EVALUATION OF CONTAMINANT EXPOSURE AND THE POTENTIAL IMPACTS ON AQUATIC HABITAT QUALITY IN THE ANCHORAGE AREA OF THE COOK INLET BASIN

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EXECUTIVE SUMMARY

The primary motivation for this research was to determine the presence and potential toxicological significance of waterborne polycyclic aromatic hydrocarbons (PAHs), on fishery resources in urban streams of Anchorage, AK. This complex class of toxic chemicals originates from both petrogenic and pyrogenic sources. Only 16 are listed by the US EPA as priority pollutants (PP) but hundreds of PAHs are known to exist in the environment. Most PAHs are acutely toxic but a number of PAHs are also mutagenic and carcinogenic. In addition many PAHs exhibit greatly enhanced toxicity in the presence of UV radiation. In collaboration with USGS personnel of the Cook Inlet Basin NAWQA Unit, researchers at the Columbia Environmental Research Center, USGS, deployed lipid-containing semipermeable membrane devices (SPMDs) in six small urban streams for 56 days in Anchorage, Alaska. Because SPMDs mimic the bioconcentration of trace waterborne lipophilic contaminants by fishes, are not subject to most stressors affecting the health of biomonitoring organisms, and are highly reproducible, these devices are being used worldwide for passive *in situ* monitoring of hydrophobic organic contaminants such as PAHs. PP PAHs were only detected at one site (Chester Creek). However, the largest component of the detected residues was pyrene, which is known to have greatly enhanced toxicity in the presence of UV radiation. The estimated concentration of bioavailable pyrene in water (3.6 ng/L) was within the range known to cause adverse effects on some fingerling fishes. Also, non-PP PAHs were detected at all sites but were particularly high (40.7 ng/L) at Campbell Creek (C-Street). The toxicological significance of these compounds is unknown but the whole mixture toxicity

can be screened with biomarker tests (see Dr. Johnson's report). To ensure a more holistic assessment of hydrophobic chemicals in Anchorage streams, additional screening of SPMD samples was performed for the presence of organochlorine pesticides (OCs). Numerous trace levels of OCs were found to be present at all study sites. However, levels of DDT and analogs (≈0.5 ng/L total), and pentachloroanisole (PCA, 0.17 ng/L) were quite high (e.g., relative to the Missouri River) at Ship Creek and Little Rabbit Creek, respectively. PCA is a microbial degradation product of pentachlorophenol, which is known to contain dioxins, and DDT and analogs are known to disrupt the endocrine system in some aquatic organisms. More definitive analysis of these research results requires mass spectrometric confirmation of detected residues.

INTRODUCTION

Fisheries are a very important resource in the Cook Inlet Basin in Alaska. The aquatic habitat often consists of small clear streams and the drainage areas of these streams range from a few square miles to as much as one hundred square miles. Urban development in these watersheds is of increasing concern, partly because elevated levels of some contaminants in environmental waters have been linked to urbanized areas. For example, concentrations of fluoranthene, a polycyclic aromatic hydrocarbon (PAH), in parking lot runoff have been reported at levels as high as 110 μg/L (Steve Frenzel, USGS, Anchorage, AK). Sixteen PAHs are listed by the U.S. Environmental Protection Agency as priority pollutants. The PAH class of hydrophobic chemicals originates from petrogenic or pyrogenic sources. Exposure of these chemicals to fishes results in tissue concentrations of PAHs up to five thousand fold above ambient water concentrations (Jim Oris, personal communication, Miami University, Oxford, OH) and even greater concentration factors have been observed in shellfish.

Certain PAHs (e.g., pyrene) exhibit greatly enhanced toxicity to aquatic organisms in the presence of solar ultraviolet radiation. In some cases, this photoactivation process (i.e., photolysis) can result in a 1000-fold increase in toxicity relative to the parent PAH. Of the sixteen EPA Priority Pollutant (PP) PAHs, seven are subject to photoactivation. It is also noteworthy that the commonly observed alkylated analogs of these PAHs are equally toxic when photolyzed, but have greater bioaccumulation potentials. Currently, a growing body of evidence indicates that the presence of certain PAHs subject to

photoactivation may be degrading some aquatic environments. This issue is of particular concern for shallow, clear-water habitats such as some urban streams in the Cook Inlet Basin. Studies have shown that bioconcentrated PAHs can be photolyzed in the tissues of some fish (1), which suggests that fish fry and eggs in shallow clear water are particularly vulnerable. Also, persistent organic pollutants (POPs) such as certain pesticides and polychlorinated biphenyls (PCBs) are often associated with runoff from urbanized areas and may be affecting habitat quality in these aquatic systems as well.

Scientists at the U.S. Geological Survey's Columbia Environmental Research Center (CERC) have developed the semipermeable membrane device (SPMD) for passive integrative monitoring of aquatic contaminants (2-6). The SPMD consists of layflat nonporous polyethylene (PE) tubing enclosing a thin film of the neutral lipid triolein (Figure 1). Only readily bioavailable (i.e., solutes or vapors) lipophilic contaminant molecules in water and air diffuse through transient cavities (< 10 Å in cross-sectional diameter) of the PE membrane to the triolein. The mechanism of lipophilic contaminant transfer through the transient cavities of the PE membrane appears to model the transport of similar chemicals through biomembranes (2). Also, the triolein used in SPMDs is a major storage fat for persistent hydrophobic pollutants in aquatic organisms (7).

The bioconcentration of hydrophobic chemicals dissolved in water generally involves active transport to the respiratory membrane surface, diffusion through the exterior

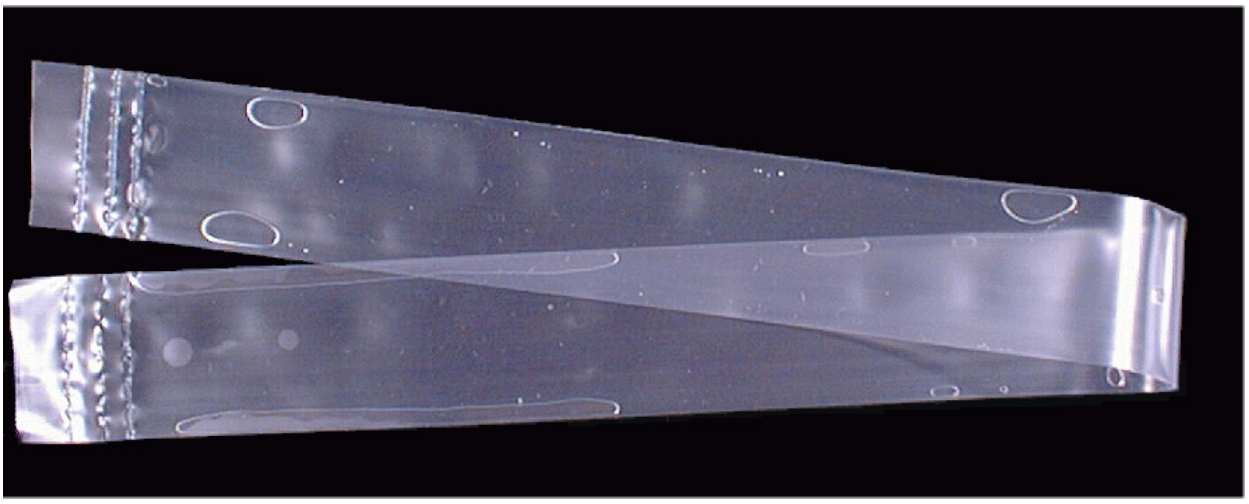


Figure 1. A standard lipid-containing SPMD with three molecular welds near each end. Note the low interfacial tension causes intimate contact (i.e., the presence of a lipid film on the membrane interior surface) between the triolein and the membrane even where air bubbles exists.

boundary layer, the mucosal layer, and the membrane, and active export, via blood, away from the membrane's inner surface to lipid containing tissues. SPMDs model only the passive elements of bioconcentration, which include solute diffusion through an aqueous boundary layer, a biofilm (usually not present until > 2 weeks exposure), the PE membrane, and finally partitioning with the lipid. Comparisons of the concentrations and uptake rates of POPs by SPMDs and fishes often have shown close similarities (8-11).

Several investigators have found that SPMDs can be used as *in situ* mimetic (mimics more complex biological processes, such as bioconcentration, in simple media) devices for assessing the potential toxicity of bioconcentrated contaminants with bioindicator/biomarker tests such as Microtox® and Mutatox® (12-14). Finally, theory and inferential evidence (15, Edward Little, personal communication, CERC, Columbia

MO) suggest that SPMD extracts can also be used to screen the phototoxicity of PAHs residues.

The primary objective of this research was to determine the presence, water concentration, and potential toxicity of PAH residues in selected small streams in the Anchorage area of the Cook Inlet Basin. Also, the potential for assessing enhanced PAH toxicity due to photolysis was explored using biomarker test. The secondary objective of this work was to determine the presence of several classes of POPs in study watersheds.

MATERIALS AND METHODS

Materials: Low-density polyethylene (PE) layflat tubing was purchased from Environmental Sampling Technologies (EST), St. Joseph, MO. The PE tubing was a 2.54 cm wide, No. 940, untreated (pure PE; no slip additives, antioxidants, etc.) clear tubing. The wall thickness of this lot ranged from 84 to 89 μm. Triolein (1,2,3-tri-[cis-9-octadecenoyl]glycerol) was obtained from Sigma Chemical Co., St. Louis, MO and was $\geq$ 95% pure. Florisil® (60-100 mesh) was obtained from Fisher Scientific Company, Pittsburgh, PA. The Florisil was heated at 475 ^{o}C for 8 hours and stored at 130 ^{o}C. Silica gel (SG-60, 70-230 mesh) was obtained from Thomas Scientific, Swedesboro, NJ. The silica gel was washed with 40:60 methyl tert-butyl ether:hexane (V:V) followed by 100% hexane. The silica gel was activated at 130 ^{o}C for a minimum of 72 hours before use and subsequently stored at room temperature over P_2O_5 as a desiccant. All organic solvents

were Optima grade from Fisher Scientific, except methyl tert-butyl ether, which was purchased from Baxter Healthcare Corp., McGraw Park, IL.

SPMD Preparation: The SPMDs for this project were constructed at the Columbia Environmental Research Center using 86 cm lengths of PE tubing with 1.0 mL (0.91 g) of triolein (Sigma Chemical Co. Lot # 38H5150) being added to each SPMD. The active surface area of the finished device was ≈ 440 cm^2 and the weight of an individual SPMD averaged 4.4 g. These SPMDs match the criteria for the USGS "standard" SPMD (13). One SPMD in each deployment apparatus/canister (i.e., one of n = 5) and one of the SPMDs used as Field Blanks (for each site) was spiked with 8.0 µg of perdeuterated (D_{10})-phenanthrene (permeability/performance reference compound [PRC]). The SPMDs were placed into labeled, solvent rinsed gas-tight cans. The cans were immediately flushed with argon and sealed. These cans were then shipped to the site for deployment.

PRC Method Overview: PRCs are non-interfering (analytically) organic compounds, such as D_{10}-phenanthrene, with moderate to relatively high fugacity (escaping tendency) from SPMDs, that are added to the membrane enclosed lipid, as described earlier, prior to deployment. Based on previous research (e.g., 6, 13, 16), it is clear that SPMD sampling rates for PAHs and POPs in general are affected by temperature, water turbulence/facial velocity, and biofouling. However, we have shown that the effects of these environmental variables on the SPMD uptake rates of target compounds are largely mirrored by changes in the loss rates of PRCs (13). By computing the rate of loss of a PRC or its non-labeled analog during the laboratory calibration of SPMDs and comparing

this data to measured values for the loss rate of the same PRC at each field site, analyst can derive a site specific exposure adjustment factor (EAF). These PRC EAFs permit much more accurate estimates of water concentrations of bioavailable contaminants.

SPMD Deployment Apparatus/Canister: We used commercially available (EST, St Joseph, MO) stainless-steel canisters designed for deploying SPMDs (maximum of n = 5) in aquatic environments. Figure 2 is a picture of the deployment apparatus/canister with multiple racks each containing a standard SPMD.

Sampling Overview & Site Characteristics: Each canister contained five standard 1-mL triolein SPMDs, only one of the five SPMDs was spiked with a PRC. Table 1 summarizes relevant details and observations related to SPMD deployment and recovery. The exposure period was 56 days at all sites. Both deployment and recovery of SPMDs followed standard practices established as part of CERC QA/QC procedures used for field exposures of SPMDs. Note that important considerations in the shipping, deployment and recovery of SPMDs are described in the American Petroleum Institute's "Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants" (13). Also, during the deployment of SPMDs, CERC scientists trained Cook Inlet Basin NAWQA personnel on QC issues related to SPMD field exposures. Therefore, sample recovery was entirely conducted by Cook Inlet Basin NAWQA personnel. Table 2 summarizes selected characteristics of exposure sites that may be relevant to the potential outcome of this work.

Figure 2. A commercially available stainless steel deployment apparatus, which has a capacity of 5 Standard SPMDs. Each SPMD is placed on a separate rack and the five racks are held in place by a threaded center pin as shown in the picture.

SPMD Storage and Custody: Following receipt of exposed SPMDs at CERC and prior to processing, the samples were stored in a laboratory freezer at -15°C until processing.

Overview of Sample Processing and Analyte Enrichment: Sample processing was similar to procedures previously described (17), but enough differences did exist that we include descriptions of key analytical procedures in this report. However, all results of QC procedures and checks are given in the "Analytical Appendix".

Table 1. Deployment of SPMDs in small urban Anchorage streams

Sample Designation	Site Location	Number of Canisters	Canister Orientation*	Date Deployed	Date Retrieved	Observations
Site # 1	Ship Creek	One	Horizontal	05/17/00	07/12/00	One SPMD covered with sand/gravel
Site # 2	Campbell Creek, C-Street	One	Vertical	05/17/00	07/12/00	Moderate algal growth on SPMDs
Site # 3	Rabbit Creek	One	Horizontal	05/17/00	07/12/00	No significant changes
Site # 4	Little Rabbit Creek	One	Vertical	05/17/00	07/12/00	Three SPMDs covered with sand
Site # 5	Chester Creek	Three	Vertical	05/18/00	07/13/00	Three SPMDs in one canister covered with sand/sediment, some algal growth on SPMDs in other canisters
Site # 6	Campbell Creek, South Fork	Three	1 Vertical 2 Horizontal	05/18/00	07/13/00	No significant changes

* Longest axis of canister is at right angle to stream flow or stream bed

Preparation of SPMDs for Analysis: Exposed SPMDs and all QA/QC SPMDs generated in conjunction with the analysis sets were cleaned before dialysis. The steps associated with the cleanup were applied to each SPMD sequentially, and were as follows. The sealed metal cans, containing field exposed SPMDs, were opened and the SPMDs were removed and rinsed by immersion into 100 mL of hexane. Then, the hexane was discarded. The SPMDs were placed individually into a large flat stainless

Table 2. Selected characteristics of exposure sites*

Sample Designation	Site Location	Water Velocity	Mean Weekly Temperature In °C ± S.D. (n = # values)	Watershed Description**
Site # 1	Ship Creek	05/17/00: 67.7 cm/s 07/12/00: 131.7 cm/s	Temperature Monitor lost	P.D. = 28 In. = 0.13 % Im. = 2.14 %
Site # 2	Campbell Creek, C-Street	05/17/00: 54.2 cm/s 07/12/00: 94.2 cm/s	9.12 ± 1.95 (n = 9)	P.D. = 523 In. = 1.03 % Im. = 7.06 %
Site # 3	Rabbit Creek	05/17/00: 96.3 cm/s 07/12/00: 125.6 cm/s	5.60 ± 1.35 (n = 9)	P.D. = 112 In. = 0.00 % Im. = 1.91 %
Site # 4	Little Rabbit Creek	05/17/00: 51.8 cm/s 07/12/00: 46.3 cm/s	8.33 ± 0.65 (n = 4)	P.D. = 50 In. = 0.04 % Im. = 2.51 %
Site # 5	Chester Creek	05/18/00: Canister 1 – 21.9 cm/s Canister 2 – 17.7 cm/s Canister 3 – 34.1 cm/s 07/13/00: Canister 1 – 38.7 cm/s Canister 2 – 30.4 cm/s Canister 3 – 41.7 cm/s	11.05 ± 1.73 (n = 9)	P.D. = 2054 In. = 0.77 % Im. = 21.79 %
Site # 6	Campbell Creek, South Fork	05/18/00: Canister 1 – 1.5 cm/s Canister 1 & 2 – 26.5 cm/s 07/13/00: Canister 1 – 6.6 cm/s Canister 2 & 3 – 25.8 cm/s	6.61 ± 2.77 (n = 2.77)	P.D. = 11 In. = 0.00 % Im. = 0.24 %

* Data from Steve Frenzel, USGS

** P.D. = population density, In. = industrial, Im. = impervious to infiltration

steel pan and washed with a clean brush using running tap water (deep well water with no known contaminants). This step is required to remove all remaining surface adhering material. Any SPMD tether loops outside the lipid containment seals were cut off and discarded at this point. Next, water was drained from the exterior of the devices and each SPMD was separately immersed in a glass tank containing 1N HCl for a period of approximately 30 seconds. Then, the devices were rinsed with tap water to remove the acid. Afterwards, all surface water was removed from individual SPMDs by using successive rinses of acetone followed by isopropanol. SPMDs were air dried on a piece of solvent-rinsed aluminum foil (Note that exposure time was minimized to prevent airborne chemical uptake by the SPMDs).

SPMD Dialysis: Clean glass canning jars (one pint) with solvent-rinsed aluminum foil under the lid were used for the dialysis step. The 86 cm SPMDs (1.0-mL lipid) were individually submersed in 175 mL of hexane in each jar and were dialyzed individually at 18 ^{o}C for 18 hours. The hexane extract was removed and transferred into an evaporation flask. A second volume of 175 mL of hexane was added to the dialysis jar and the SPMDs were dialyzed for an additional 6 hours at 18 ^{o}C. The second extract/dialysate was transferred into the flask containing the first dialysate. The SPMDs were then discarded. The combined dialysates were reduced to a volume of 3 - 5 mL on a rotary evaporation system, and quantitatively transferred through a pre-rinsed glass-fiber filter into appropriately labeled test tubes. The solvent volume was then reduced to ≈ 1.0 mL, using high purity nitrogen.

SEC: A Perkin-Elmer Series 410 HPLC (Perkin-Elmer, Inc., Norwalk, CN), was used as the solvent delivery system for the size exclusion chromatography (SEC) cleanup. This HPLC unit was equipped with a Perkin-Elmer ISS-200 auto sampler. The SEC column was a 300-mm x 21.2-mm I.D. (10-µm particle size, 100 Å pore size) Phenogel column (Phenomenex, Inc., Torrance, CA), equipped with a 50-mm x 7.5-mm I.D. Phenogel guard column. The mobile phase was 98:2 (V:V) dichloromethane:methanol (DCM:MeOH) and separations were performed isocratically at a flow rate of 4.0 mL/min. The SEC system was equipped with an ISCO Foxy 200 (ISCO, Inc., Lincoln, NE) fraction collector connected to the output end of the SEC column.

SEC Calibration and Cleanup: The SEC system was calibrated on a daily basis by the injection of a solution of compounds representative of target compounds and potentially interfering materials. The substances contained in this calibration solution (given in sequence of elution volume, first to last) are diethylhexylphthalate (DEHP, a model compound with lipid-like chromatographic behavior), biphenyl and naphthalene (small aromatic hydrocarbons), coronene (a large PAH, who's elution is later than any target pollutant), and elemental sulfur (an interfering substance frequently encountered in environmental samples). Elution of these components was monitored using a UV detector (254 nm) and a strip chart recorder.

SEC cleanup of samples was accomplished using a collect fraction defined by the calibration of the system on the day of operation. The collect fraction was initiated at the point 70% of the time between the apex of the DEHP chromatographic peak and the apex

of the biphenyl chromatographic peak. The collect fraction was terminated at 70% of the time between the apex of the coronene chromatographic peak and the apex of the sulfur chromatographic peak. Replicate SPMD dialysates were combined as a function of this cleanup giving four SPMDs per sample composites. Each SPMD containing a PRC was chromatographed individually. The samples collected were amended with ≈ 2 mL of isooctane, reduced to a volume of ≈ 1 mL on a rotary evaporation system, and quantitatively transferred with hexane into appropriately labeled test tubes.

Post-SEC Cleanup and Sample Splitting: Because the enrichment techniques required for quantitation of PAH and POP residues were different than those for toxicological testing, the samples were split prior to fractionation and enrichment. The PRC samples and quality control (spiked samples) were used for the analysis of PAHs and POPs. A one-SPMD equivalent of control samples (i.e., one fourth of each four-SPMD composite sample) was also used for this purpose. Samples designated for the analysis of PAHs and POPs were identified as the "PAH" samples. The remaining samples were used for toxicological testing and were identified as the "TOX" samples or the samples subjected to biomarker tests. All samples were reduced in volume to ≈ 1.0 mL, using a stream of nitrogen gas.

Further Enrichment of "PAH" Samples: After dialysis and SEC, these samples were processed using open column chromatography. The ≈ 1.0 mL hexane extracts were treated using a tri-adsorbent column consisting of (top to bottom), 3-g phosphoric acid/silica gel; 3 g of KS; and 3 g of silica gel. The tri-adsorbent column was eluted with

50 mL of 4% (V:V) methyl tert-butyl ether in hexane. This procedure resulted in a solution suitable for instrumental analysis of PAH residues and for the analysis of the PRC perdeuterated phenanthrene. The fractions collected were amended with ≈ 2 mL of isooctane, reduced to a volume of ≈ 0.5 mL on a rotary evaporation system, and quantitatively transferred with hexane into labeled GC vials. At this point, sample volumes were adjusted to 0.5 mL using a stream of nitrogen gas.

Further Enrichment of "TOX" Samples: These samples were subjected to a second SEC cleanup step using the same procedure as previously described. After this polishing step, a portion of each sample (25% of control samples, 20% of deployment samples) was removed and held in reserve. The remainder of these samples was transferred into pyrogen free dimethylsulfoxide (DMSO) for biomarker testing.

Gas Chromatography of Analytes: Gas chromatographic analyses were conducted using a Hewlett Packard 5890 series gas chromatograph (GC) equipped with a Hewlett Packard 7673A autosampler (Hewlett Packard, Inc., Palo Alto, CA). In all analyses, 1.0 µL of sample extract was injected using the "cool-on-column" technique with hydrogen as the carrier gas. GC analyses of samples for PAHs, POPs and the PRC were performed using a DB-5 (30 m x 0.25 mm i.d x 0.25 µm film thickness.) capillary column (J&W Scientific, Folsom, CA) with the following temperature program: injection at 60 ^{o}C and hold for 2 min, then 10 ^{o}C/min to 110 ^{o}C and hold for 5 min, followed by 3.0 ^{o}C/min to 200 ^{o}C and hold for 10 min, finally 4 ^{o}C/min to 310 ^{o}C. The Detector was an HNU photoionization detector (PID) with a 9.5 eV lamp operating at 270 ^{o}C (HNU, Inc.,

Newton, MA). Quantitation of PAHs was accomplished using a six-point curve with D_{14}-4-terphenyl as the instrumental internal standard. The levels of the PAH standards spanned a 32-fold range of concentrations for each priority pollutant PAH. Quantitation of the PRC in the PAH fraction was accomplished using a six point curve with D_{14}-4-terphenyl as the instrumental internal standard. The levels of the PRC standards spanned a 10-fold range of concentrations.

GC analysis of "PAH" samples for organochlorine pesticides (OCs) and other POPs was performed using a DB-35MS (30 m x 0.25 mm i.d. x 0.25 μm film thickness) capillary column from J&W Scientific, Folsom, CA, with the following temperature program: injection at 90 ^{o}C; then 15 ^{o}C/min to 165 ^{o}C; followed by 2.5 ^{o}C/min to 250 ^{o}C; then at 10 ^{o}C/min to 320 ^{o}C. The electron capture detector (ECD) was maintained at 330 ^{0}C (Hewlett Packard, Inc., Palo Alto, CA). Quantitation of OCs was accomplished using a six-point curve and external calibration. The levels of the OC standards spanned an 80-fold range of concentrations for each compound determined.

The "TOX" samples were analyzed by GC for residual levels of methyl oleate following each SEC cleanup step. Note that methyl oleate is a triolein impurity and is a marker compound for the presence of more toxic oleic acid, which must be removed or be at low concentrations before biomarker testing. The GC capillary column used was a DB-5 (30 m x 0.25 mm i.d x 0.25 μm film thickness) from J&W Scientific, Folsom, CA. The following temperature program was used for these analyses: injection at 60 ^{o}C and hold for 2 min, then 10 ^{o}C/min to 320 ^{o}C. Detection was performed using a flame ionization

detector (FID) operating at 330 ^{o}C (Hewlett Packard, Inc., Palo Alto, CA). Quantitation of methyl oleate was accomplished using a six-point curve and external calibration. The levels of the methyl oleate standards spanned a 400-fold range of concentration.

Quality Control: For each exposure site, a field blank SPMD accompanied SPMDs designated for aquatic sampling. These QC samples were exposed to the air during the deployment of all SPMDs. Field blank SPMDs are used to measure any potential contamination occurring during transport (to and from the site), deployment, and retrieval, i.e., a QC method used to ensure detected residues originated from exposure waters. These field blanks were processed and analyzed exactly the same as the deployed samples. Individual field blank samples from each exposure site exhibited no coincident GC peaks at levels significantly higher than those associated with the laboratory control SPMDs. These QC data indicate that the deployment and retrieval of SPMDs did not result in inadvertent contamination

The method detection limit (MDL) and method quantitation limit (MQL) for GC analysis of SPMD samples were determined for each analyte by measuring the values of coincident GC-PID peaks for each compound in all sample blanks processed in this study. The MDL was defined as the mean plus 3-standard deviations of values so determined (18). The MQL was defined as the mean plus 10-standard deviations of values so determined (18). For individual analytes having no coincident GC peak, an assumed value equal to the low sample reject for the GC method was used to calculate the mean. In the cases where the MQLs were below the level of the calibration curve

employed in the GC-analysis, the MQLs were set at the value of the lowest level of the calibration curve employed in quantifying the analyte levels. The background, MDLs and MQLs for analysis of the study samples for PAHs are presented in Table I of the "Analytical Appendix".

During the processing of study samples, a wide variety of QC samples and procedures were used to monitor recovery through the entire process, as well as to check the performance of individual processing steps. Overall recoveries of PAHs through the dialysis, fractionation, and enrichment procedures were monitored using spiked SPMD samples. These SPMD spikes were prepared by fortifying a freshly prepared SPMD with 4.0 μg of each priority pollutant PAH. The recovery values were consistent with those typically obtained at CERC for the overall analytical process. The analysis of OCs was not part of the original study plan and, as a result, QC SPMDs were not spiked with OCs. However, OC recovery data from other SPMD studies (using the same methods) conducted during the time period of this project are given in Table II of the "Analytical Appendix".

Dialytic recovery was monitored for the five sample sets (Table III, Analytical Appendix) needed for this project, by spiking a control SPMD with ^{14}C-dibenz(a, h)anthracene (DBA). Note that DBA is one of the more difficult PAHs to obtain acceptable dialytic yields and that recovery of ^{14}C-DBA was not measured until after both dialysis and SEC cleanup (Table IV, Analytical Appendix).

Processing was monitored for the five SEC cleanup sets (Table V, Analytical Appendix) by spiking a control sample with ^{14}C-2, 5, 2', 5'-tetrachlorobiphenyl (Table VI, Analytical Appendix). The determination of residual levels of methyl oleate (Table VII, Analytical Appendix) following SEC serves as a marker of the effectiveness of this processing step for the removal potential interferences. Elimination of methyl oleate, oleic acid, and polyethylene waxes from SPMD materials, reduces the potential of masking the toxicity of target environmental contaminants.

The recoveries of the analytes of interest were determined for the tri-adsorbent treatment for PAHs and for OCs. The tri-adsorbent column spikes were prepared by adding 1.0 μg of each priority pollutant PAH to a control tri-adsorbent column. After OCs were observed in study samples, three tri-adsorbent columns were spiked with a mixture of twenty-seven individual OC-pesticides at 40 ng each. The recoveries of PAHs and OCs are given in Table VII of the Analytical Appendix.

RESULTS AND DISCUSSIONS

Quality Control: The exposed SPMDs were processed concurrently with the quality control samples described in the "Materials and Methods" section. Tables 3 & 4 give the MDLs-MQLs and the analytical recoveries of target pollutants, respectively. Because of differences in GC-detectors sensitivities (i.e., ECD and PID), MDLs of OC residues are

Table 3. Background, MDL, & MQL Values for Target Compounds

OC-Pesticides	Bkg ng	MDL ng	MQL ng	PAHs	Bkg µg	MDL µg	MQL µg
HCB*	0.1	0.4	1.0	Naphthalene	0.04	0.15	0.42
PCA**	0.2	0.5	1.5	Acenaphthylene	0.03	0.23	0.71
α-BHC***	0.1	0.4	1.1	Acenaphthene	0.02	0.05	0.25
Lindane	0.2	0.5	0.8	Fluorene	0.03	0.34	1.06
β-BHC***	0.3	0.6	1.3	Phenanthrene	0.02	0.09	0.25
Heptachlor	0.2	0.5	1.2	Anthracene	0.02	0.05	0.25
δ-BHC***	0.2	0.6	1.3	Fluoranthene	0.03	0.16	0.48
Dacthal	0.2	0.5	1.2	Pyrene	0.02	0.12	0.36
Oxychlordane	0.2	0.4	1.0	Benz[a]anthracene	0.02	0.05	0.25
Heptachlor Epoxide	0.1	0.4	1.0	Chrysene	0.02	0.05	0.25
trans-Chlordane	0.2	0.4	1.0	Benzo[b]fluoranthene	0.02	0.05	0.25
trans-Nonachlor	0.2	0.6	1.3	Benzo[k]fluoranthene	0.02	0.05	0.25
o,p'-DDE	0.2	0.4	1.2	Benzo[a]pyrene	0.02	0.01	0.25
cis-Chlordane	0.2	0.6	1.7	Indeno[1,2,3-cd]pyrene	0.02	0.05	0.25
Endosulfan	0.3	0.7	1.5	Dibenz[a,h]anthracene	0.02	0.05	0.25
p,p'-DDE	0.1	0.4	0.8	Benzo[g,h,i]perylene	0.02	0.05	0.25
Dieldrin	0.2	0.3	1.0				
o,p'-DDD	0.4	0.7	1.4				
Endrin	0.3	0.5	1.8				
cis-Nonachlor	0.1	0.3	1.0				
o,p'-DDT	0.3	0.5	1.1				
p,p'-DDD	0.2	0..5	1.0				
Endosulfan-II	0.4	0.8	1..9				
p,p'-DDT	0.2	0.4	1.0				
Endosulfan Sulfate	0.1	0.4	1.0				
Methoxychlor	0.1	0.4	1.0				
Mirex	0.3	0.8	2.1				

* Hexachlorobenzene
** Pentachloroanisole
*** Benzenehexachloride

much lower than those for PAHs (Table 3). Overall recoveries of the 16-priority pollutant PAHs and 27 OCs averaged 66.3 and 82.3 %, respectively (Table 4). Although the mean recovery of the PAHs was lower than for the OCs, the analytical precision was good (i.e., C.V. = 14.2 %). Gas chromatographic conditions were optimized to give sufficient resolution for the quantitation of all target compounds (Table IX of the Analytical Appendix and Figures 1a & 2a).

Table 4. Recovery of PAHs and OC-Pesticides From SPMD Spikes

OC-Pesticides *	%	PAHs	Set # 1 %	Set # 2 %	Set # 3 %	Set # 4 %	Set # 5 %	Mean %
HCB	62.3	Naphthalene	0.0	19.1	0.0	0.0	36.1	11.0
PCA	114	Acenaphthylene	44.9	49.8	38.5	43.0	56.2	46.5
α-BHC	75.5	Acenaphthene	45.0	53.4	44.2	48.2	63.7	50.9
Lindane	88.1	Fluorene	51.0	65.1	67.6	66.8	80.7	66.2
β-BHC	50.0	Phenanthrene	47.3	69.2	69.9	70.9	75.2	66.5
Heptachlor	65.1	Anthracene	46.9	66.8	68.4	65.3	71.1	63.7
δ-BHC	46.8	Fluoranthene	53.9	77.6	79.8	78.4	81.5	74.2
Dacthal	54.7	Pyrene	57.9	77.8	83.0	80.2	83.3	76.4
Oxychlordane	84.0	Benz[a]anthracene	52.6	79.7	79.4	81.2	85.2	75.6
Heptachlor Epoxide	82.0	Chrysene	63.3	63.3	68.3	70.8	80.8	69.3
trans-Chlordane	73.5	Benzo[b]fluoranthene	57.7	77.6	82.9	85.4	89.8	78.7
trans-Nonachlor	61.8	Benzo[k]fluoranthene	46.7	54.8	71.7	74.4	76.3	64.8
o,p'-DDE	76.7	Benzo[a]pyrene	66.4	76.7	79.1	75.2	84.2	76.3
cis-Chlordane	66.5	Indeno[1,2,3-cd]pyrene	66.9	81.9	78.8	82.5	92.5	80.5
Endosulfan	80.4	Dibenz[a,h]anthracene	71.4	87.0	81.1	88.2	104.4	86.4
p,p'-DDE	80.2	Benzo[g,h,i]perylene	58.2	73.7	68.7	78.9	90.6	74.0
Dieldrin	69.7	Mean =	51.9	67.1	66.3	68.1	78.2	66.3
o,p'-DDD	76.2							
Endrin	80.7							
cis-Nonachlor	56.7							
o,p'-DDT	83.8							
p,p'-DDD	69.5							
Endosulfan-II	58.8							
p,p'-DDT	65.7							
Endosulfan Sulfate	49.2							
Methoxychlor	46.2							
Mirex	69.3							
OCP Mean =	82.3							

* Note that values in this table reflect averages of 17 replicates as processed at CERC encompassing the time frame for the processing of samples from this study

Variance associated with field exposed replicate SPMDs (e.g., Table 5) appeared to be quite low. For example, levels of pyrene among 3 replicate SPMDs at site 5 varied (i.e., C.V. in %) by less than 5 %.

Table 5. Results of the Analyses of Study Samples for PAHs (µg/SPMD by GC-PID)

	Site #1	Site #2	Site #3	Site #4	Site #5 Rep #1	Site #5 Rep #2	Site #5 Rep #3	Site #6 Rep #1	Site #6 Rep #2	Site #6 Rep #3
Naphthalene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Acenaphthylene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Acenaphthene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Fluorene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Phenanthrene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Anthracene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Fluoranthene	<MDL	<MDL	<MDL	<MDL	**0.26**	**0.49**	**0.49**	<MDL	<MDL	<MDL
Pyrene	<MDL	<MDL	<MDL	<MDL	**1.44**	**1.56**	**1.55**	<MDL	<MDL	<MDL
Benz[a]anthracene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Chrysene	<MDL	<MDL	<MDL	<MDL	**0.32**	**0.34**	**0.27**	<MDL	<MDL	<MDL
Benzo[b]fluoranthene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Benzo[k]fluoranthene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Benzo[a]pyrene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Indeno[1,2,3-cd]pyrene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Dibenz[a,h]anthracene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Benzo[g,h,i]perylene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Naphthalene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Acenaphthylene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

Observations and Findings: The results of PAH analysis of "PAH" SPMDs exposed to sites 1-6 are given in Tables 5 & 6. Although few individual priority pollutant PAHs

Table 6. Estimated Total PAHs (µg/SPMD) Based on Pyrene PID Response Factor

Deployment Site	Total PID Response
Mean of 6 Field Blanks	0.45
Site # 1	9.58
Site # 2	12.97
Site # 3	10.64
Site # 4	2.65
Site # 5, Replicate # 1	8.60
Site # 5, Replicate # 2	7.18
Site # 5, Replicate # 3	8.46
Site # 6, Replicate # 1	3.98
Site # 6, Replicate # 2	3.94
Site # 6, Replicate # 3	3.87

were seen, the chromatograms (e.g., Figure 3) indicated that complex mixtures of substituted PAHs may be present. Note that Huckins et al. (3) have shown that SPMD residue levels are proportional to ambient concentrations of dissolved organic contaminants. Using the response factor for pyrene, estimates of the total PID response to enriched SPMD extracts from each sample site were made (Table 6). Based on

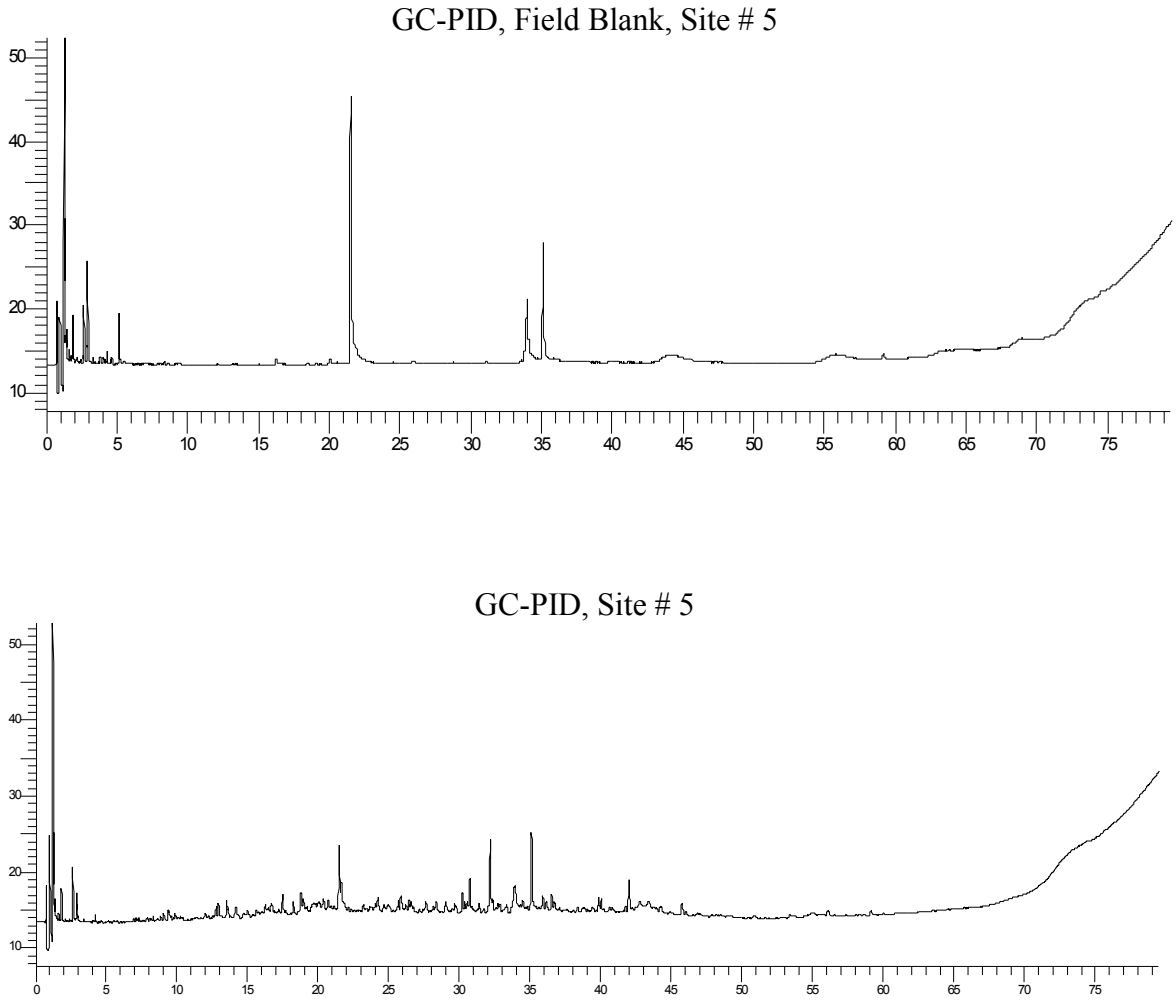
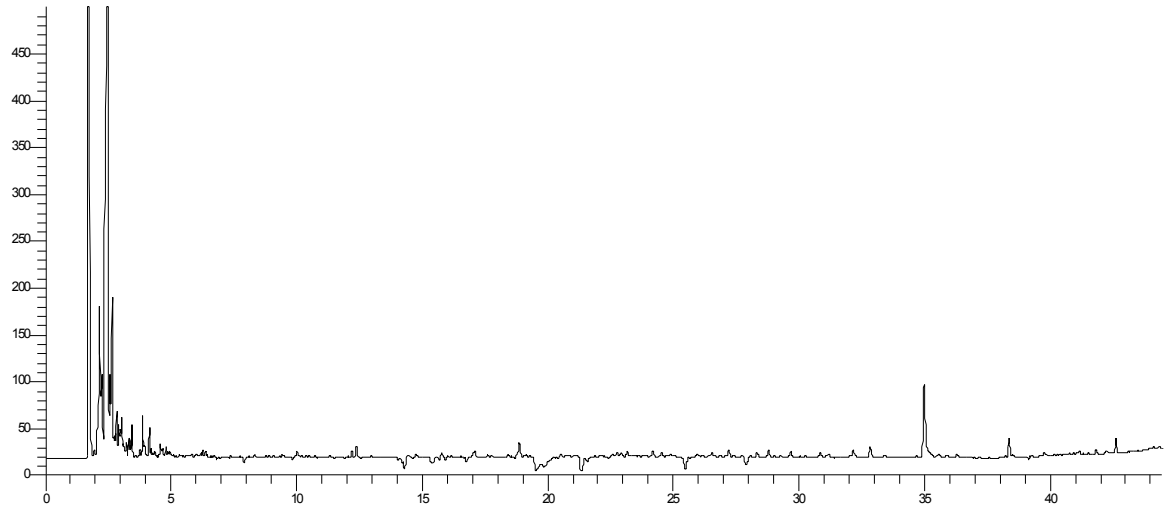


Figure 3. Representative GC-PID traces of enriched SPMD extracts of the site 5 field blank and sample. Note that the prominent GC-PID peaks at ≈ 21 min., at ≈ 34 min., and at ≈ 35 min. are the PRC, methyl oleate, and the internal standard, respectively.

this approach, Site 2 contained the highest levels of these aromatic compounds (12.97-μg/SPMD, most likely substituted PAHs), while site 5 was only fourth highest among the 6 sites (Table 6). However, site 5 contained the only detectable priority pollutant PAHs (Table 5). The apparent elevated levels of substituted PAHs (requires GC/MS confirmation) at site 2 are surprising in view of the fact that site 5 has a much higher percentage of impervious area (Table 2).

Although analysis of OC POPs was not planned, we screened the "PAH" samples by GC-ECD (Figures 4 & 5) and identified and quantified several OC-pesticides (Table 7). Pentachloroanisole (PCA) was present at all six sites, but was elevated at sites 4 & 5. PCA is a microbial degradation product of pentachlorophenol (PCP), a wood preservative, which was banned by the EPA in the early eighties. The presence of chlorinated dioxins in commercial formulations of PCP was a major factor in its removal from the market. The OC pesticide p, p'-DDT was detected in SPMDs at all sites with the exception of site 3. However, p, p'-DDT concentrations in SPMDs at site 1 (i.e., 39.2 ng/SPMD) are significantly elevated and may be due to a point source. For a perspective, levels of p, p'-DDT detected in SPMDs exposed to Missouri River water (28 d, summer of 1992) at sites ranging from Nebraska City, NE, to Hermann MO averaged ≈ 15 ng/SPMD (17). Also, residues from the historic use of p, p'-DDT in temperate areas are typically characterized by a larger percentage of p, p'-DDE (>50 % of the total residues) than p, p'-DDT. This was not the case for any of the sites with detectable residues. This finding suggests that residues of DDT and its analogs may stem from local use, where degradation is likely retarded by low temperatures relative to temperate regions.

GC-ECD, Field Blank, Site # 5



GC-ECD, Site # 5

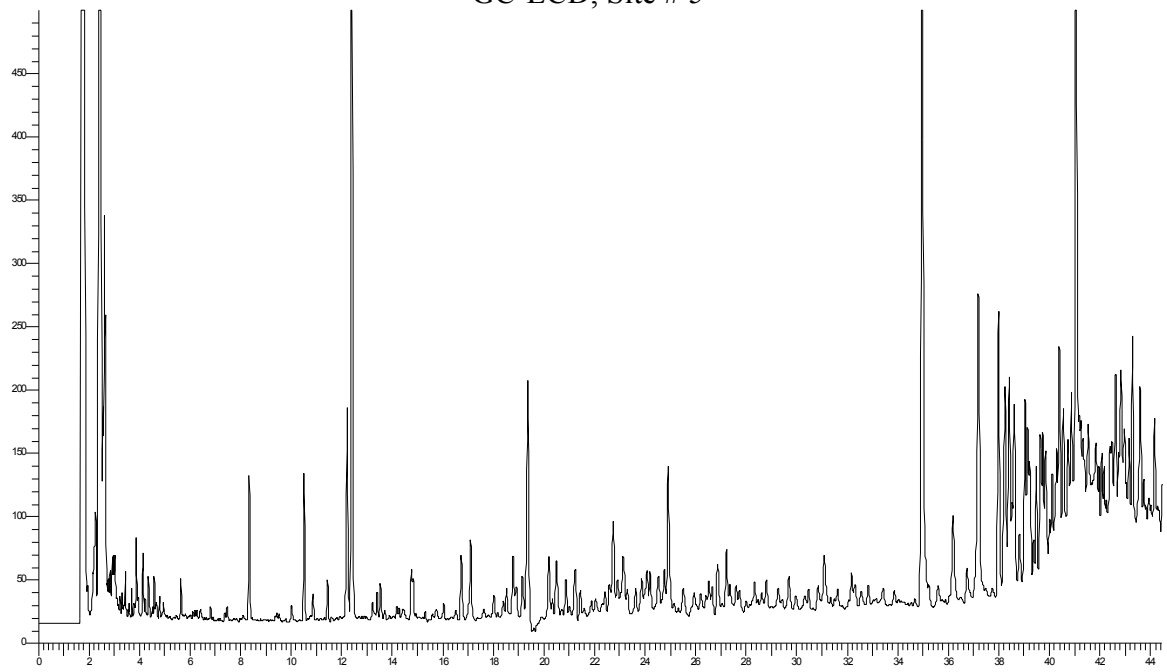
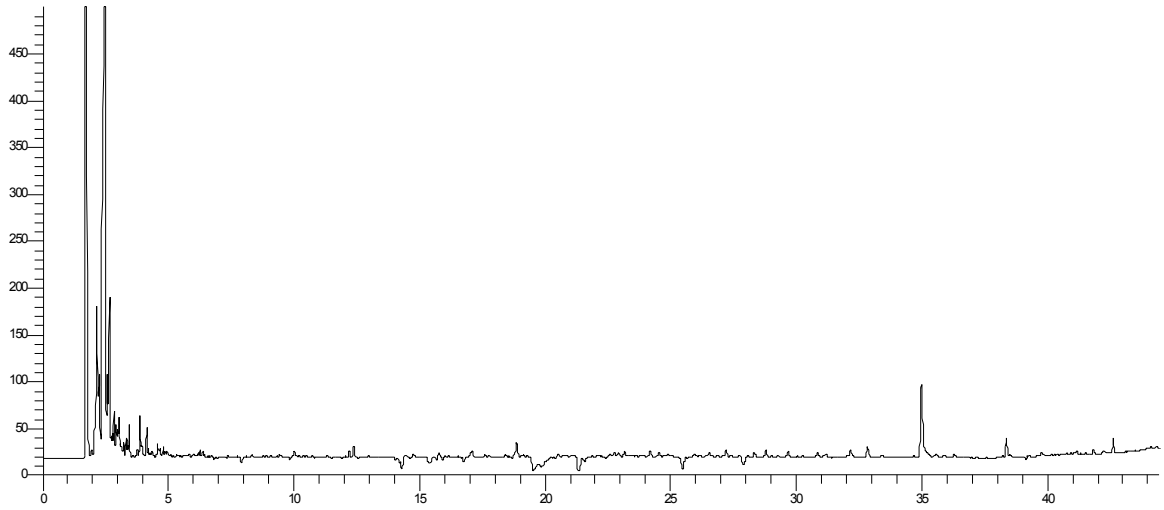


Figure 4. Representative GC-ECD traces of site # 5 field blank and exposed SPMDs

GC-ECD, Field Blank, Site # 6



GC-ECD, Site # 6

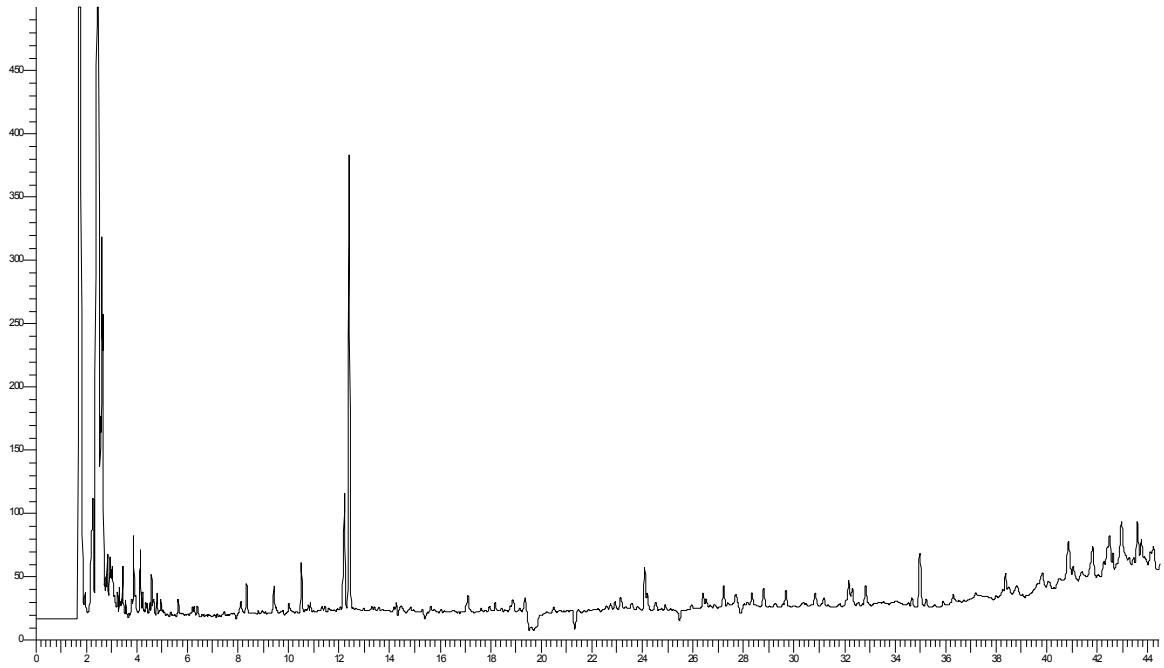


Figure 5. Representative GC-ECD traces of site # 6 (i.e., the reference site) field blank and exposed SPMDs

Table 7. Results of the GC-ECD analysis of SPMDs for OC pesticides (ng/SPMD)

	Site #1	Site #2	Site #3	Site #4	Site #5 Rep #1	Site #5 Rep #2	Site #5 Rep #3	Site #6 Rep #1	Site #6 Rep #2	Site #6 Rep #3
HCB	6.7	5.4	15.8	11.5	9.2	8.8	9.4	5.1	5.4	7.3
PCA	14.9	16.2	15.7	35.6	29.3	28.3	30.0	11.0	11.7	13.6
α-BHC	<MDL	<MDL	<MDL	<MDL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL
Lindane	<MDL	0.9	0.9	7.8	2.8	2.7	2.7	0.5	0.5	0.6
β-BHC	1.5	0.7	<MDL	0.7	2.2	1.5	1.6	<MQL	<MQL	<MQL
Heptachlor	<MDL	<MDL	<MDL	<MDL	<MDL	5.0	5.8	<MDL	<MDL	<MDL
δ-BHC	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL
Dacthal	<MDL	3.1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Oxychlordane	<MDL	<MDL	<MDL	<MDL	<MQL	4.6	4.6	3.1	<MQL	<MQL
Heptachlor Epoxide	1.8	0.3	<MDL	1.5	1.3	<MDL	<MDL	<MQL	<MQL	<MQL
trans-Chlordane	1.0	0.8	<MDL	0.7	3.5	5.0	5.2	<MQL	<MQL	<MDL
trans-Nonachlor	<MQL	1.0	1.7	0.8	5.7	6.1	6.5	2.7	5.4	7.9
o,p'-DDE	4.2	1.7	<MDL	2.1	3.9	5.1	5.2	1.3	1.5	<MQL
cis-Chlordane	2.0	1.3	1.1	1.2	4.6	<MQL	5.6	0.7	0.8	0.9
Endosulfan	<MDL	<MDL	<MDL	<MDL	<MQL	1.1	1.0	<MDL	<MDL	<MDL
p,p'-DDE	10.1	2.1	0.7	<MQL	<MQL	<MQL	<MQL	0.6	0.8	1.2
Dieldrin	0.5	<MQL	0.5	0.5	2.2	2.2	2.4	<MQL	0.5	0.5
o,p'-DDD	10.2	4.1	<MDL	<MDL	2.7	4.4	4.4	5.6	3.8	<MQL
Endrin	2.1	0.8	1.9	1.1	3.5	<MQL	<MQL	<MQL	<MQL	0.7
cis-Nonachlor	<MQL	<MQL	0.5	<MDL	1.6	1.2	1.3	<MQL	<MQL	0.1
o,p'-DDT	13.6	0.8	4.6	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
p,p'-DDD	11.1	4.7	<MDL	<MDL	2.5	2.6	2.9	<MQL	<MQL	<MQL
Endosulfan-II	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL
p,p'-DDT	39.2	7.1	<MDL	1.4	3.9	4.8	4.9	3.2	3.0	4.4
Endosulfan Sulfate	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL
Methoxychlor	<MDL	<MQL	<MDL	<MDL	4.9	<MQL	<MQL	<MDL	<MDL	<MDL
Mirex	<MDL	<MDL	1.5	<MDL	<MQL	33.4	33.8	<MDL	<MDL	<MDL

Exposure Conditions and PRC Data: Earlier, we stated that temperature, water-turbulence/facial (membrane) velocity, and biofouling could affect SPMD sampling rates. Warm highly turbulent water is sampled at a higher rate than cold quiescent waters, because the uptake of hydrophobic chemicals by SPMDs is largely based on solute diffusion rates and the thickness of the aqueous diffusion layer. Examination of data in Table 2 shows that site 3 (Rabbit Creek) not only had the highest flow rate during SPMD

exposures, but also the lowest mean temperature. For contaminants with log octanol-water partition coefficients (i.e., K_{ow}, a measure of hydrophobicity) greater than 4.4 (e.g., pyrene), the impact of water flow rates on SPMD sampling is more important than temperature effects. However, the design of the EST deployment canisters (Figure 2) tends to moderate flow effects. Fortunately, the effects of the complex factors controlling SPMD sampling rates are mirrored by the effects on PRC loss rates (13). Table 8 gives data on PRCs from all six-test sites.

Table 8. Permeability/performance reference compound data

Sample Site	Mean* μg PRC at Day 0 (C_{SPMD0}·Sample wt.)	Mean μg PRC at at Exposure End (C_{SPMD}·Sample wt.)	PRC loss rate k_{ePRC} (d^{-1})***
Site #1	5.72	1.13**	0.0246
Site #2	5.72	1.35**	0.0219
Site #3	5.72	0.31**	0.0442
Site #4	5.72	1.33**	0.0221
Site #5	5.72	0.77	0.030
Site #6	5.72	1.23	0.023

* Mean of field blanks for all sites
** Single values
*** The k_{ePRC} is computed from $k_{ePRC} = \ln (C_{SPMD0}/C_{SPMD})/t$ and sample weights are identical

Losses of PRCs at the 6 exposure sites ranged from 76.4 to 94.6 %, which are reflected by the magnitude of the k_{ePRC}s (Table 8). Site 3 SPMDs lost the largest amount of PRC, which is consistent with the observed highest average water velocity of the study (Table 3). Surprisingly, the k_{ePRC}s of perdeuterated phenanthrene, derived for the six sites, are only 1.6 to 3.2 fold greater than phenanthrene's k_{ePRC} derived in laboratory calibration studies @ 10 °C and a flow velocity of < 1cm/sec (6). Thus, the baffling effect of the deployment canister and the generally lower exposure temperatures appeared to have

offset the much higher (relative to laboratory calibration) water flow velocity at the exposure sites.

Estimation of TWA Water Concentrations: SPMD calibration data and PRC data are required to accurately estimate water concentrations of dissolved (i.e., bioavailable) organic contaminants from their respective levels in SPMDs. Using data from the analysis of the PRC levels (Table 8), models previously developed (3, 6), and data from SPMD calibration studies (13), the concentrations of most contaminants present in exposed SPMDs can be estimated.

An example of the overall estimation procedure is as follows. The first step is to compute the rate constant of PRC (perdeuterated phenanthrene) loss for each site. In our case the following model was used.

$$k_{ePRC} = \ln (C_{SPMD0} / C_{SPMD})/t \qquad (1)$$

where k_{ePRC} is the first-order rate constant for PRC loss, C_{SPMD0} is the PRC concentration in SPMDs at the initiation of the exposure period (typically field blank values are used), C_{SPMD} is the concentration of PRC in the SPMD at the end of the exposure, and t is exposure time in days. After derivation of k_{ePRC} values for perdeuterated phenanthrene at each site, these values must be compared to the k_e of non-labeled or native phenanthrene (i.e., k_{en}) derived during laboratory calibration studies. The difference between the k_{ePRC} and k_{en} can be viewed as an exposure adjustment factor (EAF), which is given by

$$EAF \equiv k_{ePRC}/k_{en} \quad (2)$$

The EAF can then be used to adjust analyte sampling rates to the conditions of each sample site by the following

$$k_{ua\text{-}f} = K_{SPMD\text{-}f}\, EAF\, (k_{ua}/K_{SPMD}) \quad (3)$$

and

$$k_{ea\text{-}f} = k_{ua\text{-}f}/K_{SPMD\text{-}f} \quad (4)$$

where $k_{ua\text{-}f}$ is the analyte uptake rate constant (L/d·g) at a specific site, $K_{SPMD\text{-}f}$ is the unitless equilibrium SPMD-water partition coefficient at field temperature, and the subscripts "f"' and "a" refer to field conditions and target compound, respectively. The use of equations 1-3 assumes that k_{en}, k_{ua}, and K_{SPMD} values are known or can be derived from existing models (13). These calibration data and related information for priority pollutant PAHs and OC pesticides have been determined in laboratory studies (13) with defined sets of exposure conditions (e.g., water temperature, flow velocity and exposure duration; ideally, calibration conditions should bracket those encountered in the field).

After determining the levels of target compounds in study SPMDs (Tables 5-7) and the loss rates of PRCs (Table 8 and equation 1), the concentrations of analytes in exposure waters can be determined by one of two models described by Huckins et al. (13)

$$C_{wa} = C_{SPMD}M_{SPMD}/R_{sa\text{-}f}t = C_{SPMD}/k_{ua\text{-}f}t \quad (5)$$

and

$$C_{wa} = C_{SPMD}/K_{SPMD\text{-}f}\,(1-\exp\,[-k_{ea\text{-}f}\,t]\,) \quad (6)$$

where C_{wa} is analyte chemical concentration in site water (pg or ng/L, TWA if the linear model [5] is used), C_{SPMD} is chemical concentration in the whole SPMD (pg or ng/g), M_{SPMD} is the mass of the SPMD used for the exposure in g, $R_{sa\text{-}f}$ is the analyte sampling rate of a standard 1-mL triolein SPMD in L/d of water extracted, and $K_{SPMD\text{-}f}$, $k_{ua\text{-}f}$, $k_{ea\text{-}f}$, and t have been defined.

Selection of the appropriate model (i.e., equation 5 or 6) to use for the estimation of C_{wa} is based on the following approach. The first step is the computation of PRC half-lives for the various sites. This can be accomplished by the following simple model

$$t_{1/2} = 0.693/k_{ePRC} \quad (7)$$

Using data given in Table 8 and equation 7, we find that the PRC $t_{1/2}$s at the six study sites ranged from 15.7 to 31.6 days. Because equation 5 assumes linear uptake of analyte and linear uptake only occurs during the first half-life, equation 5 can only be used to compute C_{wa} for compounds with K_{SPMD} or K_{ow} values four times greater than the PRC phenanthrene. Clearly, derivation of the C_{wa} of measured contaminants with K_{ow}s ≤ the

PRC phenanthrene (log K_{ow} = 4.46) must be made with equation 6 or an equilibrium model. Also, the following equilibrium model should be used if phenanthrene's k_{ePRC} value suggests four or more half-lives have elapsed during the exposure and the target compound has a $K_{ow} \leq$ phenanthrene (i.e., 4.46).

$$C_{wa} = C_{SPMD}/K_{SPMD} \qquad (8)$$

Using the rationale and algorithm given in this section, the estimated bioavailable waterborne concentrations of selected contaminants detected at the study sites are presented in Table 9. Note that calibration data used for these derivations were generated at 10 ^{o}C (13).

Table 9. Concentrations of selected target compounds in water at study sites

Analytes	Site 1 (pg/L) EAF = 1.76	Site 2 (pg/L) EAF = 1.56	Site 3 (pg/L) EAF = 3.16	Site 4 (pg/L) EAF = 1.58	Site 5 (pg/L) EAF = 2.14	Site 6 (pg/L) EAF = 1.64
Fluoranthene	<MDL	<MDL	<MDL	<MDL	1,210	<MDL
Pyrene	<MDL	<MDL	<MDL	<MDL	3,460	<MDL
Chrysene	<MDL	<MDL	<MDL	<MDL	880	<MDL
Total PAHs*	26,600	40,700	16,500	8,200	18,400	11,700
HCB	42	38	55	80	46	39
PCA	65	79	38	172	105	56
t-Nonachlor	<MQL	5	4	4	23	26
Lindane	<MDL	40	40	347	120	22
p, p'-DDE	46	11	2	<MQL	<MQL	4
p, p'-DDD	59	28	<MDL	<MDL	12	<MQL
p, p'-DDT	238	48	<MDL	10	22	23
o, p'-DDE	22	NC**	<MDL	NC	NC	NC
o, p'-DDD	51	NC	<MDL	<MDL	NC	NC
o, p'-DDT	87	NC	NC	<MDL	<MDL	<MDL

* Based on PID response factor for pyrene and the SPMD sampling rate for pyrene
** Not computed, generally very low levels

As expected, the relative levels of aqueous contaminants (dissolved phase) shown in Table 9 generally reflect those measured in SPMDs (Tables 5-7). However, because of differences in the EAFs vary by almost two fold and analyte SPMD uptake rates vary,

water levels are not exactly proportional to those reported for SPMDs. The water concentrations of the some of the reported compounds (e.g., p, p'-DDE at sites 3 and 6) are probably close to global background levels. However, several chemicals at specific sites are clearly elevated and may be of concern. These include pyrene (known to have greatly enhanced toxicity during photolysis) at site 5, total PAHs at site 2, PCA at sites 4 and 5 (main concern is the known presence of dioxin impurities in pentachlorophenol, the parent compound of PCA), and DDT and analogs at site 1. Adverse effects on fish have been observed for anthracene and pyrene at > 3 ng/L water concentrations (Jim Oris, personal communication, Miami University, Oxford, OH). The significance of apparently elevated concentrations of total PAHs found at several sites cannot be assessed without toxicity studies such as those performed by Dr. Johnson and the identification of potentially toxic components. Concentrations of DDT and it's analogs (total of 500 pg/L) at site 1 are also of potential concern because DDT has been found to bioconcentrate in chum salmon by 3.2×10^6 (19). Clearly, a level of bioconcentration this high would lead to high tissue levels (> 1 μg/g) of DDT in fishes.

Most chlorinated pesticides such as DDT have been banned – some for more than 20 years. The persistence of these chlorinated contaminants has resulted in very slow declines in their environmental concentrations. Also, the DDT complex along with a much larger set of diverse environmental contaminants has been reported to cause endocrine-disruption in some organisms (20).

In summary, several contaminants have been tentatively identified in this study whose bioavailable water concentrations are elevated. This report, in combination with the parallel biomarker work of Dr. Johnson, with and without photoactivation, defines several potential contaminant issues in urban streams of the Cook Inlet.

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Table I. Dialysis sets

Set # 1 9-7-00	Set # 2 9-11-00	Set # 3 9-13-00
Reagent Blank # 1	Reagent Blank # 2	Reagent Blank # 3
14C-SPMD Spike # 1	14C-SPMD Spike # 2	14C-SPMD Spike # 3
SPMD Spike # 1	SPMD Spike # 2	SPMD Spike # 3
SPMD Processing Blank # 1	SPMD Processing Blank # 2	SPMD Processing Blank # 3
SPMD Fabrication Blank, Rep # 1	Site # 3, Field Blank , Rep # 1	Site # 1 (PRC)
SPMD Fabrication Blank, Rep # 2	Site # 3, Field Blank , Rep # 2	Site # 2 (PRC)
SPMD Fabrication Blank (PRC)	Site # 3, Field Blank , Rep # 3	Site # 3 (PRC)
Site # 1, Field Blank (PRC)	Site # 3, Field Blank , Rep # 4	Site # 4 (PRC)
Site # 2, Field Blank (PRC)	Site # 4, Field Blank , Rep # 1	Site # 5, Location # 1 (PRC)
Site # 3, Field Blank (PRC)	Site # 4, Field Blank , Rep # 2	Site # 5, Location # 2 (PRC)
Site # 4, Field Blank (PRC)	Site # 4, Field Blank , Rep # 3	Site # 5, Location # 3 (PRC)
Site # 5, Field Blank (PRC)	Site # 4, Field Blank , Rep # 4	Site # 6, Location # 1-1 (PRC)
Site # 6, Field Blank (PRC)	Site # 5, Field Blank , Rep # 1	Site # 6, Location # 1-2 (PRC)
Site # 1, Field Blank , Rep # 1	Site # 5, Field Blank , Rep # 2	Site # 6, Location # 2 (PRC)
Site # 1, Field Blank , Rep # 2	Site # 5, Field Blank , Rep # 3	Site # 1, Rep # 1
Site # 1, Field Blank , Rep # 3	Site # 5, Field Blank , Rep # 4	Site # 1, Rep # 2
Site # 1, Field Blank , Rep # 4	Site # 6, Field Blank , Rep # 1	Site # 1, Rep # 3
Site # 2, Field Blank , Rep # 1	Site # 6, Field Blank , Rep # 2	Site # 1, Rep # 4
Site # 2, Field Blank , Rep # 2	Site # 6, Field Blank , Rep # 3	Site # 2, Rep # 1
Site # 2, Field Blank , Rep # 3	Site # 6, Field Blank , Rep # 4	Site # 2, Rep # 2
Site # 2, Field Blank , Rep # 4		Site # 2, Rep # 3
		Site # 2, Rep # 4

Table I (Continued). Dialysis sets

Set # 4 9-18-00	Set # 5 9-20-00
Reagent Blank # 4	Reagent Blank # 5
14C-SPMD Spike # 4	14C-SPMD Spike # 5
SPMD Spike # 4	SPMD Spike # 5
SPMD Processing Blank # 4	SPMD Processing Blank # 5
Site # 3, Rep # 1	Site # 5, Location # 3, Rep # 1
Site # 3, Rep # 2	Site # 5, Location # 3, Rep # 2
Site # 3, Rep # 3	Site # 5, Location # 3, Rep # 3
Site # 3, Rep # 4	Site # 5, Location # 3, Rep # 4
Site # 4, Rep # 1	Site # 6, Location # 1, Rep # 1
Site # 4, Rep # 2	Site # 6, Location # 1, Rep # 2
Site # 4, Rep # 3	Site # 6, Location # 1, Rep # 3
Site # 4, Rep # 4	Site # 6, Location # 1, Rep # 4
Site # 5, Location # 1, Rep # 1	Site # 6, Location # 2, Rep # 1
Site # 5, Location # 1, Rep # 2	Site # 6, Location # 2, Rep # 2
Site # 5, Location # 1, Rep # 3	Site # 6, Location # 2, Rep # 3
Site # 5, Location # 1, Rep # 4	Site # 6, Location # 2, Rep # 4
Site # 5, Location # 2, Rep # 1	Site # 6, Location # 3, Rep # 1
Site # 5, Location # 2, Rep # 2	Site # 6, Location # 3, Rep # 2
Site # 5, Location # 2, Rep # 3	Site # 6, Location # 3, Rep # 3
Site # 5, Location # 2, Rep # 4	Site # 6, Location # 3, Rep # 4

Table II. Recovery of ^{14}C-dibenz(a,h)anthracene from spiked SPMDs following dialysis and SEC

Dialysis Set	Date	% Recovery
Set # 1	9-7-00	96.9
Set # 2	9-11-00	91.6
Set # 3	9-13-00	91.3
Set # 4	9-18-00	93.6
S3t # 5	9-20-00	90.7
	Mean=	**92.8**

Table III. SEC cleanup sets

Preliminary Set 9-22-00	Set # 1 9-25-00	Set # 2 9-26-00
(Single Injection Samples)	**(Single Injection Samples)**	**(Single Injection Samples)**
Daily Calibration Run	Daily Calibration Run	Daily Calibration Run
14C-QA/QC GPC Recovery	14C-QA/QC GPC Recovery	14C-QA/QC GPC Recovery
14C-SPMD Spike # 1	GPC Blank # 1	GPC Blank # 2
14C-SPMD Spike # 2	Reagent Blank # 3	**(Four injection Composites)**
14C-SPMD Spike # 3	SPMD Fabrication Blank, Rep # 1	Reagent Blank # 1
14C-SPMD Spike # 4	SPMD Fabrication Blank, Rep # 2	Reagent Blank # 2
14C-SPMD Spike # 5	SPMD Spike # 1	Reagent Blank # 4
	SPMD Spike # 2	Reagent Blank # 5
	SPMD Spike # 3	SPMD Processing Blank # 1
	SPMD Spike # 4	SPMD Processing Blank # 2
	SPMD Spike # 5	SPMD Processing Blank # 4
	(Four injection Composites)	SPMD Processing Blank # 5
	SPMD Processing Blank # 3	Site # 1, Field Blank , Rep # 1
	SPMD Fabrication Blank (PRC)	Site # 1, Field Blank , Rep # 2
	Site # 1, Field Blank (PRC)	Site # 1, Field Blank , Rep # 3
	Site # 2, Field Blank (PRC)	Site # 1, Field Blank , Rep # 4
	Site # 3, Field Blank (PRC)	Site # 2, Field Blank , Rep # 1
	Site # 4, Field Blank (PRC)	Site # 2, Field Blank , Rep # 2
	Site # 5, Field Blank (PRC)	Site # 2, Field Blank , Rep # 3
	Site # 6, Field Blank (PRC)	Site # 2, Field Blank , Rep # 4
	Site # 1 (PRC)	Site # 3, Field Blank , Rep # 1
	Site # 2 (PRC)	Site # 3, Field Blank , Rep # 2
	Site # 3 (PRC)	Site # 3, Field Blank , Rep # 3
	Site # 4 (PRC)	Site # 3, Field Blank , Rep # 4
	Site # 5, Location # 1 (PRC)	Site # 4, Field Blank , Rep # 1
	Site # 5, Location # 2 (PRC)	Site # 4, Field Blank , Rep # 2
	Site # 5, Location # 3 (PRC)	Site # 4, Field Blank , Rep # 3
	Site # 6, Location # 1-1 (PRC)	Site # 4, Field Blank , Rep # 4
	Site # 6, Location # 1-2 (PRC)	Site # 5, Field Blank , Rep # 1
	Site # 6, Location # 2 (PRC)	Site # 5, Field Blank , Rep # 2
		Site # 5, Field Blank , Rep # 3
		Site # 5, Field Blank , Rep # 4
		Site # 6, Field Blank , Rep # 1
		Site # 6, Field Blank , Rep # 2
		Site # 6, Field Blank , Rep # 3
		Site # 6, Field Blank , Rep # 4
		Site # 1, Rep # 1
		Site # 1, Rep # 2
		Site # 1, Rep # 3
		Site # 1, Rep # 4

Table III (Continued). SEC cleanup sets

Set # 3 9-27-00	Second Pass SEC Cleanup 10-17-00
(Single Injection Samples)	**(Single Injection Samples**
Daily Calibration Run	SPMD Processing Blank
14C-QA/QC GPC Recovery	Site # 1 Field Blank
GPC Blank # 3	Site # 2 Field Blank
(Four injection Composites)	Site # 3 Field Blank
Site # 2, Rep # 1	Site # 4 Field Blank
Site # 2, Rep # 2	Site # 5 Field Blank
Site # 2, Rep # 3	Site # 6 Field Blank
Site # 2, Rep # 4	Site # 1
Site # 3, Rep # 1	Site # 2
Site # 3, Rep # 2	Site # 3
Site # 3, Rep # 3	Site # 4
Site # 3, Rep # 4	Site # 5 Rep. 1
Site # 4, Rep # 1	Site # 5 Rep. 2
Site # 4, Rep # 2	Site # 5 Rep. 3
Site # 4, Rep # 3	Site # 6 Rep. 1
Site # 4, Rep # 4	Site # 6 Rep. 2
Site # 5, Location # 1, Rep # 1	Site # 6 Rep. 3
Site # 5, Location # 1, Rep # 2	
Site # 5, Location # 1, Rep # 3	
Site # 5, Location # 1, Rep # 4	
Site # 5, Location # 2, Rep # 1	
Site # 5, Location # 2, Rep # 2	
Site # 5, Location # 2, Rep # 3	
Site # 5, Location # 2, Rep # 4	
Site # 5, Location # 3, Rep # 1	
Site # 5, Location # 3, Rep # 2	
Site # 5, Location # 3, Rep # 3	
Site # 5, Location # 3, Rep # 4	
Site # 6, Location # 1, Rep # 1	
Site # 6, Location # 1, Rep # 2	
Site # 6, Location # 1, Rep # 3	
Site # 6, Location # 2, Rep # 1	
Site # 6, Location # 2, Rep # 2	
Site # 6, Location # 2, Rep # 3	
Site # 6, Location # 2, Rep # 4	
Site # 6, Location # 3, Rep # 1	
Site # 6, Location # 3, Rep # 2	
Site # 6, Location # 3, Rep # 3	
Site # 6, Location # 3, Rep # 4	
Site # 6, Location # 3, Rep # 5	

Table IV. Recovery of ^{14}C-2,5,2',5'-tetrachlorobiphenyl during SEC cleanup processing

SEC Processing Set	Processing Date	% Recovery
Preliminary	9-22-00	94.3
Set # 1	9-25-00	96.4
Set # 2	9-26-00	94.9
Set # 3	9-27-00	97.9
Second Pass	10-17-00	94.5
	Mean =	**95.6**

Table V. Results of post-SEC analysis for residual levels of methyl oleate (µg/SPMD by GC-FID)

4-SPMD Composite	1st Pass SEC	2nd Pass SEC
SPMD Processing Blank	210	3.0
Site # 1 Field Blank	210	3.2
Site # 2 Field Blank	250	5.9
Site # 3 Field Blank	220	5.8
Site # 4 Field Blank	260	5.3
Site # 5 Field Blank	230	3.8
Site # 6 Field Blank	230	4.4
Site # 1	43	1.5
Site # 2	47	1.5
Site # 3	32	2.0
Site # 4	48	1.2
Site # 5 Rep. 1	54	2.0
Site # 5 Rep. 2	42	1.7
Site # 5 Rep. 3	40	1.7
Site # 6 Rep. 1	81	1.0
Site # 6 Rep. 2	72	0.7
Site # 6 Rep. 3	73	0.9

Table VI. Recovery of PAHs and OC-Pesticides through tri-adsorbent column chromatographic cleanup (corrected for background)

OC-Pesticides	# 1 %	# 2 %	# 3 %	**Mean %**	PAHs	%
HCB	82.6	71.3	74.4	**76.1**	Naphthalene	0.0
PCA	85.2	74.7	73.7	**77.9**	Acenaphthylene	24.2
α-BHC	55.2	42.0	37.1	**44.7**	Acenaphthene	31.4
Lindane	72.3	60.5	55.2	**62.7**	Fluorene	55.6
β-BHC	92.8	89.5	81.8	**88.0**	Phenanthrene	80.0
Heptachlor	93.8	87.1	79.8	**86.9**	Anthracene	89.3
δ-BHC	0.0	0.0	0.0	**0.0**	Fluoranthene	105
Dacthal	93.4	89.7	82.6	**88.6**	Pyrene	108
Oxychlordane	96.6	91.4	79.9	**89.3**	Benz[a]anthracene	113
Heptachlor Epoxide	97.9	91.6	81.1	**90.2**	Chrysene	103
trans-Chlordane	95.5	91.3	80.6	**89.1**	Benzo[b]fluoranthene	122
trans-Nonachlor	96.1	91.9	80.4	**89.4**	Benzo[k]fluoranthene	93.4
o,p'-DDE	97.8	92.3	80.8	**90.3**	Benzo[a]pyrene	104
cis-Chlordane	96.3	91.6	80.9	**89.6**	Indeno[1,2,3-cd]pyrene	120
Endosulfan	69.1	44.0	39.0	**50.7**	Dibenz[a,h]anthracene	120
p,p'-DDE	90.9	88.1	80.2	**86.4**	Benzo[g,h,i]perylene	103
Dieldrin	94.8	89.9	80.0	**88.2**	Mean =	**85.7**
o,p'-DDD	94.2	91.5	84.5	**90.1**		
Endrin	85.9	78.8	70.8	**78.5**		
cis-Nonachlor	93.3	90.5	81.2	**88.3**		
o,p'-DDT	104.3	99.0	86.0	**96.4**		
p,p'-DDD	91.9	89.5	82.7	**88.0**		
Endosulfan-II	0.0	0.0	0.0	**0.0**		
p,p'-DDT	96.0	95.6	89.0	**93.5**		
Endosulfan Sulfate	0.0	0.0	0.0	**0.0**		
Methoxychlor	99.2	100.5	95.3	**98.4**		
Mirex	103.8	98.5	84.4	**95.6**		
Mean =	82.6	71.3	74.4	**76.1**		

Table VII. Elution order of targeted compounds during gas chromatographic analysis*

OC-Pesticides (on DB-35 MS)	Retention Time Min.	**PAHs** (on DB-5)	Retention Time Min.
HCB	12.91	Naphthalene	6.05
PCA	13.08	Acenaphthylene	11.42
α-BHC	13.52	Acenaphthene	12.75
Lindane	15.63	Fluorene	16.47
β-BHC	17.39	Phenanthrene	23.50
Heptachlor	17.67	Anthracene	23.84
δ-BHC	18.99	Fluoranthene	32.67
Dacthal	20.96	Pyrene	34.13
Oxychlordane	22.49	D_{14}-4-Terphenyl as Internal Std	36.96
Heptachlor Epoxide	23.24	Benz[a]anthracene	43.94
trans-Chlordane	24.86	Chrysene	44.25
trans-Nonachlor	25.11	Benzo[b]fluoranthene	56.72
o,p'-DDE	25.19	Benzo[k]fluoranthene	56.99
cis-Chlordane	25.52	Benzo[a]pyrene	59.28
Endosulfan	25.71	Indeno[1,2,3-cd]pyrene	66.59
p,p'-DDE	27.41	Dibenz[a,h]anthracene	67.02
Dieldrin	27.72	Benzo[g,h,i]perylene	67.75
o,p'-DDD	28.75		
Endrin	29.82		
cis-Nonachlor	30.50		
o,p'-DDT	30.60		
p,p'-DDD	31.51		
Endosulfan-II	31.89		
p,p'-DDT	33.37		
Endosulfan Sulfate	35.08		
Methoxychlor	38.28		
Mirex	39.01		
OCN as Internal Std.	43.57		

* NOTE: Slight variations in retention times were recorded on a run-by-run basis. Retention times as given reflect the example provided in Figures 3 and 4.