Bull. Environ. Contam. Toxicol. (2006) 76:791–798
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DOI: 10.1007/s00128-006-0989-8

Bulletin of Environmental Contamination and Toxicology

Bioavailability of Polycyclic Aromatic Hydrocarbons (PAHs) from Surficial Lake Erie Sediments

S. W. Pickard,[1] J. U. Clarke,[2] G. R. Lotufo[2]

[1] U. S. Army Corps of Engineers, 1776 Niagara Street, Buffalo, NY 14207, USA
[2] U. S. Army Engineer Research and Development Center, 3909 Halls Ferry Road, Vicksburg, MS 39180, USA

Received: 6 January 2006/Accepted: 8 March 2006

Polycyclic aromatic hydrocarbons (PAHs) are nonpolar, primarily coplanar organic compounds containing only carbon and hydrogen, and include at least two, 6-sided fused aromatic benzene rings. In the aquatic environment, PAH compounds are hydrophobic, adsorb to sediment particles and organic carbon, and tend to be persistent. They are bioaccumulative, and can elicit lethal and sublethal toxicity, including carcinogenicity (Neff et al. 2005). The carcinogenic potency of PAH compounds can be approximated by toxic equivalency factors (TEFs) (Safe 1998).

PAHs arise from the incomplete combustion of fossil fuels and garbage, and major stationary sources include petroleum refineries, wholesale trades in petroleum products and coal-fired electric generating plants. They are also found in crude oil, coal tar, creosote and asphalt. The primary inputs of PAHs to the US side of Lake Erie include fluvial transport of contaminated sediments from major cities along the south shore (Detroit, Cleveland and Buffalo) and the airborne deposition of contaminated dust. Total PAH concentrations in Lake Erie bottom sediments range from 0.22 to 5.3 mg/kg (Smirnov et al. 1998).

The bioavailability of sediment-sorbed PAHs determines their potential to bioaccumulate and elicit toxicity in the exposed organisms. Thus, knowledge regarding the bioavailability and bioaccumulation of sediment-associated PAHs is paramount in the assessment of ecological risk to the exposed biota. The bioavailability of sediment-associated PAHs is typically assessed by measuring bioaccumulation of those compounds in benthic organisms that dwell in bedded sediments and serve as vectors for trophic transfer in aquatic food webs (i.e., Schuler et al. 2003).

The objective of this investigation was to assess the bioavailability of PAH compounds in Lake Erie surficial sediments at two areas using a standard freshwater bioaccumulation test with the sediment aquatic feeding aquatic oligochaete worm, *Lumbriculus variegatus*.

Correspondence to: S. W. Pickard

Figure 1. Lake Erie sampling areas in US waters near Vermilion, OH, and Dunkirk, NY

MATERIALS AND METHODS

Sediment samples were collected in 2001 at two deepwater areas off the south shore of Lake Erie: one (13.7 to 14.0 m deep) located near Vermilion, OH, near the eastern end of the Central Basin, termed the Vermilion Lake Area (VLA), with the other (15.2 to 17.4 m deep) located near Dunkirk, NY, in the Eastern Basin, termed the Dunkirk Lake Area (DLA) (Figure 1). Both areas were situated within the lake's "South Zone" which receives diluted contaminated sediments through surface and bottom circulation from the ports at major US cities with some minor local influence (Smirnov et al. 1998). Surface grab sediment samples were collected using a Petite Ponar dredge sampler from four sites within each lake area, for a total volume of at least six L per site. Sediment samples were gathered in a stainless steel pan and homogenized. Equal volumes of the four discrete samples were combined and thoroughly mixed into a composite sample for use in the bioaccumulation testing. All samples were analyzed for PAH concentrations, total organic carbon (TOC) and particle size.

The 28-d *L. variegatus* bioaccumulation test was conducted according to guidelines provided in the USEPA/USACE Great Lakes Dredged Material Testing and Evaluation Manual (US Environmental Protection Agency [USEPA]/US Army Corps of Engineers [USACE] 1998). Worms were exposed to the composite sediment samples, in 6-L box aquaria (31.5 x 18 x 10.5 cm) using five replicates per treatment. Adequate exposure conditions were maintained using an intermittent flow system for overlying water renewal. At exposure termination, worms were recovered from the sediment, placed in water for gut purging (24 h), blotted dry and frozen for analyses.

Particle size analyses followed ASTM Procedure D422. USEPA SW-846 Method 8270C was used to quantify the standard 17 PAH compounds in sediment and tissue, and Method 9060 was used for TOC analysis (USEPA 1996). Sediment and tissue samples, including method blank, laboratory control spike and laboratory control spike duplicate were extracted with an Accelerated Solvent Extractor using a 50:50 solvent mixture of acetone and methylene chloride. Extracts were cleaned up using silica gel chromatography. Concentrated extracts were analyzed for PAHs using a Hewlett-Packard (HP) 5890 Gas Chromatograph with an HP Mass Selective Detector operating in a Selective Ion Monitoring mode. P-terphenyl-d_{14} was used as the surrogate recovery analyte for USEPA Method 8270C. Surrogate recoveries were as follows: DLA, sediment - range 60-72% (mean 64.3±3.3); tissue - range 33-96% (mean 63.0±16.7); VLA, sediment - range 61-146% (mean 110±25.8); tissue - range 59-103% (mean 81.5±11.9). Total tissue lipid content was determined using the chloroform/methanol extraction and colorimetric analyses according to Van Handel (1985).

Biota-Sediment Accumulation Factors (BSAFs) were calculated to quantify the bioavailability of sediment-associated PAH compounds (Ferraro et al. 1990):

$$\mathrm{BSAF} = \frac{C_t / L}{C_s / \mathrm{TOC}}$$

where C_t is the concentration of the PAH compound (μg/kg wet weight) and L is the concentration of lipid (percent of wet weight) in *L. variegatus* tissue at exposure termination, C_s is the concentration of the compound in sediment (μg/kg dry weight) and TOC is expressed as percent of dry weight.

PAH compound BSAFs were determined for each of the five experimental replicates per lake area, using the tissue concentrations and composite sample sediment concentration. Non-detects were valued at the laboratory reporting limit (LRL) to produce a maximum and most conservative BSAF. Lake area BSAFs were determined as the mean of each set of lake area replicates. BSAF uncertainty was estimated using standard error-based propagated error (PE) calculations for C_s and TOC from the discrete sediment samples, and lipid and C_t from the replicate tissue samples (Clarke and McFarland 2000).

RESULTS AND DISCUSSION

Concentrations of individual PAHs in the DLA composite sediment sample ranged from below the LRL (12 μg/kg) for acenaphthene, to 260 μg/kg for fluoranthene. In the VLA composite sediment sample, PAH concentrations ranged from below the LRL of 24 μg/kg for various compounds, to 158 μg/kg for benzo(b)fluoranthene. Total PAH concentration was 290 and 2,000 μg/kg at the VLA and DLA, respectively.

The physical sediment characteristics of the VLA and DLA were similar and composed of 99 and 84% silt/clay, with the remainder sand, respectively. TOC levels in the composite samples were 2.3 and 1.3% at the VLA and DLA, respectively. Tissue residues in *L. variegatus* exposed to the DLA composite sediment sample ranged from below LRL (0.46 µg/kg) for various compounds to 47 µg/kg for pyrene. At the VLA, PAH tissue concentrations ranged from 0.7 µg/kg for fluoranthene to 288 µg/kg for 2-methylnaphthalene. The majority of the PAH residues in the sediment and tissue samples were above detectable concentrations. Lipid levels in *L. variegatus* ranged from 1.0 to 1.5% (both for the DLA) and averaged 1.3% for both lake areas.

The mean PAH compound BSAFs (±PE) are summarized in Table 1. Mean BSAFs for the VLA ranged from 0.20±0.26 for fluoranthene to 4.2±8.6 for 2-methylnaphthalene, and the mean for all compounds was 1.0±0.28. For the DLA, mean BSAFs ranged from 0.0094±0.0086 for indeno(1,2,3-cd)pyrene to 0.21±0.16 for benzo(k)fluoranthene, and the mean for all compounds was 0.079±0.039. When compared to the DLA, the VLA PAH BSAFs were consistently higher, often by an order of magnitude, indicating a wide range of bioavailability in Lake Erie sediments.

Table 1. Mean PAH BSAFs (±PE) for the Vermilion and Dunkirk lake areas (n=5), with associated TEFs from Safe (1998)

PAH compound	TEF	Lake area	
		Vermilion, OH	Dunkirk, NY
2-Methylnaphthalene	0.001	4.2±8.6	0.11±0.17
Naphthalene	0.001	2.3±2.5	0.090±0.24
Acenaphthylene	0.001	0.46±0.26	0.048±0.019
Acenaphthene	0.001	0.70±0.39	0.041±0.027
Fluorene	0.001	0.77±0.44	0.027±0.050
Phenanthrene	0.001	0.61±0.98	0.019±0.027
Anthracene	0.01	0.58±0.43	0.026±0.85
Fluoranthene	0.001	0.20±0.26	0.047±0.071
Pyrene	0.001	0.30±0.35	0.17±0.26
Benzo(a)anthracene	0.1	0.36±0.43	0.17±0.19
Chrysene	0.01	0.42±0.47	0.11±0.12
Benzo(b)fluoranthene	0.1	0.52±0.64	0.087±0.071
Benzo(k)fluoranthene	0.1	0.63±0.78	0.21±0.16
Benzo(a)pyrene	1	0.62±0.81	0.16±0.15
Indeno(1,2,3-cd)pyrene	0.1	1.7±2.2	0.0094±0.0086
Dibenzo(a,h)anthracene	0.5	1.9±2.1	0.013±0.0094
Benzo(g,h,i)perylene	0.01	1.5±2.0	0.010±0.011
Mean BSAF		1.0±0.28	0.079±0.039

At the VLA, the highly hydrophobic and carcinogenic dibenzo(a,h)anthracene and B(a)P (Safe et al. 1998) were the 3rd and 9th most bioavailable PAHs (BSAFs = 1.9±2.1 and 0.62±0.81), respectively. The same compounds ranked 15th and 4th, respectively (BSAFs = 0.013±0.0094 and 0.16±0.15), at the DLA.

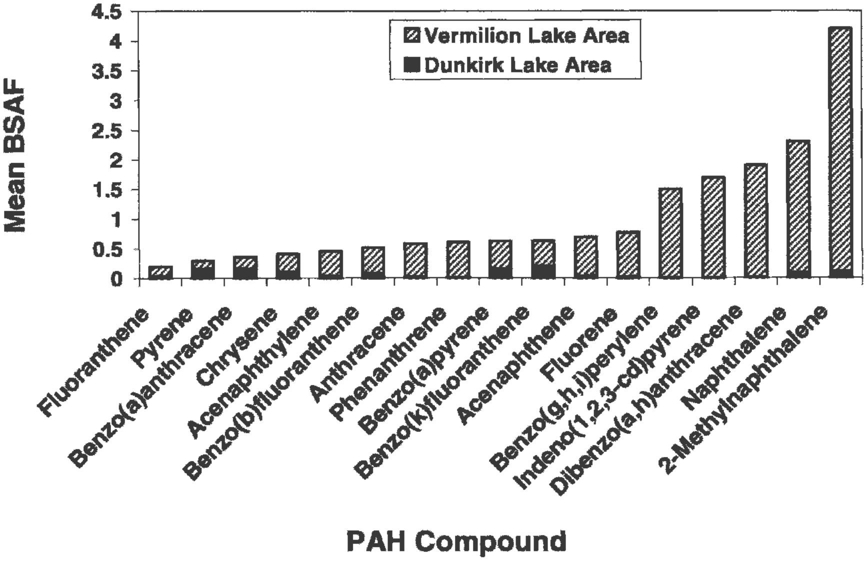

Figure 2. Bar graph of mean PAH compound BSAFs for the two lake areas, ranked from low to high based on the VLA BSAF group

The mean VLA BSAF was four times greater than the grand mean BSAF of 0.25 (but within the 0.003 to 3.8 range) for all PAHs for benthic organisms in laboratory testing, as obtained from a database maintained by US Army Engineer Research and Development Center (USAERDC) (2005). In contrast, the mean PAH BSAF for the DLA was less than one third of this grand mean (but still within the range). Figure 2 is a bar graph of the mean lake area PAH BSAFs illustrating the large difference between the two data groups. For the VLA, it shows the notably higher bioavailability of 2-methylnaphthalene, naphthalene and benzo(g,h,i)perylene, as well as the carcinogenic indeno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene. For the DLA, it also illustrates a comparably higher bioavailability of the carcinogenic B(a)P, benzo(k)fluoranthene and benzo(a)anthracene, and less potent pyrene.

The 28-d exposure period used in this study likely was sufficient to allow tissue residues of the PAH compounds to approach steady state in *L. variegatus*. Exposure of *L. variegatus* to field sediments contaminated with various highly hydrophobic PAH compounds (log K_{ow}s up to 6.7 [benzo(g,h,i)perylene]) for periods of 14 and 28 d allowed body residues to reach steady-state levels, with no further increases being observed in exposure periods greater than 28 d (Ingersoll et al. 2003). Therefore, the BSAFs determined in this study are expected to be representative of the *in-situ* bioavailability of PAH compounds in Lake Erie surficial sediments within a reasonable degree of confidence. The metabolism of PAH compounds taken up by *L. variegatus* from Lake Erie sediments was likely negligible and contributed minimally to the estimated uncertainty. Leppanen and Kukkonen (2000) reported that the metabolism of pyrene and B(a)P by *L.*

variegatus is negligible, or limited and slow. In addition, Hyotylainen and Oikari (2004) observed negligible biotransformation of PAHs in *L. variegatus* that bioaccumulated PAHs from creosote-contaminated sediment.

The octanol-water partition coefficient (K_{ow}) is a measurement of hydrophobicity used to describe the behavior of nonpolar organic contaminants in the aquatic environment. Hydrophobicity typically influences bioavailability by affecting sediment sorption strength and generally increases with increasing molecular weight, surface area and volume of a chemical. To assess the relationship between PAH bioavailability and hydrophobicity at the two lake areas, all BSAFs were plotted against the respective PAH compound log K_{ow} (Figure 3). The VLA association appears parabolic, showing a decrease in bioavailability up to a log K_{ow} of about 5 to 5.5, followed by an increase. This result is consistent with Ingersoll et al. (2003), evidencing no reduction in bioavailability in *L. variegatus* for high (≥5.6) log K_{ow} PAH compounds. For the DLA, no relationship between the PAH compound BSAFs and log K_{ow} is apparent, suggesting that other factors are affecting sediment-associated bioavailability. The low correlation between the two lake area BSAFs (R=-0.13) supports this line of reasoning.

At the DLA, sediments containing pyrogenic soot and chars (black carbon [BC]) from lakeshore coal-fired power plants likely account for the observed reduction in PAH bioavailability. Unlike the VLA, the DLA is located less than one mile from the second largest coal-fired power plant in terms of air emissions in NY, and downwind and downdrift (with respect to prevailing winds and lake currents, respectively) of a chain of five coal-fired power plants along the lake's south shore (Clean Air Task Force 2005). Field notes also indicate that sediments from this area were dark gray in color. The lower bioavailability of PAHs associated with BC has been well documented (e.g., Sundelin et al. 2004; Van Noort et al. 2004). The appreciably lower BSAFs at the DLA coupled with significantly lower mean TOC (t-test, $P<0.001$; mean TOC = 1.3% [DLA] vs. 2.6% [VLA]) are consistent with the speculation that sediment sorption strength at the DLA is comparably much greater. While emissions from coal-fired power plants result in a net increase in various environmental pollutants, the deposition of soot in aquatic sediments typically renders organic contaminants less bioavailable.

The condensed carbon matrices of coal soot have been hypothesized to augment PAH sorption capacities (Karapanagioti et al. 2000). Bucheli and Gustafsson (2000) used empirical solid-water distribution coefficient data to demonstrate that the strongly sorbing properties of soot matrices substantially enhance the partitioning of several PAH compounds. Sundelin et al. (2004) showed that sediments with the highest BC levels resulted in BSAFs that were about 20 times less than those with lowest BC levels. While the markedly lower BSAFs for the DLA are consistent with the presence of BC, other factors, such as lipid composition/content, sediment particulate size, TOC level, sorbent properties, hydrophobicity, metabolizing capabilities and feeding behavior can influence PAH bioavailability. Data from this study appear to eliminate all of these as

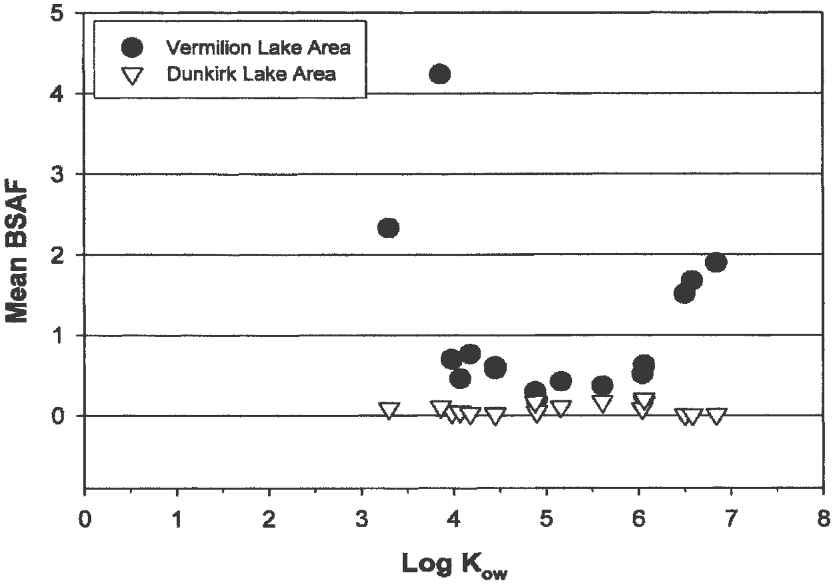

Figure 3. Plot of Dunkirk and Vermilion lake area PAH compound BSAFs vs. log K_{ow}s

substantially contributing factors, except for sorbent properties, which would be influenced by a preponderance of BC.

This study corroborates evidence that two-phased equilibrium partitioning (EqP)-based predictions using K_{ow} overestimate the bioavailable fraction of PAH compounds associated with BC. In fact, constrained bioavailability is often used to explain weak relationships between uptake, and the levels of organic contaminants and bulk TOC (Cornelissen and Gustafsson 2005). These results underscore the potential drawbacks of applying EqP methodology to develop sediment quality criteria for PAHs.

Acknowledgments. We thank colleagues William Butler, David Melfi, Jay Miller, David Swiatek and Shanon Chader for their support on this work.

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