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# Comparison of Methods Used To Determine the Availability of Polycyclic Aromatic Hydrocarbons in Marine Sediment

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Semipermeable membrane devices (SPMDs), Tenax TA, and a polyethylene tube dialysis (PTD) methods were used to estimate the "available" fraction of PAH in marine sediment slurries. The polyethylene membrane used in the SPMD and PTD methods mimics a biomembrane. The PAH must diffuse through the membrane into triolein or pentane, respectively. The Tenax TA scavenges PAH from the water phase and is separated from the sediment, thus particle-associated PAH are excluded from all three methods. Spiked PAH were more readily available than endogenous (unspiked) PAH, and the presence of sediment organic matter decreased desorption and thus availability of the PAH. All three methods could aid in bioremediation feasibility assessments and predictions on the potential toxicity of sediments or soils. The SPMD method has the advantage of being available commercially, and the use of such a standard method allows comparison with other samples from the literature. The Tenax method gave similar results with the exception of the larger compounds that were recovered more efficiently, and it was less expensive. The PTD method was the most stringent assay for availability and could be useful in assessing the risk associated with exposure to a contaminated sample.

## Introduction

Polycyclic aromatic hydrocarbons (PAH) are hydrophobic organic pollutants that have been placed on the U.S. EPA priority pollutants list due to their toxicity and, in some cases, carcinogenicity. PAH with up to five rings are biodegradable (*1*); however, the bioremediation of contaminated sites is often limited by the low bioavailability of higher molecular weight PAH associated with soils and sediments (*2*). This is primarily due to the tendency of these compounds to partition into the organic matter content of soils or sediments or into nonaqueous-phase liquids (NAPLs) where they are thought to be inaccessible to intracellular enzymes (*3*). Desorption of PAH from the solid matrix is affected by the length of time the contaminants have been in contact with the matrix, the rate at which the PAH are removed from the water phase, and the diffusion rate of PAH within the matrix (*3*).

There have been a number of attempts to model the behavior of PAH in soil−water or sediment−water systems in order to improve predictions about bioremediation and the effects of contaminants on ecosystems. Some models are based on theoretical predictions of what happens at the microscale (e.g., refs *4* and *5*). Most, however, were designed to predict whether the microbial degradation rate or contaminant desorption rate will limit the rate of contaminant biodegradation (e.g., refs *6*−*10*) and use measured coefficients. Most models assume that desorption is required for biodegradation (*11*).

Desorption is quite specific to the matrix and environmental conditions encountered. For example, Paine et al. (*12*) studied a site in Kitimat Arm, BC, Canada. Sediments at the site were contaminated to a level that had caused adverse effects in other locations; however, the aquatic biota appeared to be relatively unaffected by exposure to the sediment. The authors concluded that the PAH at the site were not bioavailable. Several other researchers have found that PAH associated with soot are very tightly bound and may be less able to desorb than from other organic matrices (e.g., refs *13*−*16*). The contamination in Kitimat Arm probably came primarily from the wet scrubbers at a nearby aluminum smelter (*12*) and might have been associated with soot.

Even in the absence of soot, the nature of the organic content of sediments and soils (that is, whether the organic matter is made up of humic material, creosote, or other oily substances) affects the rate of desorption from the solid matrix (e.g., refs *17* and *18*), as does the length of contact time between the pollutant and the solids (*19*, *20*). All of this discussion illustrates the complexity of the interactions between pollutants and soils or sediments, and emphasizes the difficulties encountered when predicting desorption and bioavailability. Since desorption is so important in determining the fate of pollutants in the environment, it should be measured routinely in environmental samples; however, complete adsorption−desorption experiments are costly and time-consuming. For routine use, simple methods to measure available fractions are required. Although such methods cannot be definitive, since they do not account for the environmental conditions encountered under all circumstances, for example, in the digestive tracts of organisms, they do represent an improvement over simple chemical extraction of the soil or sediment.

Several methods have been used to try to assess the availability of contaminants in solid matrixes (e.g., refs *21*−*24*). Mild chemical extractions were used by Kelsey et al. (*21*) to try to determine the availability of contaminants. The extraction results were compared to uptake by test organisms. The actual procedure that best described bioavailability was dependent on the soil and the test organism used, so the best extraction was system-specific. Gustafson et al. (*22*) found that filtration of water samples followed by sorption of the contaminants to a resin was the best method of determining the available fraction of contaminants in the water column. Similar methods of concentrating contaminants that desorbed from sediment particles on a resin were used by Yeom et al. (*23*) and Lake et al. (*24*).

Semipermeable membrane devices (SPMDs) are patented devices that have been used to measure bioavailable hydrophobic contaminants in the aquatic environment (*25*). They are made from nonporous polyethylene tubing containing a thinly spread layer of triolein (*26*). The underlying assumption behind the use of SPMDs as measures of available contaminants is that only dissolved material is bioavailable. Any pollutants that are attached to particles or are associated with colloidal material will be unable to pass through the

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**TABLE 1. Concentrations of PAH in False Creek Sediment Used in the Methods Comparison Experiment with and without Spike[a]**

| PAH | sediment (no spike) | spiked sediment |
|---|---|---|
| ACY | 0.26 | 1.4 |
| ACE | 0.33 | 9.1 |
| FLU | 0.49 | 26.4 |
| PHE | 2.10 | 33.4 |
| ANT | 0.54 | 44.0 |
| FLA | 2.76 | 35.7 |
| PYR | 2.81 | 52.6 |
| BAA | 1.22 | 38.4 |
| CHR | 1.81 | 20.8 |
| BAP | 1.03 | 29.7 |
| DBA | 0.55 | 28.0 |
| BGHIP | 1.30 | 37.2 |

[a] All concentrations are in $\mu$g/g dry weight. The sediment organic matter concentration was 11.4%.

membrane or through biological membranes. Hydrophobic contaminants become concentrated in the lipid relative to the water phase according to their lipid− or octanol−water partition coefficients as they might in fish lipids or the tissues of other organisms (*27*). This approach allows exposures to be determined without having to account for the variation between individuals or the metabolism or depuration rates in organisms. Furthermore, they can be deployed in the field at sites where animals might not survive (*27*). PAH with up to five rings have been successfully recovered using this approach (*28*).

In this research, three methods were used to try to measure the availability of PAH from False Creek sediment: semipermeable membrane devices (SPMD), a new polyethylene tube dialysis (PTD) method, and a Tenax TA leachate method similar to that used by Yeom et al. (*23*) to measure PAH desorption from soil. The PTD method is similar to the SPMD method except that a small sample of sediment−water slurry is sealed inside the tubing and dialyzed against solvent.

## Experimental Section

**Chemicals.** All solvents used were Fisher Scientific HPLC grade, except dimethyl sulfoxide (DMSO) was Spectranalyzed. PAH were obtained from Supelco. Dry chemicals were analytical grade, except food-grade sea salts were used. Low-density polyethylene layflat tubing (2.54 cm tubing width, 53.6 $\mu$m thickness) was obtained from Cope Plastics, Inc., and triolein was from Sigma. Tenax TA 20/35 mesh was purchased from Altech.

**PAH Spiked Clay.** This was used to compare the availability of added and endogenous PAH. PAH (Supelco) solutions made in toluene were added to ashed bentonite (550 °C/2 h), and the solvent was allowed to evaporate. The resultant spike had higher concentrations of the higher molecular weight compounds since some of the low molecular weight compounds were lost due to volatilization. The PAH that were used are as follows: acenaphthylene (acy), acenaphthene (ace), fluorene (flu), phenanthrene (phe), anthracene (ant), fluoranthene (fla), pyrene (pyr), benz[*a*]-anthracene (baa), chrysene (chr), and benzo[*a*]pyrene (bap). In the methods comparison experiments, dibenz[*a*,*h*]anthracene, (dba) and dibenzo[*g*,*h*,*i*]perylene (bghip) were also used. Table 1 shows the concentrations of PAH in False Creek sediment used for the methods comparison experiment, with and without spiked clay.

**Sampling/Sample Handling.** Surface sediment samples were taken using an Ekman dredge from False Creek near Vancouver, BC, Canada. False Creek is a narrow arm of the ocean that is completely surrounded by the city of Vancouver. It is affected by combined sewer overflows and historical contamination. Sediment was removed from the dredge sampler with a metal spoon and transferred to plastic bags. At the laboratory, the material was passed through a 2 mm sieve and stored at 4 °C in amber glass jars until use. Dry weight and loss on ignition (organic matter) were determined as the experiments were set up (2540 G; *29*). False Creek sediment organic matter ranged from 11.4 to 13.8%, and the salinity of the water at the sediment surface was 16.5‰.

**Sediment Extraction and Analysis.** Freeze-dried samples were extracted 3 times for 1 h on a wrist action shaker with 50 mL of dichloromethane/acetone (95/5). The extracts were concentrated by rotary evaporation and cleaned up using a DMSO liquid extraction method (*30*). When wet sediment was used, the sediment was first mixed with sodium sulfate and extracted with acetone before dichloromethane extraction. These pooled solvent extracts were dried with sodium sulfate before concentrating. Sediment extracts were analyzed by gas chromatography with flame ionization detection (GC-FID, HP 5890 series II). One microliter splitless injections were made onto a DB-5 capillary column (80 °C for 1.5 min; 15 °C/min to 150 °C, final time A 0.5 min; 5 °C/min to 315 °C, final time B 10 min) and confirmed on a DB-1 capillary column (as DB-5 except final temperature was 310 °C, final time B was 2 min). Alternatively, samples were analyzed by GC with a mass selective (MS) detector (HP 6890 GC/HP 5973 MS) using a HP-5MS column (60 °C for 2 min; 20 °C/min to 90 °C, final time A 0.5 min; 5 °C/min to 310 °C, final time B 2 min) The internal standard was 1-chloroanthracene.

**Semipermeable Membrane Devices (SPMDs).** Low-density polyethylene layflat tubing was cut to 117 cm lengths. Up to 12 lengths of tubing were added to 1 L of pentane for

**TABLE 2. Percent of Total PAH Recovered in "Available" Fractions[a]**

| | sediment, no spike | | | spiked sediment | | | spiked clay | | |
|---|---|---|---|---|---|---|---|---|---|
| PAH | PTD | SPMD | Tenax TA | PTD | SPMD | Tenax TA | PTD | SPMD | Tenax TA |
| ACY | ND | 0 | 0 | 0 | 39 | 0 | 100 | 81 | 36 |
| ACE | ND | 42 | 35 | 100 | 87 | 90 | 100 | 100 | 100 |
| FLU | ND | 38 | 8 | 100 | 84 | 74 | 100 | 96 | 99 |
| PHE | 100 | 14 | 9 | 91 | 79 | 56 | 100 | 95 | 98 |
| ANT | ND | 11 | 0 | 88 | 64 | 49 | 96 | 84 | 86 |
| FLA | 61 | 24 | 6 | 78 | 67 | 24 | 98 | 91 | 95 |
| PYR | 59 | 22 | 5 | 75 | 64 | 25 | 97 | 89 | 94 |
| BAA | 0 | 5 | 0 | 49 | 22 | 16 | 81 | 56 | 50 |
| CHR | 100 | 7 | 0 | 52 | 16 | 21 | 79 | 41 | 34 |
| BAP | 0 | 0 | 0 | 43 | 6 | 17 | 67 | 15 | 31 |
| DBA | ND | 0 | 0 | 43 | 2 | 27 | 62 | 5 | 43 |
| BGHIP | 0 | 0 | 0 | 46 | 1 | 29 | 61 | 1 | 39 |

[a] ND indicates none detected in either fraction. Note that the detection limit using the PTD method is 11 times higher than for the other two methods.

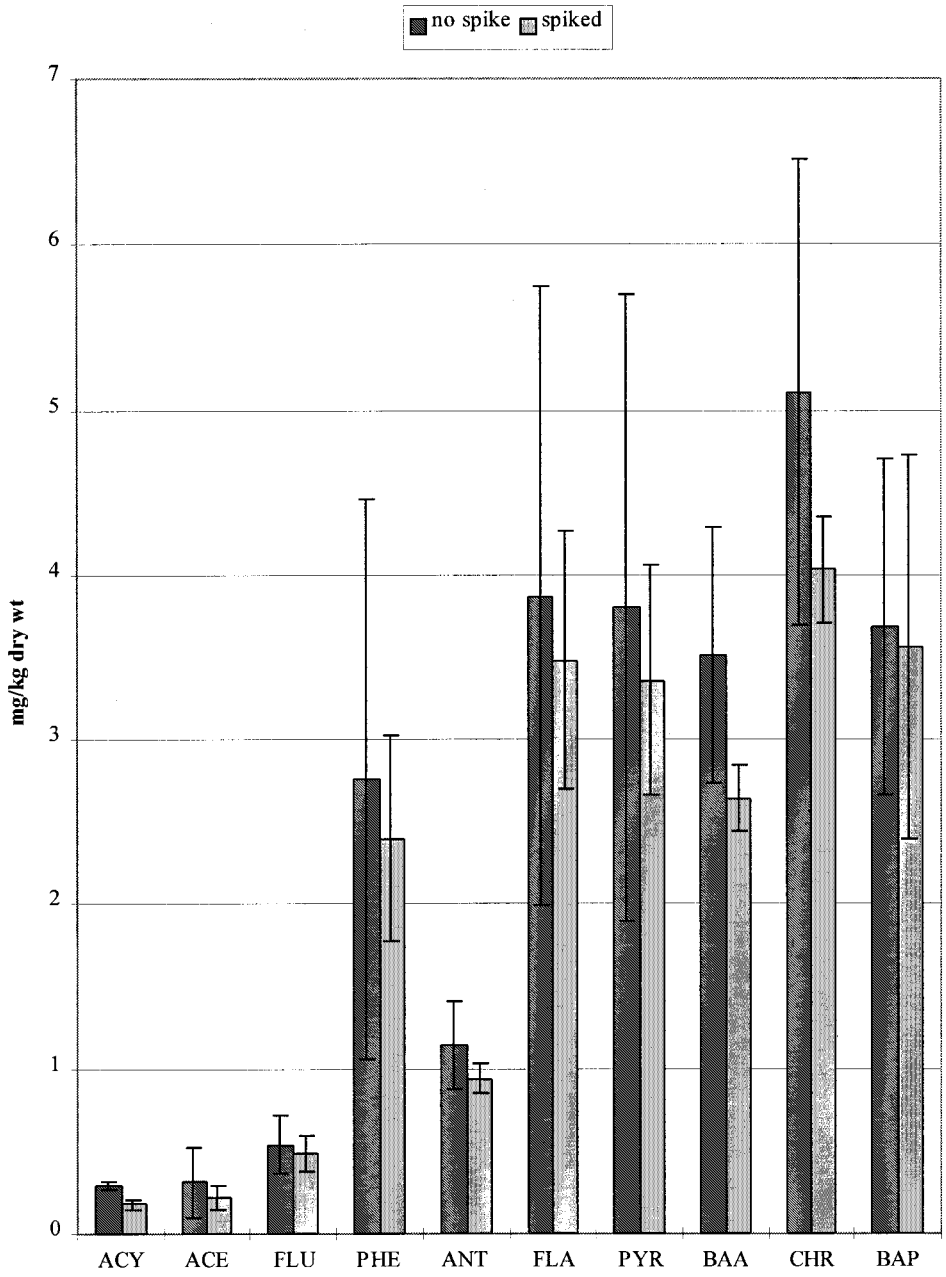


**FIGURE 1. Concentration of PAH remaining associated with False Creek sediment (no spike) and spiked False Creek sediment after exhaustive exposure to SPMDs. Concentrations are in mg/kg dry weight; error bars represent the standard deviations and $n = 3$.**

24 h for pre-extraction. One milliliter of triolein was added to each tube and spread down the length of the tubing using a small plastic roller. The tubing was heat-sealed approximately 10 cm from the ends and the ends brought together, one turned 180° to form a Mobius strip, and heat-sealed together.

SPMDs were exposed to 10 g of wet sediment or an equivalent amount of ashed clay, 0.5 g of spiked clay (when added), and 100 mL of 15‰ sea salts solution, on an end-over-end tumbler for 24 h at 10 rpm. Longer exposure of the SPMD to this sediment caused damage to the membrane. After exposure, the SPMDs were removed and rinsed with tap water and then acetone prior to dialysis in 200 mL of pentane for 24 h. After dialysis, the pentane was concentrated by rotary evaporation. These extracts were cleaned up by the DMSO method (*30*) prior to analysis by GC as described for the sediment extracts.

To determine the effect of sediment organic matter (OM) content on availability, freeze-dried sediment was mixed with sediment that had been ashed (550 °C/2 h) to give different organic matter levels with a maximum of 13.8%. A total of 4 g of dry and/or ashed sediment was added per bottle with 210 mL of 15‰ sea salts solution, 0.5 g of PAH-spiked clay, and one SPMD. These were exposed and extracted as described above.

For determination of the sediment PAH content after exposure to numerous SPMDs, 20 g of wet sediment (7.34 g dry weight), 210 mL of 15‰ sea salts solution, and 0.5 g of PAH-spiked clay or unspiked clay was added to each bottle, and the SPMDs were removed, extracted, and replaced every 24 h for 11 days. Longer exposures of individual SPMDs to False Creek sediment resulted in damage to the polyethylene tubing.

**Polyethylene Tube Dialysis (PTD).** Ten milliliters of a slurry made from 10 g of wet sediment or ashed clay equivalent, 0.5 g of spiked clay (when used), and 100 mL of 15‰ sea salts solution were heat-sealed in 60 cm lengths of pre-extracted (as for SPMD) polyethylene tubing. These were

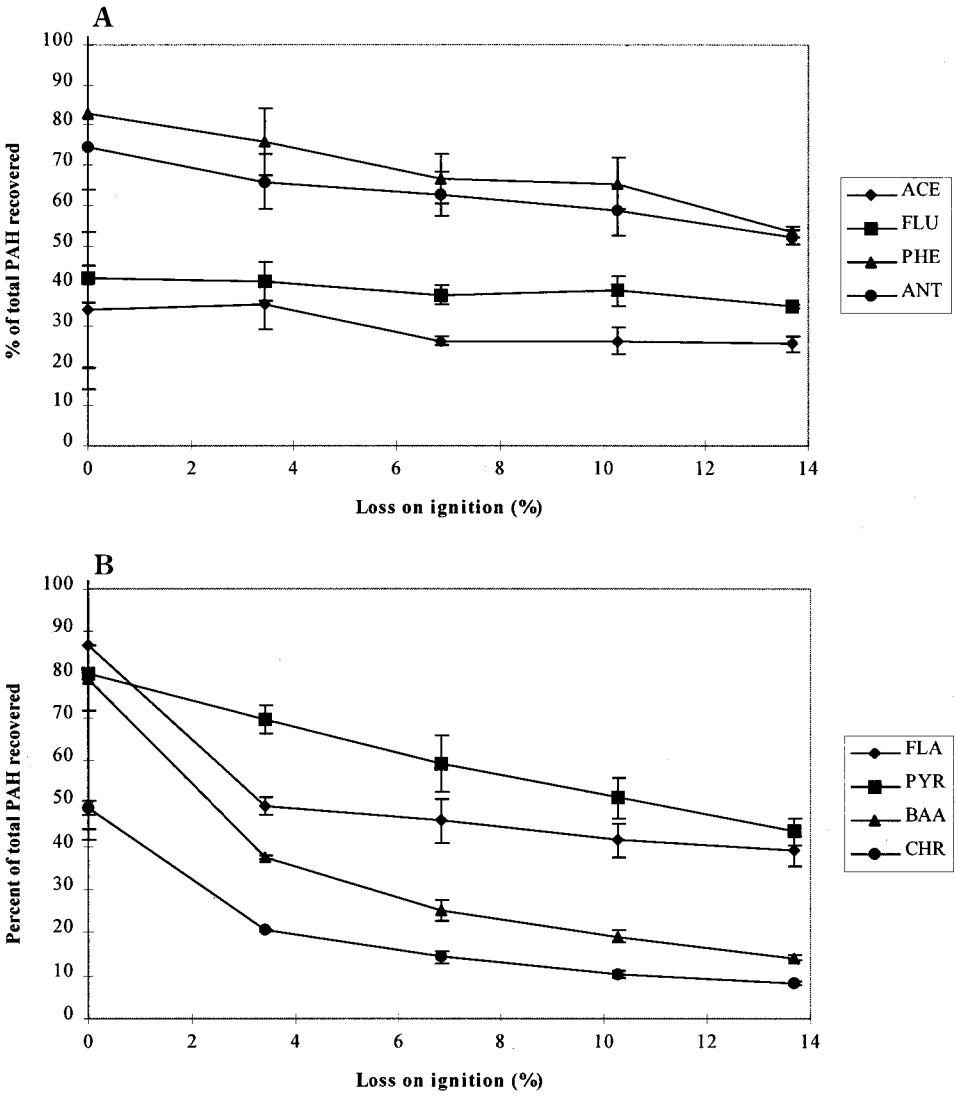


**FIGURE 2. Effect of sediment organic matter content on PAH extraction by SPMD [(A) Low and (B) high molecular weight PAH. The percentage of total PAH (SPMD plus sediment PAH after exposure) in the SPMD extract is shown because there was some endogenous PAH content in the False Creek sediment. The error bars represent the standard deviation of duplicate samples.**

placed in 150 mL of pentane in glass bottles on an end-over-end tumbler for 24 h at 10 rpm. After exposure, the solvent was removed and concentrated, then cleaned up by the DMSO method (*30*) prior to analysis by GC-FID or GC−MS. Since only 10 mL of the slurry is sealed into the tubing, less material is extracted using this method than in the other two. The PAH detection levels (approximately 1−5 $\mu$g/g dry weight) are therefore 11 times higher than with the other methods.

**Tenax TA.** The method used here is similar to that used by Yeom et al. (*23*). Ten grams of wet sediment or an equivalent mass of ashed clay, 100 mL of 15‰ sea salts solution, 0.5 g of spiked clay (when used), and 0.2 g of Tenax TA were placed in glass bottles on an end-over-end tumbler for 24 h at 10 rpm. After exposure, the samples were centrifuged, and the Tenax was raked off the surface and washed once with deionized water. The Tenax was then extracted for 24 h with 30 mL acetone on an end-over-end tumbler at 10 rpm. The solvent was dried with sodium sulfate and concentrated and then cleaned up by the DMSO method (*30*) prior to analysis by GC−MS.

Yeom et al. (*23*) used 0.2 g of Tenax TA to maintain a near-zero PAH concentration in the water of a slurry system containing 2.5 g of a soil with 75% OM. In our experiment, 5.6 g of sediment with 11.4% OM was used, which is nearly 3 times more Tenax TA/g of OM, so the Tenax TA should not have become saturated.

## Results and Discussion

Measuring "bioavailability" is complicated by the many conditions under which organisms live and different routes of exposure. Any bioavailability assay will thus be limited by the experimental conditions. In this research, mass balance showed that none of the methods led to significant PAH losses by adsorption to sample containers. Since the sediments, salinities, and incubation conditions were identical, differences in the results reflect differences in the methods used, and the best assay for any given application will depend on the questions being asked. All three methods work on the assumption that the contaminant must pass through the dissolved phase to be biodegraded or to exert toxic effects.

In SPMD and PTD extractions, contaminants associated with sediment particles cannot pass through the tubing, so only dissolved PAH are measured. The permeant size of the nonporous polyethylene membrane (10 Å) is thought to be similar to that of biomembranes, assuming transport across

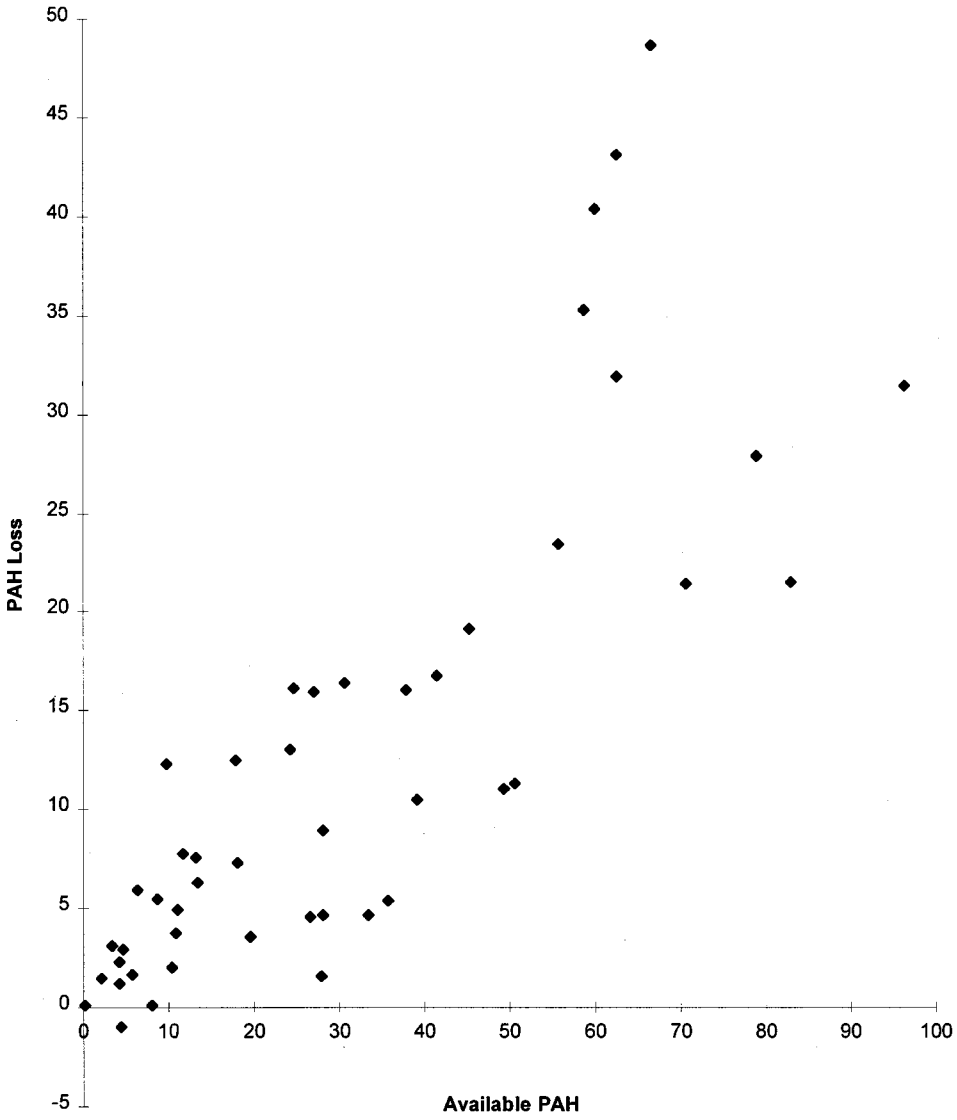


**FIGURE 3. Effect of availability as measured by the PTD method on degradability of PAH in False Creek sediment. Four degradation experiments are shown. Details of the degradation experiments are given elsewhere (*32*). All results are given in mg/kg dry weight.**

the membrane is by diffusion (*25*). The SPMD sampling rates for PAH increase with octanol−water partition coefficient from 0.3 L/day for naphthalene to a maximum of over 5 L/day for pyrene. The sampling rates then decline due to lower membrane permeability to the larger molecules (*25*), similar to the protective effect of biomembranes. The SPMD system is unlikely to have reached equilibrium for the larger compounds in 24 h; however, exposure of SPMDs to our sediment for longer periods caused damage to the membrane. This SPMD method therefore reflects the PAH exposure to biota during 24 h. The same membrane was used in the PTD method.

In the Tenax TA method, the Tenax particles are separated from the sediment after incubation, so the PAH still associated with the sediment are not included in the extraction. The addition of Tenax to the system maintains the maximum concentration gradient between the sediment particles and the aqueous phase by scavenging the PAH from the water phase (*23*). This method does not include a membrane, so it is probably more reflective of the total available PAH, without the protective function of biomembranes. This would therefore be more reflective of all the dissolved and potentially colloidal material, not just that which can pass through biological membranes.

The available fraction of the PAH in False Creek sediment, spiked False Creek sediment, and spiked clay using all three methods are shown in Table 2. With all three methods, PAH associated with clay were the most available, followed by PAH spiked sediment, and the endogenous (no spike added) PAH were the least available. This was expected, since "aged" contaminants tend to become more strongly associated with sediments (*3, 19, 20*), and the PAH in the spiked sediment samples would have associated with the sediment organic matter, which was absent from the spiked clay samples.

The availability of PAH is generally greater when measured by the PTD method than by the other two. This makes it a more stringent method, which could be useful when the object of the assay is to determine the potential for harm resulting from exposure to a sediment. It is more stringent because the ratio of "solvent" to sediment in this method, 150 mL of pentane/0.9 g of wet sediment, is much higher than in the SPMD method, 1 mL of triolein/10 g of wet sediment. In addition, it is also likely that some of the pentane used in the extraction passed through the tubing and acted as a cosolvent, which could facilitate desorption of the PAH from the sediment (*3*). Although there was never a separate pentane phase in the tubing, pentane

molecules are small enough to diffuse through the polyethylene. This method can be used when only small samples are available.

Comparisons of the results of the SPMD and Tenax TA extractions are quite interesting. For most compounds, the SPMD method gave slightly higher recoveries; however, the opposite was true for the five- and six-ring compounds, benzo[*a*]pyrene, dibenz[*a*,*h*]anthracene, and benzo[*g*,*h*,*i*]-perylene. This is likely due to a slow transfer rate of these large PAH across the polyethylene tubing in the SPMD, which might mimic the protective effect of biomembranes. On the other hand, if transfer of the compounds is not always by passive diffusion, the Tenax TA method might provide a more accurate measure of the bioavailability of those compounds. For both of these methods, larger samples can be used than for the PTD method, which is useful when dealing with heterogeneous environmental matrices and low analyte concentrations. They might also be more useful than the PTD method when trying to gauge whether required or legislated maximum PAH concentrations in sediment or soil could likely be reached economically by bioremediation. When the rate of biodegradation is limited by substrate availability, treatment time will be longer, which leads to higher treatment costs (*31*). The SPMD method is slightly more stringent for the lower molecular weight compounds, and the Tenax method is somewhat less expensive.

Since the SPMD method has been put forward by the manufacturers as a standard method in aquatic toxicology for measurement of available hydrophobic contaminants (*25*), it was assessed further using sediment from False Creek. To determine if all of the added PAH could be recovered in SPMD extracts, spiked and unspiked sediments were incubated sequentially with 11 SPMDs. The PAH remaining in the sediment phase of the spiked and unspiked samples were then compared (Figure 1). The presence of PAH in the sediment after exposure to so many SPMDs shows that there is a fraction of the endogenous PAH that is resistant to desorption. Since the results of the spiked and unspiked sediments are not significantly different for any of the PAH, none of the added material became resistant to desorption in the 11-day duration of the experiment.

Using mixtures of dried and ashed sediment, the influence of organic matter content on PAH recovery using SPMDs was explored (Figure 2). With increased sediment organic matter, less of the PAH was extracted by the SPMD, indicating greater resistance to desorption. The effect was most pronounced with the higher molecular weight compounds. These results were expected since more hydrophobic contaminants tend to associate with the organic matter of sediments to a greater extent (*3*).

The PTD method was used to measure the availability of PAH added to sediments used in several biodegradation experiments, which are described elsewhere (*32*). Figure 3 shows the plot of PAH loss after 12 weeks against the available PAH in the control sediment, as measured by the PTD method. This measurement of the available PAH content was used because of the small sample size required. Samples with low availability were degraded slowly, if at all, and those that were more readily available tended to be degraded more quickly.

The dependence of biodegradation on availability underlines the importance of having methods to measure the available fraction of contaminants in solid media. Such methods could be used to try to assess the risk or the likelihood of successful bioremediation of contaminated material. Each method has its own strengths and weaknesses, and it is important to keep these in mind when making decisions based on the results of such assays. For example, in the experiments described here, the conditions were not the same as those that might be encountered in the digestive tracts of fish, where the bioavailability of the contaminants could be altered; however, the methods do offer relatively inexpensive tools for initial evaluation of contaminated materials. Of the methods described here, PTD is the most stringent and might best be used for the assessment of risk associated with exposure to soils or sediments. The SPMD and Tenax methods will be useful for estimation of the fraction of contaminants in solid samples that will likely be biodegradable in a reasonable length of time. These methods will also be useful tools in the study of factors that affect the bioavailability of contaminants associated with soils or sediments.

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