data. Although a high amount of uncertainty is associated with predicting the total PAH TU based on the measure of only parent PAHs for sediments contaminated from various PAH sources [2], the present study demonstrates that the uncertainty can be greatly reduced when the sediments are collected from areas containing primarily pyrogenic PAHs, such as those associated with MGP sites.

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Appendix. Polycyclic aromatic hydrocarbon (PAH) toxic units and detection limits

| | Concn. for one toxic unit ($\mu\text{g/g OC}$) | Target detection limit ^a ($\mu\text{g/g sediment}$) | Method detection limit ($\mu\text{g/g sediment}$) |
|--|--|--|---|
| Naphthalene | 385 | 0.11 | 0.001 |
| 2-Methylnaphthalene | 444 | 0.13 | 0.001 |
| 1-Methylnaphthalene | 444 | 0.13 | 0.001 |
| C2 Naphthalenes | 510 | 0.15 | 0.005 |
| C3 Naphthalenes | 581 | 0.17 | 0.01 |
| C4 Naphthalenes | 657 | 0.19 | 0.01 |
| Acenaphthylene | 452 | 0.13 | 0.001 |
| Acenaphthene | 491 | 0.14 | 0.001 |
| Fluorene | 538 | 0.16 | 0.001 |
| C1 Fluorenes | 611 | 0.18 | 0.005 |
| C2 Fluorenes | 686 | 0.20 | 0.01 |
| C3 Fluorenes | 769 | 0.23 | 0.03 |
| Phenanthrene | 596 | 0.18 | 0.001 |
| Anthracene | 594 | 0.17 | 0.001 |
| C1 Phenanthrenes/anthracenes | 670 | 0.20 | 0.005 |
| C2 Phenanthrenes/anthracenes | 746 | 0.22 | 0.01 |
| C3 Phenanthrenes/anthracenes | 829 | 0.24 | 0.02 |
| C4 Phenanthrenes/anthracenes | 913 | 0.27 | 0.03 |
| Fluoranthene | 707 | 0.21 | 0.001 |
| Pyrene | 697 | 0.21 | 0.001 |
| C1 Fluoranthenes/pyrenes | 770 | 0.23 | 0.005 |
| Benz[<i>a</i>]anthracene | 841 | 0.25 | 0.002 |
| Chrysene | 844 | 0.25 | 0.002 |
| C1 Benz[<i>a</i>]anthracenes/chrysenes | 929 | 0.27 | 0.01 |
| C2 Benz[<i>a</i>]anthracenes/chrysenes | 1,008 | 0.30 | 0.03 |
| C3 Benz[<i>a</i>]anthracenes/chrysenes | 1,112 | 0.33 | 0.05 |
| C4 Benz[<i>a</i>]anthracenes/chrysenes | 1,214 | 0.36 | 0.08 |
| Benzo[<i>b+k</i>]fluoranthene ^b | 980 | 0.29 | 0.002 |
| Benzo[<i>e</i>]pyrene | 967 | 0.28 | 0.002 |
| Benzo[<i>a</i>]pyrene | 965 | 0.28 | 0.002 |
| Perylene | 967 | 0.28 | 0.002 |
| Indeno[1,2,3- <i>cd</i>]pyrene | 1,115 | 0.33 | 0.002 |
| Dibenz[<i>a,h</i>]anthracene | 1,123 | 0.33 | 0.002 |
| Benzo[<i>ghi</i>]perylene | 1,094 | 0.32 | 0.002 |

^a Target detection limits for both sediment and pore water are 1/34th of the concentration of each individual PAH that corresponds to one toxic unit as described in U.S. EPA [2]. Sediment values are based on 1% OC (organic carbon).

^b Benzo[*b*]fluoranthene and benzo[*k*]fluoranthene are reported as their sum because of insufficient chromatographic resolution.