EVALUATION OF THE USE OF SPMDs FOR THE ANALYSIS OF HYDROPHOBIC ORGANIC CONTAMINANTS IN WATER OF THE ELIZABETH RIVER, VIRGINIA

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EXCUTIVE SUMMARY

This report summarizes finding from a pilot study using lipid-containing semipermeable membrane devices (SPMDs) to monitor bioavailable organic contaminants in the Elizabeth River, in the state of Virginia. The work was conducted as part of a collaborative effort between the U.S. Geological Survey's (USGS) Columbia Environmental Research Center (CERC) and the Virginia Department of Environmental Quality (DEQ) to assess waterborne hydrophobic contaminants in environmental waters of Virginia. The SPMDs were fabricated by CERC scientists and they were deployed by DEQ personnel for 30 days (July of 2000) at eight sites along the Elizabeth River. Unfortunately, SPMD samplers were lost at two sites prior to retrieval by the DEQ. SPMDs from the remaining six sites were processed and analyzed for polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine chlorine pesticides (OCPs) by CERC personnel. Quantifiable levels of contaminants from each class of chemicals were found at all sites. However, concentrations of PAHs were greater at a site corresponding to the Atlantic Wood Preservers facility than those of PAHs or other target contaminants at the other study sites. Also several sites had elevated levels of OCPs. In particular, several so called "new generation" pesticides were found in SPMDs. Both isomers of permethrin (a pyrethroid insecticide) were detected for the first time in SPMDs exposed to aquatic environments during the last decade. Overall, the results of this study suggest that SPMDs provide an effective approach to monitoring bioavailable contaminants often difficult to detect in environmental waters.

INTRODUCTION

During the last century, the Elizabeth River (located in south-east Virginia) has experienced a steady decline in the ecological balance that once existed (1). A technical assessment (1) has found that many of the problems present in the river today are due to the input of toxic contaminants. Heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) tributyl tin (TBT), DDT, phthalate esters, aromatic hydrocarbons, herbicides and pesticides have been identified by the Elizabeth River Project Toxics Reduction Team as contaminants of concern (1). By using a ranking system, based on potential impacts to human health and the environment, investigators have found that PCBs and PAHs are of greatest concern (1). In terms of total contaminant loading, PAHs top the list. Finfish sampling by the Virginia Institute of Marine Science in segments of the Elizabeth River with high PAH levels has shown that there is a high rate of gross abnormalities.

Unfortunately, there is a paucity of water concentration data for both PAHs and PCBs, because the levels of these very hydrophobic compounds in waters are usually below the detection limits of commonly employed low volume (i.e., ≤ 5 L) sampling methods. Even when high volume solid phase extraction systems are used for the analysis of environmental waters, concerns exist with sample contamination, analyte losses, and procedurally mediated changes in the aqueous distribution of target compounds due to the collection, filtration, and extraction of large volumes of water. Also, episodic changes in

environmental contaminant concentrations may not be detected, because sampling with conventional methods provide data on a single point or small window in time.

To address most of these analytical methods issues and others, Scientists at the U.S. Geological Survey's Columbia Environmental Research Center (CERC) have developed a semipermeable membrane device (SPMD) for *in situ* passive integrative monitoring of aquatic contaminants (2-6). The SPMD consists of layflat, low-density polyethylene (LDPE) tubing containing a thin film of high-molecular weight (≥ 800 Da), high-purity triolein (Figure 1). The nonporous polymeric membrane used in the SPMD sampler functions by allowing the readily bioavailable contaminant molecules to pass through transient membrane cavities approaching 10 Å in cross sectional diameter. The molecular size limitation of the LDPE used for SPMD membrane suggest that only dissolved chemicals will be sampled by SPMDs, which has been confirmed by Ellis et al. (7). Note that for compounds with log octanol-water partition coefficients (K_{ow}s) ≤ 6.0, the dissolved phase is the major source of residues accumulated in aquatic organism tissues (8). Also, residue transfer through the polymeric cavities in the LDPE membrane of SPMDs appears to mimic the transport of contaminants through biomembranes (9), which leads to bioconcentration of recalcitrant hydrophobic contaminants.

Lipid containing SPMDs are applicable to all neutral organic compounds with log octanol-water partition coefficients (K_{ow}s) ≥ 3.0 , which includes all PAHs and PCBs. Although SPMDs will also sample neutral compounds with even lower log K_{ow}s, the advantages of the SPMD approach over conventional methods are generally not great.

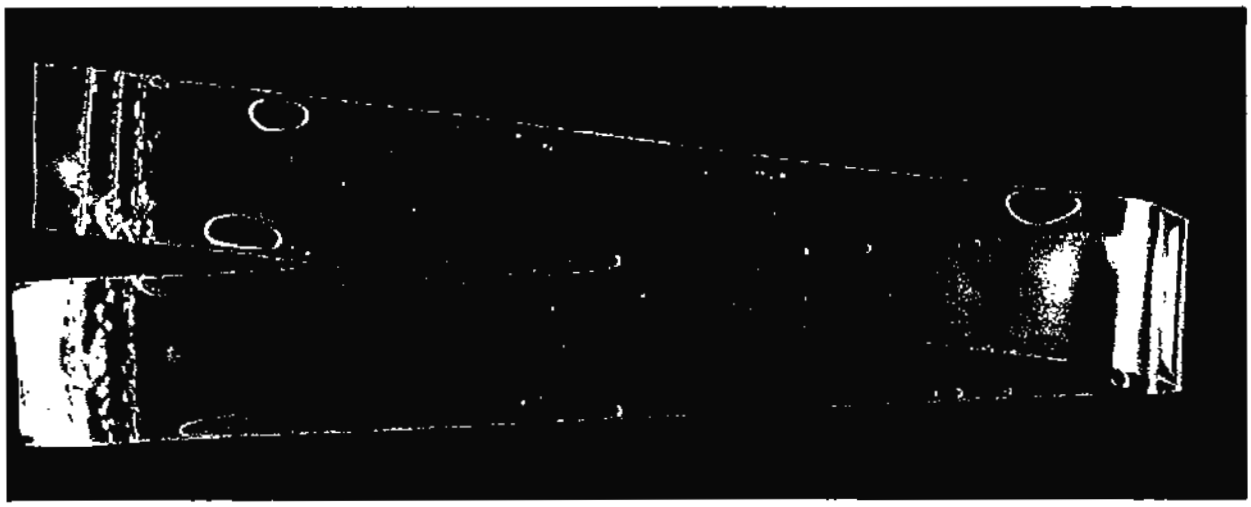

Figure 1. A standard lipid-containing SPMD with three molecular welds near each end. Note the low interfacial tension causes intimate contact (i.e., the presence of a lipid film on the membrane interior surface) between the triolein and the membrane even where air bubbles exists.

However, in the case of very hydrophobic analytes with log K_{ow}s > 6.0, where a large portion of the total waterborne chemical is associated with particulate or dissolved organic carbon phases, SPMDs readily concentrate ultra-trace residues of these compounds present in the dissolved phase to quantifiable levels (4, 10). Depending on environmental conditions such as temperature, biofouling level and flow velocity-turbulence at the membrane surface, a "standard" 1-mL triolein SPMD (6) will passively extract hydrophobic contaminant residues from about 1to 10 L of water per day. Sampling of hydrophobic compounds will generally remain integrative (i.e., no significant losses of residues accumulated in the device, even when ambient concentrations fall) throughout a 30 day (d) sampling period. Thus, more than a 100 L of water is typically extracted of hydrophobic organic residues by one-standard SPMD during a 30 d exposure period. Also note that we have developed an approach (11) that

permits determination of site-specific SPMD sampling rates. Details of this method are given in the experimental section. Finally, of the list of Elizabeth River contaminants given in the introductory paragraph, only heavy metals and certain very hydrophilic herbicides and pesticides will not be effectively sampled by SPMDs.

The primary purpose of this project was to demonstrate the utility of the SPMD approach for the detection and quantification of trace levels of hydrophobic contaminants in a selected aquatic system of the state of Virginia. Also, this work was designed to determine residue levels of the contaminants of concern (i.e., priority pollutant [PP] PAHs as designated by the US EPA, organochlorine pesticides [OCPs], and PCBs), or the presence of typical bioconcentratable contaminants at selected sites along the Elizabeth River of Virginia.

EXPERIMENTAL AND MODELING

Materials: LDPE layflat tubing was purchased from Environmental Sampling Technologies, St. Joseph, MO. The 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°C for 8 hours and stored at 130°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°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 Scieutific.

SPMD Preparation: Specifically, the "standard" (6) SPMDs used in this project were constructed using 1.0 mL (0.91 g) aliquots of high purity triolein (Sigma Chemical Co. Lot # 38H5150, ≥ 95 % pure) enclosed as a thin film in 86 cm lengths of LDPE tubing. Note that the design of the standard or commercially available SPMD consists of a specified length (typically about 90 cm [distance between the inter welds or the length of the triolein containing portion]) of 2.54 cm wide layflat LDPE tubing (additive free, wall thickness 70-95 μm), containing ≥ 95 % purity triolein (1 mL used for the 91.4 cm length). After heat-sealing the triolein inside the LDPE tube, the resulting SA-V (membrane surface area to total SPMD volume) ratio is ≈ 90 cm^2/mL or ≈ 460 cm^2/mL of triolein, and the device consists of ≈ 20 % triolein. For the 1-mL triolein configuration, the whole device typically weighs ≈ 4.4 to 4.6 g. In our case, the area of the active exchanging or sampling surface of the finished device was ≈ 440 cm^2. One of the SPMDs in each deployment device (see "SPMD Deployment and Retrieval" for a picture of a commercially available deployment device) and one of the two SPMDs used as Field Blanks (for each site) was spiked with ≈ 12 μg of D_{10} phenanthrene, which is a permeability/performance reference compound (PRC, see subsequent section on PRCs). The SPMDs were loaded onto support racks which were then placed into labeled, solvent

rinsed gas-tight cans. Afterwards, the cans were flushed with argon and sealed. These cans were placed in coolers and then shipped overnight to the Virginia Department of Environmental Quality (DEQ) for deployment in the Elizabeth River.

Permeability/Performance Reference Compounds: PRCs are analytically non-interfering organic compounds with moderate to high fugacity from SPMDs that are added to the lipid prior to membrane enclosure and field deployment (6). The basis of the approach has been described in detail by Huckins et al. (11). In this study perdeuterated phenanthrene was used as the PRC. The rate constants for PRC dissipation from SPMDs at each sample site were determined and compared to PRC dissipation rate constants measured during laboratory calibration studies of target compounds. This method permitted the calculation of an exposure adjustment factor (EAF). Using the EAF ratios, calibration data (i.e., SPMD uptake rate constants for analytes of interest) were adjusted to more accurately reflect actual *in situ* sampling rates. As suggested earlier, the effects of exposure conditions on SPMD uptake and dissipation rates are largely a function of 1) exposure medium temperature, 2) facial velocity-turbulence at the membrane surface, 3) membrane biofouling, and 4) the design of the deployment apparatus (i.e., baffling of media flow-turbulence). Based on our PRC research (11), the use of EAFs should permit the estimation of analyte water concentrations within ± 75 % of the actual time weighted average values.

Locations of Sampling Sites: Figure 2 shows a map with the site locations in the Elizabeth River (note that map and site descriptions courtesy of Roger Stewart, Virginia DEQ, Richmond, VA).

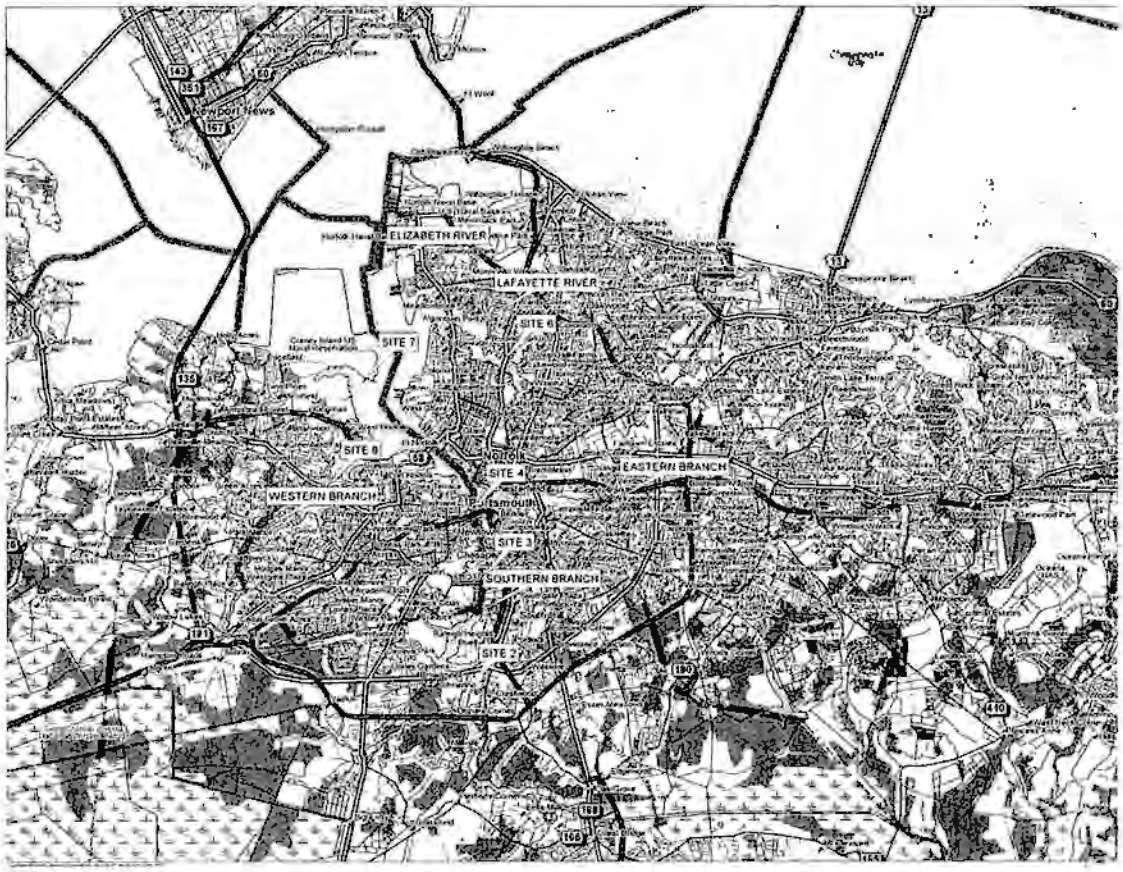

Figure 2. Locations of SPMD sample sites on the Elizabeth River, south eastern Virginia (Courtesy of Roger Stewart, Virginia DEQ, Richmond, VA).

Site # 2 was located approximately 6.26 river miles up from the mouth of the Southern Branch of the Elizabeth River off of Virginia Power near the western shoreline (36 46 03.0 -76 17 57.6). Site # 3 was located approximately 1.98 miles up from the mouth of the Southern Branch of the Elizabeth River off of Atlantic Wood Preservers next to an

old pilings near the western shoreline (36 48 30.6 -76 17 31.3). Site # 4 was located approximately at the mouth of the Southern Branch of the Elizabeth River off of Portsmouth's Portside quay near the hotel Renaissance (36 49 59.0 -76 17 45.2). Site # 6 was located approximately 3.83 miles up from the mouth of the Lafayette River within a pier structure on the western shoreline (36 53 19.4 -76 16 51.4). Site # 7 was located south of Cranny Island adjacent to the DEQ's artificial oyster reef restoration area (36 52 58.9 -76 20 41.6). Site # 8 was located approximately 2.11 river miles up from the mouth of the western branch of the Elizabeth River and under the route 17 bridge where it was attached to the 4th "NO WAKE" sign located in the channel towards the southern bank (36 50 31.1 -76 21 37.5).

SPMD Deployment and Retrieval: SPMDs used for each study site were enclosed in three stainless steel protective devices identified as "canister # 1", "canister # 2", and "canister # 3", and were deployed by the Virginia DEQ at eight study sites along the Elizabeth River, Virginia. Canister # 1 and canister # 2 (Figure 3) each contained five SPMDs (both canisters contained one SPMD spiked with a PRC) while canister # 3, only contained four SPMDs (one SPMD also contained a PRC) and differed somewhat in design from canisters 1 and 2. Therefore, a total of 14 SPMDs were deployed at each site. The eight sites were identified numerically as Site # 1 through Site # 8. Environmental conditions (including but not limited to location, water temperature, and dates and times of deployment and retrieval) were not specified, but the exposure period was 30 d. Upon retrieval of study SPMDs, Virginia DEQ personnel found that all deployment devices from Site # 1 and # 5 were lost. In addition, Canister # 1 from Site #

6 was lost. Heavy biofouling was also noted on recovered SPMDs as shown in Figure 4 (photo courtesy of Roger Stewart, Virginia DEQ, Richmond, VA). Finally, SPMDs were shipped in coolers on ice overnight to CERC in the original shipping cans.

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

Sample Processing and Residue Enrichment: Sample processing was similar to procedures previously described (6), with specific details noted in the following sections.

Figure 3. The commercially available deployment apparatus described as canisters # 1 and 2. Each standard SPMD (n = 5) was placed on a separate rack and the racks were held in place by a threaded center pin as shown in the picture.

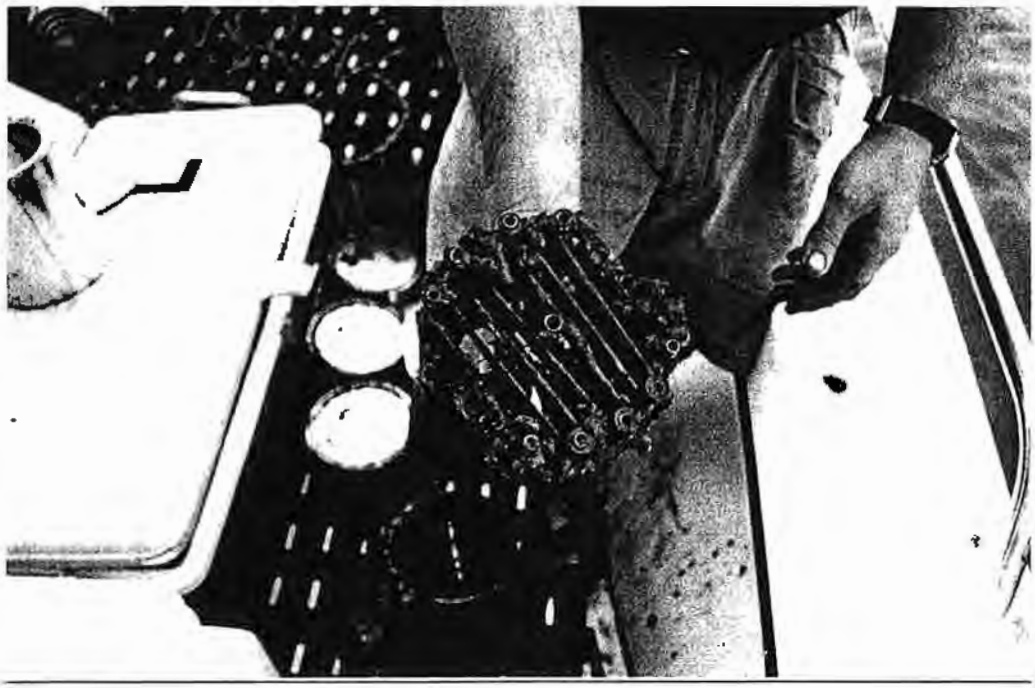

Figure 4. Picture (courtesy of Roger Stewart, Virginia DEQ) a of heavily fouled SPMD on a deployment apparatus rack after the 30-d exposure in the Elizabeth River.

SPMD Membrane Cleaning: The exterior membrane surfaces of exposed SPMDs were cleaned prior to dialysis. This cleaning procedure was applied to all SPMDs received from the field as well as to all quality assurance/quality control (QA/QC) SPMDs generated in conjunction with analysis sets. The steps associated with membrane cleaning were applied to each SPMD individually and sequentially, and were as follows. Sealed cans with SPMDs were opened and the SPMDs were removed and momentarily immersed (< 30 sec.) in 100 mL of hexane. Afterwards, the hexane was discarded. Then the SPMDs were individually placed into a large flat stainless steel pan and washed thoroughly using running tap water and a clean brush 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, the water was drained from the exterior of each SPMD. The SPMDs were then separately immersed in a glass tank containing 1 N HCl for a period of approximately 30 seconds. Then, they 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.

SPMD Dialysis (i.e., Recovery of Analytes): Glass canning jars (one pint) with solvent-rinsed aluminum foil under the lid were used for the dialysis step. Each SPMD was submersed in 175 mL of hexane in separate jars and were dialyzed individually at 18 °C for 18 hours. The hexane was removed and transferred into an evaporation flask. A second volume of 175 mL of hexane was added to each sample jar and the SPMDs were dialyzed for an additional 6 hours at 18 °C. The second dialysate was transferred into the flask containing the first dialysate. At this point analyte recovery is complete and the

SPMDs were discarded. The combined dialysates from each SPMD were reduced to a volume of 3 to 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.

Post Dialysis Sample Splitting: The dialysates from all SPMDs containing a PRC were maintained as individual samples (i.e., they were not composited) throughout cleanup procedures. Dialysates of the four remaining SPMDs from canisters # 1 and # 2 were combined to give two 4-SPMD composite samples. Also, the dialysates of the three remaining SPMDs in canister # 3 were combined to give a 3-SPMD composite sample. A 1-SPMD equivalent sub-sample was removed from each of the two 4-SPMD composite dialysates. These two 1-SPMD sub-samples from each site were held in reserve for any future analysis. At this point, each site was represented by three, 3-SPMD composite dialysates, with the exception of site # 6 (canister # 1 was lost). Then all three SPMD composites were split into two equal 1.5-SPMD composites. This final split was necessary because a different set of enrichment techniques were required for the environmental contaminants targeted in each sample. These sample splits were ideutified as the "PAH" fractions and the "OCP" fractions. Thus, at each site with recovered SPMDs, there were six samples (site # 6 n = 4) each representing a 1.5-SPMD equivalent. After these manipulations, dialysates of all samples were reduced to a volume of ≈ 1 mL using a stream of high purity nitrogen. Note that in subsequent analytical steps, the "PRC" dialysate concentrates were treated the same as the "PAH" fractions.

SEC Cleanup: A Perkin-Elmer Series 410 HPLC (Perkin-Elmer, Inc., Norwalk, CN), was employed as the solvent delivery system for size exclusion chromatography (SEC) cleanup of samples. 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 isocratic mobile phase was 98:2 (V:V, dichloromethane:methanol, DCM:MeOH) the flow rate was set at 4.0 mL per minute. 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.

The SEC system was calibrated on a daily basis by the injection of a solution of compounds representative of the analytes and potentially interfering materials. The substances contained in this calibration solution, in sequence of elution, are diethylhexylphthalate (DEHP; a common plasticizer with lipid-like chromatographic behavior), biphenyl and naphthalene (small aromatic analytes), coronene (a large PAH later eluting than any anticipated analyte), and elemental sulfur (a problematic interference frequently encountered in environmental samples). Elution of these components was monitored by a UV detector (254 μm) and a strip chart recorder.

SEC cleanup was accomplished using a collect fraction (i.e., window in which target analytes elute) determined by the calibration of the system on the day of operation. For the "PAH" and "PRC" samples, 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. For the "OCP" samples, the collect fraction was initiated at the point 50 % of the time between the apex of the DEHP chromatographic peak and the apex of the biphenyl chromatographic peak. For all SEC separations, 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. The fractions 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 Column Chromatography: After SEC cleanup, samples were further processed using open column chromatography. The methods employed to enrich the "OCP" and "PAH" fractions are as follows. The "OCP" fractions (≈ 1 mL volume) were applied to Florisil® columns (5 g) and subsequently eluted with 60 mL of 75:25 (V:V) methyl tert-butyl ether:hexane. The fractions collected were amended with ≈ 5 mL of isooctane, and reduced to a volume of ≈ 0.5 mL on a rotary evaporation system. Following volume reduction to ≈ 0.5 mL, each sample was applied to a silica gel (SG) column (5 g). Two fractions were collected; fraction SG-1 (46 mL of hexane) and fraction SG-2 (55 mL of 40:60 [V:V] methyl tert-butyl ether:hexane). This enrichment procedure provided fractions for the analysis of PCBs and OCPs. 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. Sample volumes at this point were adjusted to 1.0 mL using high purtiy nitrogen.

The "PRC" and "PAH" fractions (≈ 0.5 mL) were treated using a tri-adsorbent column consisting of from top to bottom, 3 g phosphoric acid/silica gel; 3 g of potassium silicate; 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 analysis of PAH residues and for the analysis of the PRC. 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. Sample volumes at this point were adjusted to 1.0 mL using high purtiy nitrogen.

Gas Chromatography: 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. Analyses of PAH fractions and PRC samples 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 °C, then 15 °C/min to 165 °C, followed by 2.5 °C/min. to 250 °C, then 10 °C/min. to 320 °C and held at 320 °C for 1 min. Detection was performed using an HNU photoionization detector (PID) with a 9.5 eV lamp operating at 270 °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 standards for PAH samples spanned a 20-fold range of concentration for each priority pollutant PAH from 0.5 to 10 μg/mL. Quantitation of the

PRC samples was also accomplished using a six point curve with D_{14}-4-Terphenyl as the instrumental internal standard. The levels of the standards for PRC samples spanned a 10-fold range of concentration from 1.0 to 10 μg/mL. Analyses of SG-1 and SG-2 fractions for OCPs and PCBs were performed using a DB-35MS (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 90 °C; then 15 °C/min to 165 °C; followed by 2.5 °C/min to 250 °C; then at 10 °C/min to 320 °C. The electron capture detector (ECD, Hewlett Packard, Inc., Palo Alto, CA) was maintained at 330 ^{0}C. Quantitation of OCPs in SG-1 and in SG-2 samples was accomplished using a six point curve with octachloronaphthalene (OCN) as the instrumental internal standard. The levels of the OCP standards spanned an 80-fold range of concentration for each compound determined or from 1.0 to 80 ng/mL. Quantitation of total PCBs in the SG-1 fractions was accomplished using a six point curve employing standard solutions containing a 1:1:1:1 mixture of Aroclor® 1242, 1248, 1254, and 1260 with OCN as the instrumental internal standard. The levels of the PCB standards spanned a 160-fold concentration range from 50 to 8,000 total ng/mL. Figures I-III (Analytical Appendix) show representative chromatograms of analytical standards used in this study.

Gas Chromatography-Mass Spectrometry (GC-MS): Selected samples were analyzed with a Agilent 6890 GC (Agilent Technologies, Inc., Wilmington, DE). In all analyses, 1.0 µL of sample extract was injected using the "cool-on-column" technique with helium as the carrier gas. A HP-5MS (30 m x 0.25 mm i.d. x 0.25 µm film thickness) capillary column (Agilent Technologies, Inc., Wilmington, DE) was used for all confirmational

analyses. Detection was performed with a 5973 mass selective detector (Agilent Technologies, Inc., Palo Alto, CA) in the selected ion mode (SIM) or full scan (FS) mode.

In the case of cis/trans-permethrin analyses the following temperature program was used: injection at 90 °C, then 10 °C/min to 250 °C, followed by 5 °C/min to 310 °C and held at 310 °C for 2 min. The detector zone temperatures were set at 310 °C for the MSD transfer line, 150 °C at the quadrapole, and 230 °C at the source. Quantitation of the analytes was accomplished using a six point curve with external calibration. The ions chosen for SIM detection were masses 163 and 183 and a 100 msec dwell time was used for each ion. Calibration standard concentrations were 3.5, 17.5, 35, 70, 140, and 280 ng/mL for the cis isomer and 1.5, 7.5, 15, 30, 60, and 120 ng/mL for the trans isomer. Volumes of samples analyzed were 1 mL.

In the case of all other analytes confirmed by GC-MS, samples were first analyzed for PAHs at a volume of 1 mL, theu they were reduced in volume to 100 μL for OC analysis. Each target compound was examined with FS mode and then SIM. Chromatographic separations were performed using the following temperature program: initial temperature of 90 °C, then 15 °C/min to 165 °C, then 2.7 °C/min to 250 °C, followed by 10 °C/min to 320 °C and held for 1 min. The full scan acquisition was performed by scanning a mass range of 50 to 450 amu at a rate of 1.88 scans/sec. The SIM parameters for the identified analytes were: masses 280 and 282 for PCA, masses 179 and 304 for diazinon, masses 371 and 406 for trans-chlordane, masses 405 and 440 for trans-nonachlor, masses 246

and 316 for p,p'-DDE and masses 235 and 283 for o,p'-DDD. A dwell time of 50 msec was used for each analyte with the exception of diazinon which had a dwell time of 100 msec.

Derivation of Water Concentrations from SPMD Levels (Modeling): Using models previously developed (3, 6, 11), data from the analysis of the PRC levels (see "PRC Data" in "Results and Discussion" section), and from calibration studies, the bioavailable (i.e., dissolved phase) concentrations of analytes in SPMDs exposed to Elizabeth River water can be estimated. For compounds with log K_{ow} values ≥ 5.0, sampling is integrative and reported water concentration values represent a time weighted average of residue concentration (i.e., residues were accumulated in an additive manner throughout the exposure with no significant losses of analytes) during the 30 day exposure period. For compounds with log K_{ow}s < 5.0, sampling is not integrative throughout the whole exposure period and reported water concentrations represent a smaller window of time than the 30 day exposure. Regardless of these considerations, water concentrations can be determined by using different assumptions and models (6).

An example of the overall modeling procedure for compounds with log K_{ow}s ≥ 5.0 is as follows. Note that Huckins et al. (6) have also described modeling procedures for water concentration estimates of compounds with log K_{ow}s < 5.0. The analyte sampling rate (R_{sw}) is determiued from laboratory exposures conducted under some of the same conditions (i.e., water temperature and exposure duration) as the current study. The

linear or integrative uptake of OCs by SPMDs has been described by Huckins, et al. (6) as follows:

$$C_{SPMD} = C_w k_o K_{mw} A t / V_{SPMD} \quad (1)$$

substituting R_{sw} for $k_o K_{mw} A$ in equation 1 gives

$$C_{SPMD} = C_w R_{sw} t / V_{SPMD} \quad (2)$$

where C_{SPMD} is the concentration of the analyte in the whole SPMD (i.e., the membrane + lipid), C_w is the concentration of the analyte in the water, t is the exposure time in days, and V_{SPMD} is the volume of the SPMD. Rearranging equation 2 results in

$$C_w = C_{SPMD} V_{SPMD} / R_{sw} t \quad (3)$$

In the present case we use the uptake rate constant (k_{uw}) defined as L/d g (Liter/day·gram) of SPMD (membrane + lipid).

$$C_w = C_{SPMD} / (R_{sw} / M_{SPMD}) t = C_w = C_{SPMD} / k_{uw} t \quad (4)$$

where M_{SPMD} is the mass of the SPMD and is substituted for V_{SPMD}.

SPMD sampling rates can change due to changes in temperature, turbulence/facial velocity of water at the membrane surface, and buildup of periphyton on the membrane surface. To account for changes in these variables from the laboratory calibration studies, PRCs are used to allow estimation of actual *in situ* sampling rates. The PRC concept was described earlier. However, models to enable the use of a PRC were not. Measuring the loss of a PRC over a study exposure period provides *in situ* k_e values which when compared to the calibration k_e values can serve as an indicator of differences in the environmental conditions. If large differences exist between the k_e calibration and

exposure values, adjustments must be made to the laboratory calibration data. The k_{eprc} values are derived as follows

$$C_{SPMD} = C_{SPMDo} \exp(-k_{eprc}t) \quad (5)$$

$$k_{eprc} = \ln(C_{SPMDo}/C_{SPMD})/t \quad (6)$$

where C_{SPMDo} is the day 0 concentration of the PRC and C_{SPMD} is the concentration of PRC remaining in the SPMD following exposure. Comparison of the k_{eprc} values derived from the field-exposed SPMDs (Equations 7 or 8), to the k_e values of the PRCs measured in SPMD calibration exposures (i.e., k_{eprc} / k_{ec}), provides an estimate of the relative effect of environmental variables on SPMD sampling. Laboratory k_{ec} values of PRCs are determined by direct measurement or by

$$k_{ec} = R_s/K_{SPMD} V_{SPMD} d_{SPMD} \quad (7)$$

where K_{SPMD} is the equilibrium SPMD-water partition coefficient and d_{SPMD} is the SPMD density (g/mL), which is ≈ 0.91. Estimates of *in situ* R_s values from the k_{ec}s of PRCs can be made with the following relationship

$$R_{sf} = (k_{eprc}/k_{ec}) R_{sc} \quad (8)$$

These models and assumptions as well as others have been incorporated into an Excel spreadsheet (6) for rapid estimation of water concentrations and the Excel calculator was used for water concentration estimates in this work. Note that an average temperature of 26 °C was assumed for SPMD exposure at all sample sites.

QC Procedures: A field blank SPMD accompanied SPMDs to each sample site, including deployment, retrieval, and transport to CERC. These field blanks were

processed and analyzed exactly as exposed SPMDs. The GC method detection limit (MDL) and method quantitation limit (MQL) for analysis of SPMD samples were determined for each analyte by measuring the values of coincident GC-ECD or GC-PID peaks for each compound in all blank samples processed with this study (see Table I, "Analytical Appendix"). The MDL was defined as the mean plus three-standard deviations of values so determined (12). The MQL was defined as the mean plus ten-standard deviations of values so determined (12). 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 calculated values of 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.

During the processing of study samples, several QC checks were employed to demonstrate an acceptable outcome of sample analysis. These checks included the following procedures: 1) evaluation of the performance of the SEC system by daily (each operation day) injection of a known quantity of ^{14}C-2,5,2',5'-tetrachlorobiphenyl (^{14}C-TCB, the amount of radioactivity used per spike was ≈ 42,000 disintegrations per minute) and measuring recovery through the system; 2) monitoring dialytic recovery by spiking a blank SPMD with a known quantity of ^{14}C-dibenz(a,h)anthracene (^{14}C-DBA, the amount of radioactivity used per spike was ≈ 92,00 disintegrations per minute). An SPMD blank spiked with ^{14}C-DBA was part of each set of SPMDs dialyzed, and four sample sets were required for this study; 3) determination of the recoveries of target compounds through

all column chromatography cleanup steps used to further enrich (i.e., post SEC) samples, which included tri-adsorbent treatment for PAHs, and Florisil® and silica gel fractionation of OCPs and PCBs. Duplicate columns of the described chromatographic materials were run with each sample set. The spiked tri-adsorbent columns were prepared by adding 4 μg of each priority pollutant PAH to a control tri-adsorbent column. In a similar manner, the spiked Florisil columns were prepared by adding a mixture of thirty-two individual OCPs at 20 ng each and 1,000 ng of the aforementioned PCB mixture to control Florisil columns. 4) Monitoring the recoveries of all analytes of interest through the entire dialysis, fractionation and enrichment procedures was achieved by using spiked SPMD blanks as part of each of the sets of exposed SPMDs processed in this study. These SPMD spikes were prepared by fortifying individual blank SPMDs with 8 μg of each priority pollutant PAH, a mixture of the thirty-two individual OCPs (40 ng of each OCP) and 3,000 ng of the total PCB mixture.

RESULTS AND DISCUSSIONS

QC of Analytical Procedures: Field blank samples exhibited no coincident GC peaks at levels significantly higher than those associated with the laboratory control SPMDs (i.e., SPMDs made at the same time as sample SPMDs but maintained frozen in the laboratory until analysis of field samples). This finding demonstrates that inadvertent SPMD contamination did not occur during deployment, retrieval and shipping. Thus, residues quantified in exposed SPMDs did indeed originate from Elizabeth River water. Figures

IV-XXI show representative chromatograms of field blank SPMDs and sample SPMDs from the 6 study sites. Clearly, few interferences were encountered in the analysis of exposed SPMD fractions and sample chromatograms were quite complex. The background, MDLs and MQLs for the analysis of PP PAHs, OCs, and PCBs in study samples are presented in Table I (Analytical Appendix). Note that the mean GC response coincident to each analyte peak in the laboratory control SPMDs and Field Blank SPMDs was used to background correct GC concentration data from exposed SPMDs. The MDLs and MQLs given in Table 1 reflect this background correction procedure.

As described in the QC procedures section, several external standard checks of cleanup methods performance were conducted. In the case of SEC separations, a mean of 95.5 % (n=6) was observed for ^{14}C-TCB recoveries over the course of a week of sample processing. The mean (n=4) recovery of ^{14}C-DBA spiked SPMDs following dialysis and SEC cleanup was 87.7 %. The recoveries of PP PAHs through tri-adsorbent columns averaged 90.4 % (n=4) and the recoveries of the OCPs and total PCBs averaged, 74.4 % (n=2) and 83.7 % (n=2), respectively (Tables II and III, Analytical Appendix). Also, QC checks of the overall recoveries of priority pollutant PAHs, OCPs, and total PCBs were performed. Recoveries of priority pollutant PAHs averaged 72.9 % (n=4), recoveries of the OCPs averaged 75.1 % (n=3), and the recoveries of total PCBs averaged 78.0 % (n=3) as shown in Tables IV and V (Analytical Appendix).

SPMDs exposed to Elizabeth River sites were processed concurrently with the quality control samples described above. Therefore, the results obtained from processing and

analyses of exposed SPMDs are taken to be similar to the observed results for the quality control samples. During the gas chromatographic analysis of sample fractions, conditions were optimized to give sufficient resolution for quantitation of the targeted analytes as shown in Table VI (Analytical Appendix) and Figures I-III (Analytical Appendix).

SPMD Concentrations & Associated Variance: The results of the gas chromatographic analyses of SPMDs exposed to Elizabeth River water are given in Tables VII through XVIII (Analytical Appendix), and partly in Figures IV through XXI (Analytical Appendix). Although Figures IV through XXI represent only one sample of replicate SPMDs deployed at each site, the chromatographic profiles shown are nearly identical to those representing other samples at the same site. The precision of replicate SPMD concentration data from the five sites (one canister or sample was lost at site # 6, thus sites with adequate replication include site # 2, # 3, # 4, # 7, and # 8) with adequate replication was quite good. With the exception of site # 7, the C.V.s (%) of PP PAHs concentrations in replicate SPMD samples ($n = 3$) were generally < 15 %. In the case of site # 7 samples, the mean C.V. (%) was 31 % for PP PAH concentrations in SPMDs. The C.V.s for PCB concentrations in replicate SPMD samples ($n = 3$) from the five sites were even lower than those observed for PP PAHs and averaged 14 %, with a maximum of 18 %. Variance was a little higher for pesticide concentrations in replicate SPMDs from the five sites. However, ≈ 85 % of the measured values had C.V.s < 20 % and only 2 % of the replicates ($n = 2$) had C.V.s > 50 %. Overall, the precision of these analytical results compares favorably to that reported by DiVita and Crunkilton (13).

Analyte Concentration Relative to Site # : Clearly, SPMDs deployed at sites # 3 and # 4 had the highest levels of PP PAHs (Tables VIII & IX, Analytical Appendix). Also, the concentration of total PP PAHs in site # 3 SPMDs was about two fold higher than the concentration in site # 4 SPMDs (i.e., 4.7 μg/g [site # 3] versus 2.7 μg/g [site # 4]). The level of total PP PAHs in SPMDs at site # 7 were relatively high (i.e., 1.4 μg/g) as well. The presence of the Atlantic Wood Preservers at site # 3 appears to offer a logical explanation for the very-high levels of PP PAHs measured at that site, and possibly the elevated levels of PP PAHs in SPMDs deployed downstream at site # 4. At nearly all sites fluoranthene and pyrene were the dominant PP PAHs and their combined concentrations represented 49 to 73 % of the total PP PAH residue concentrations at the six sample sites.

Concentrations of total PCBs in SPMDs deployed at the six sites ranged from 25 ng/g to 44 ng/g (Tables XII through XVIII). Although total PCB levels in SPMDs were highest at site # 3, the concentrations across the six sites varied < than two fold. These finding suggest that PCB residues largely stem from non-point sources.

Evaluation of OCP concentrations in SPMDs deployed at the six sites (Tables XIII through XVIII) is complicated by the fact that at four sites (i.e., Sites # 2, 3, 4 & 8) more than 75 % of the target OCPs were detected. For example, site # 3 (Table XIV) had 28 of the 32 targeted OCPs. Also, some of the OCPs are present at some sites at relatively high levels when compared to other riverine systems (5). For example, the concentration of

cis-chlordane in SPMDs exposed to Kansas River water (a river that flows through Kansas City, MO) was 24.0 μg/g (5), whereas the concentration of this OCP at site # 6 averaged 30 μg/g. Also, we seldom find detectable levels of the new generation OCPs such as diazinon, chlorpyrifos, endosulfan, and permethrin in environmentally exposed SPMDs. In particular, detection of permethrin in SPMDs at sites # 3, 4 and 8 (Tables XIV, XV, and XVIII) is surprising, as we have not detected this OCP in environmental waters before. Tables XIV, XV, and XVIII do not give the concentrations of permethrin in SPMDs as GC-MS was used to confirm compound identity and isomer ratios (see "Water Concentration Estimates" section for concentration data). Figure 5 shows the reconstructed ion chromatograph of the GC-MS analysis (SIM)of permethrin residues at site 4. Masses used for SIM analysis were 163 and 183. Chlorpyrifos (another so called "new generation" pesticide) was detected at all study sites and was highest at site # 2. In addition, diazinon appeared elevated at sites # 3 and # 8. Several classic OCPs were also detected at relatively high levels. In that regard, site # 6 stands out (Table XVI, Analytical Appendix) as chlordane components, DDT degradation products and endrin are significantly elevated above other sites.

PRC Data: The results of these analyses are given in Table XIX (Analytical Appendix). The measured k_{ePRC} values (range of 0.061 to 0.095)for the six sites are about 2 to 3 fold higher than the k_{cPRC} (i.e., 0.029) measured during laboratory calibration at 26 °C, which means that SPMD sampling rates for target analytes are about 2 to 3 fold higher than those generated during laboratory calibration (11). Also, this data indicates that significant impedance of analyte uptake rates due to biofouling was offset by the

turbulence of the water at study sites. This finding shows that heavy biofouling of the SPMD membrane does not necessarily

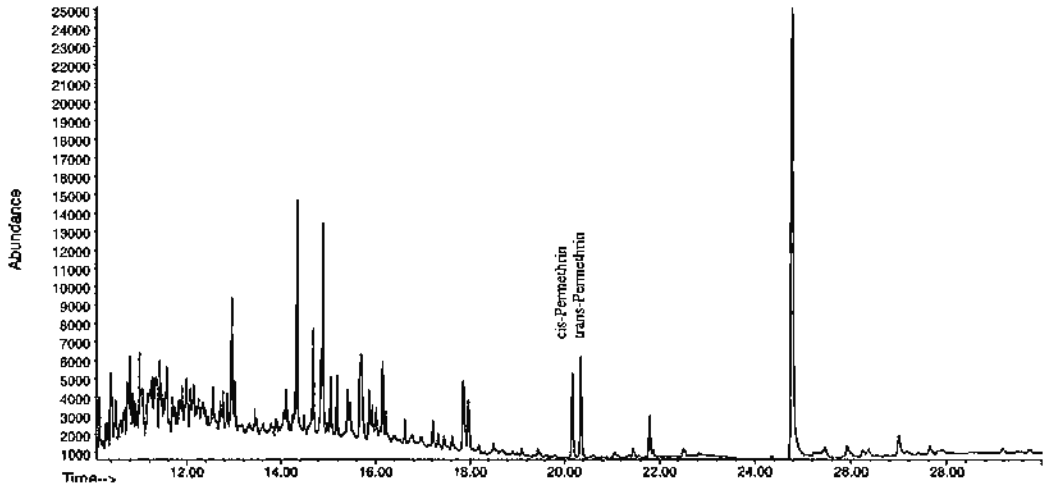

Figure 5. Reconstructed ion chromatogram in SIM mode of a Site 4 SPMD sample. Masses 163 and 183 were used for cis and trans-Permethrin confirmation.

lower analyte sampling rates. Turbulence enhances uptake rates by reducing the thickness of the aqueous boundary layer. Finally, the range of values for k_{ePRC}s was relatively small (i.e., 1.6 fold), suggesting that at the SPMD membrane surface, hydrodynamics did not vary much from site to site.

Water Concentration Estimates: A summary of the results of water concentration estimations is given in tables 1 and 2. Note that permethrin water concentrations given in Table 1 were based on GC-MS analysis and that the actual cis/trans ratio at sites with measured residues is about 40/60 (%/%), which is about equivalent to the technical mixture of permethrin. In general the concentrations in SPMDs track those in water. However, diazinon levels are a notable exception and are much higher in water relative to the concentrations of other OCP analytes. This is because the SPMD concentration factor

(i.e., the volume of water cleared of an analyte during the exposure divided by the volume of the SPMD) for diazinon is much smaller than most of the other OCPs. This observation also applies to endosulfans, as levels are elevated relative to most other OCPs.

PP PAH levels in water are very high at sites #s 3, 4, and 7. Anthracene, fluoranthene and pyrene are among the highest of the PP PAHs determined at these sites. In particular, PAH levels at site # 3 are exceedingly high. Some comparisons to other sites with high levels of PAHs are justified. For example, dissolved phase concentrations of fluoranthene and pyrene in water (determined by SPMD exposures) at the mouth of the Kansas River (5) were only 45 % and 66 %, respectively, of the concentrations computed for site # 3. The Kansas River flows through a heavily industrialized area of Kansas City,

Table 1. Summary of SPMD-Derived OCP Water Concentrations

Compound	Site 2 (pg/L)	Site 3 (pg/L)	Site 4 (pg/L)	Site 6 (pg/L)	Site 7 (pg/L)	Site 8 (pg/L)
Hexachlorobenzene (HCB)	4.7	6.2	4.1	2.0	3.1	1.9
Pentachloroanisole (PCA)	49	53	49	13	35	19
alpha-Benzenehexachloride (a-BHC)	28	32	32	N/A*	36	26
Lindane	91	42	90	N/A	170	130
beta-Benzenehexachloride (b-BHC)	45	24	N/A	N/A	N/A	N/A
Heptachlor	40	21	N/A	N/A	N/A	N/A
delta-Benzenehexachloride (d-BHC)	92	66	69	120	78	88
Dacthal	77	78	67	26	70	30
Oxychlordane	N/A	N/A	N/A	N/A	N/A	N/A
Heptachlor Epoxide	58	70	42	N/A	11	N/A
trans-Chlordane	45	42	28	50	18	20
trans-Nonachlor	26	20	16	42	19	41
o,p'-DDE	N/A	0.9	8.7	10	N/A	N/A
cis-Chlordane	75	54	33	270	57	71
Endosulfan	360	380	220	230	170	170
p,p'-DDE	15	21	12	79	14	18
Dieldrin	210	220	180	270	150	170
o,p'-DDD	10	15	9.9	58	4.7	4.8
Endrin	270	250	330	730	16	390
cis-Nonachlor	8.0	7.7	5.6	14	6.5	7.6
o,p'-DDT	8.4	6.6	3.8	N/A	N/A	N/A
p,p'-DDD	33	43	27	100	17	13
Endosulfan-II	470	350	310	280	180	190
p,p'-DDT	N/A	8.5	9.9	4.3	N/A	0.9
Endosulfan Sulfate	230	69	99	N/A	N/A	110
p,p'-Methoxychlor	55	N/A	80	27	37	7.7
Mirex	N/A	N/A	N/A	N/A	N/A	N/A
Total PCB	92	160	140	190	100	130
Chlorpyrifos	180	130	88	110	110	110
Diazinon	2000	4600	1400	N/A	N/A	3600
cis-Permethrin	N/A	150**	270**	N/A	N/A	250**
trans-Permethrin	N/A	260**	440**	N/A	N/A	390**
Trifluralin	4.3	N/A	6.4	N/A	N/A	N/A

* N.A. = not assessed, below MDL or MQL

** Values were determined by GC-MS instead of GC-ECD.

Table 2. Summary of SPMD-Derived PAH Water Concentrations

Compound	Site 2 (ng/L)	Site 3 (ng/L)	Site 4 (ng/L)	Site 6 (ng/L)	Site 7 (ng/L)	Site 8 (ng/L)
Naphthalene	N/A*	N/A	N/A	N/A	N/A	N/A
Acenaphthylene	N/A	N/A	9.2	N/A	6.9	N/A
Acenaphthene	N/A	6.0	6.0	N/A	N/A	N/A
Fluorene	N/A	4.9	4.9	4.3	4.9	4.3
Phenanthrene	N/A	4.7	N/A	N/A	N/A	N/A
Anthracene	N/A	4.0	7.2	3.6	5.4	4.9
Fluoranthene	2.2	20	11	2.7	6.5	3.0
Pyrene	1.3	13	6.6	1.9	4.8	1.9
Benz[a]anthracene	0.2	1.0	0.5	N/A	0.2	N/A
Chrysene	0.6	2.8	1.7	N/A	0.7	N/A
Benzo[b]fluoranthene	1.1	5.9	2.8	N/A	N/A	N/A
Benzo[k]fluoranthene	N/A	0.9	N/A	N/A	N/A	N/A
Benzo[a]pyrene	N/A	1.6	0.8	N/A	N/A	N/A
Indeno[1,2,3-cd]pyrene	N/A	N/A	N/A	N/A	N/A	N/A
Dibenzo[a,h]anthracene	N/A	N/A	N/A	N/A	N/A	N/A
Benzo[g,h,I]perylene	N/A	1.4	N/A	N/A	N/A	N/A

* N/A = not assessed, below MDL or MQL

MO. Also, the estimated water concentrations (EPA, conventional methods) of anthracene and pyrene in the Trinity River below Dallas, TX (14), was 37 % and 112 %, respectively, of site # 3 concentrations. Note that Trinity River concentrations reflect PAHs associated with not only the dissolved phase, but the dissolved organic carbon and particulate organic carbon phases, as well. Thus, it is likely that actual dissolved concentrations of pyrene are only about half of those reported in this work (14).

The toxicity of anthracene, fluoranthene and pyrene has been shown to be greatly enhanced by UV radiation (15, 16). This sometimes lethal photolysis reaction can occur even after residues have been concentrated in tissues of some organism, i.e., those without heavy pigmentation. Obviously, water clarity controls the level of attenuation of

UV radiation with depth. Finally, alkylated anthracenes, fluoranthenes, and pyrenes have also been shown to have the same photoactivation potential, and their concentrations were not determined in these samples. The presence of these substituted PAHs is very likely and would add to the potential for toxic effects.

GC-MS Confirmation of Analytes: Table 3 summarizes GC-MS confirmation of selected target compounds at sites # 3 and # 6. After matching GC peak retention times of sample peaks with standard mixtures, two approaches were used for analyte identification. These approaches consisted of either a full scan (FS) spectral comparison to the NIST/EPA/NIH Mass Spectral Library (version 1.6d) or the presence of characteristic ions (SIM, i.e., selected ion monitoring) at the correct retention time.

Table 3. Selected analytes confirmed by GC-MS using full scan (FS) with library match or selected ion monitoring (SIM) methods

Compound	Site # 3 Method (Library Match Quality)	Site # 6 Method (Library Match Quality)
Fluorene	FS (91 %)	NA*
Phenanthrene	FS (93 %)	FS (93 %)
Anthracene	FS (94 %)	FS (89 %)
Fluoranthene	FS (94 %)	FS (96 %)
Pyrene	FS (96 %)	FS (95 %)
Benz[a]anthracene	FS (97 %)	NM
Chrysene	FS (90 %)	NM
Benzo[b]fluoranthene	FS (**)	NM
Benzo[k]fluoranthene	FS (97 %)	NM
Benzo[a]pyrene	FS (95 %)	NM
Benzo[ghi]perylene	FS (92 %)	NM
PCA***	SIM	SIM
Diazinon	SIM	NM
Trans-Chlordane	NM	SIM
cis-Chlordane	NM	FS (96 %)
Trans-Nonachlor	NM	SIM
p,p'-DDE	NM	SIM
o,p'-DDD	NM	SIM
p,p'-DDD	NM	FS (97 %)

* Not measured

** Retention matched benzo[b]fluoranthene, however the library search indicated benzo[k]fluoranthene. Based on identical molecular weights and similar spectral patterns, we tentatively identified this compound as benzo[b]fluoranthene

*** Pentachloroanisole

CONCLUSIONS

DeVita and Crunkilton (13) have shown that quality control associated with the use of SPMDs for PP PAH analysis in water is comparable or better than the standard EPA method used by many laboratories. In this work, the variance associated with our measurements is quite low and very similar to that observed in their study (13).

Clearly, elevated levels of certain so called "new generation" pesticides were found at a number of sites in Elizabeth River water. The levels of diazinon at several sites are among the highest we have observed in water samples. Also, the levels of several PP PAHs are the highest we have observed in SPMDs exposed to a riverine system. Of particular concern is the levels of phototoxic PAHs, whose toxicity can be potentiated as much as 1000 fold by UV photoactivation.

Overall, SPMDs performed quite well permitting the detection of a large number of hydrophobic organic contaminants, which are often difficult to detect in environmental waters. In regard to the potential for the contaminants detected in the Elizabeth River water to adversely affect aquatic organisms, the water concentrations of several PAHs appear to be high enough to be of concern. In addition, the complex contaminant mixtures found at several sites may have significant potential for additive toxicological effects. Thus, toxicological screening as described by Huckins et al. (6) of SPMD extracts from selected sites seems to be warranted.

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ANALYTICAL APPENDIX

Table I

Background, MDL, & MQL Values for Targeted Analytes

OCPs & PCBs	Bkg ng/g	MDL ng/g	MQL ng/g	OCPs & PCBs (Continued)	Bkg ng/g	MDL* ng/g	MQL* ng/g
Trifluralin	0.43	0.04	0.20	Endosulfan Sulfate	0.13	0.03	0.15
HCB**	0.02	0.03	0.15	Methoxychlor	0.07	0.03	0.15
PCA***	0.04	0.03	0.15	Mirex	0.02	0.03	0.15
α-BHC****	0.08	0.03	0.15	cis-Permethrin	4.20	0.41	1.50
Diazinon	0.04	0.06	0.30	*trans*-Permethrin	6.00	0.58	2.00
Lindane	0.69	0.03	0.15				
β-BHC****	0.26	0.05	0.25	TOTAL PCBs	2.10	3.60	7.50
Heptachlor	0.04	0.03	0.15				
δ-BHC****	0.07	0.04	0.20		Bkg	MDL	MQL
Dacthal	0.09	0.04	0.22	PAHs	μg/g	μg/g	μg/g
Chlorpyrifos	0.54	0.08	0.43				
Oxychlordane	1.50	0.30	1.10	Naphthalene	0.01	0.04	0.08
Heptachlor Epoxide	0.10	0.03	0.15	Acenaphthylene	0.01	0.02	0.08
trans-Chlordane	0.01	0.02	0.15	Acenaphthene	0.01	0.02	0. 08
08trans-Nonachlor	0.20	0.03	0.15	Fluorene	0.01	0.02	0.08
o,p'-DDE	0.02	0.03	0.15	Phenanthrene	0.01	0.02	0.08
cis-Chlordane	0.46	0.06	0.35	Anthracene	0.01	0.02	0.08
Endosulfan	0.05	0.04	0.15	Fluoranthene	0.01	0.02	0.08
p,p'-DDE	0.02	0.03	0.15	Pyrene	0.01	0.02	0.08
Dieldrin	0.02	0.03	0.15	Benz[a]anthracene	0.01	0.02	0.08
o,p'-DDD	0.81	0.10	0.35	Chrysene	0.01	0.02	0.08
Endrin	0.05	0.04	0.15	Benzo[b]fluoranthene	0.01	0.02	0.08
cis-Nonachlor	0.07	0.05	0.15	Benzo[k]fluoranthene	0.01	0.02	0.08
o,p'-DDT	0.02	0.03	0.15	Benzo[a]pyrene	0.01	0.02	0.08
p,p'-DDD	0.26	0.05	0.15	Indeno[1,2,3-cd]pyrene	0.01	0.02	0.08
Endosulfan-II	0.07	0.03	0.15	Dibenz[a,h]anthracene	0.01	0.02	0.08
p,p'-DDT	2.50	0.33	1.15	Benzo[g,h,I]perylene	0.01	0.02	0.08

NOTE: MDL & MQL values given reflect determinations following background correction.

* Values given are above the background concentration

** Hexachlorobenzene

*** Pentachloroanisole

**** Benzenehexachloride

Table II

Recovery of PAHs Through Tri-adsorbent

Chromatographic Cleanup

	Replicate # 1 % Recovery	Replicate # 2 % Recovery	Replicate # 3 % Recovery	Replicate # 4 % Recovery	Mean % Recovery
Naphthalene	73.0	71.0	62.0	71.0	**69.0**
Acenaphthylene	78.0	80.0	73.0	80.0	**78.0**
Acenaphthene	79.0	80.0	68.0	75.0	**75.0**
Fluorene	84.0	82.0	72.0	76.0	**79.0**
Phenanthrene	86.0	85.0	88.0	96.0	**89.0**
Anthracene	87.0	92.0	89.0	98.0	**91.0**
Fluoranthene	89.0	86.0	92.0	99.0	**92.0**
Pyrene	91.0	88.0	94.0	100	**94.0**
Benz[a]anthracene	90.0	90.0	100	110	**97.0**
Chrysene	86.0	83.0	94.0	99.0	**91.0**
Benzo[b]fluoranthene	96.0	94.0	99.0	110	**99.0**
Benzo[k]fluoranthene	96.0	92.0	91.0	100	**945.0**
Benzo[a]pyrene	96.0	92.0	95.0	100	**96.0**
Indeno[1,2,3-cd]pyrene	89.0	89.0	99.0	110	**96.0**
Dibenz[a,h]anthracene	95.0	94.0	110	120	**110**
Benzo[g,h,I]perylene	88.0	86.0	100	120	**99.0**
				Mean =	**90.0**

Table III

Recovery of OC-Pesticides and PCBs

Through Two Stage Chromatographic Cleanup

	Replicate # 1 % Recovery	Replicate # 2 % Recovery	Mean % Recovery
Trifluralin	53.0	30.0	**42.0**
HCB	96.0	98.0	**97.0**
PCA	120	96.0	**110**
α-BHC	73.0	56.0	**64.0**
Diazinon	59.0	48.0	**54.0**
Lindane	58.0	42.0	**50.0**
β-BHC	67.0	54.0	**61.0**
Heptachlor	70.0	69.0	**70.0**
δ-BHC	92.0	67.0	**79.0**
Dacthal	92.0	92.0	**92.0**
Chlorpyrifos	41.0	30.0	**35.0**
Oxychlordane	37.0	21.0	**29.0**
Heptachlor Epoxide	86.0	67.0	**76.0**
trans-Chlordane	88.0	70.0	**79.0**
trans-Nonachlor	75.0	58.0	**67.0**
o,p'-DDE	120	94.0	**110**
cis-Chlordane	81.0	59.0	**70.0**
Endosulfan	86.0	67.0	**77.0**
p,p'-DDE	84.0	79.0	**82.0**
Dieldrin	96.0	75.0	**86.0**
o,p'-DDD	69.0	47.0	**58.0**
Endrin	98.0	75.0	**86.0**
cis-Nonachlor	93.0	71.0	**82.0**
o,p'-DDT	90.0	70.0	**80.0**
p,p'-DDD	87.0	65.0	**76.0**
Endosulfan-II	92.0	71.0	**82.0**
p,p'-DDT	100	65.0	**83.0**
Endosulfan Sulfate	95.0	72.0	**83.0**
Methoxychlor	91.0	67.0	**79.0**
Mirex	94.0	90.0	**92.0**
cis-Permethrin	110	84.0	**97.0**
trans-Permethrin	75.0	42.0	**58.0**
		Mean of OCPs =	**74.0**
TOTAL PCBs	85.0	82.0	**84.0**

Table IV

Recovery of PAHs from SPMD Spikes

Processed Concurrently with Study Samples

	Replicate # 1 % Recovery	Replicate # 2 % Recovery	Replicate # 3 % Recovery	Replicate # 4 % Recovery	Mean % Recovery
Naphthalene	46.0	41.0	41.0	37.0	**41.0**
Acenaphthylene	59.0	61.0	70.0	54.0	**61.0**
Acenaphthene	61.0	64.0	72.0	55.0	**63.0**
Fluorene	66.0	63.0	68.0	63.0	**65.0**
Phenanthrene	65.0	71.0	88.0	75.0	**74.0**
Anthracene	66.0	70.0	87.0	76.0	**74.0**
Fluoranthene	65.0	80.0	93.0	76.0	**78.0**
Pyrene	71.0	83.0	97.0	82.0	**83.0**
Benz[a]anthracene	67.0	73.0	91.0	78.0	**77.0**
Chrysene	67.0	70.0	88.0	74.0	**75.0**
Benzo[b]fluoranthene	66.0	78.0	94.0	80.0	**80.0**
Benzo[k]fluoranthene	67.0	77.0	88.0	72.0	**76.0**
Benzo[a]pyrene	66.0	80.0	89.0	73.0	**77.0**
Indeno[1,2,3-cd]pyrene	70.0	71.0	94.0	88.0	**81.0**
Dibenz[a,h]anthracene	73.0	73.0	100	100	**88.0**
Benzo[g,h,I]perylene	67.0	57.0	83.0	80.0	**72.0**
				Mean =	**73.0**

Table V

Recovery of OCPs and PCBs from SPMD Spikes

Processed Concurrently with Study Samples

	Replicate # 1 % Recovery	Replicate # 2 % Recovery	Replicate # 3 % Recovery	Mean % Recovery
Trifluralin	56.0	48.0	33.0	**46.0**
HCB	96.0	86.0	87.0	**90.0**
PCA	110	100	100	**100**
α-BHC	77.0	67.0	64.0	**70.0**
Diazinon	69.0	86.0	57.0	**70.0**
Lindane	77.0	87.0	70.0	**78.0**
β-BHC	82.0	78.0	78.0	**80.0**
Heptachlor	72.0	67.0	69.0	**69.0**
δ-BHC	110	71.0	73.0	**84.0**
Dacthal	89.0	77.0	90.0	**85.0**
Chlorpyrifos	100	75.0	91.0	**89.0**
Oxychlordane	94.0	76.0	85.0	**85.0**
Heptachlor Epoxide	86.0	84.0	85.0	**85.0**
trans-Chlordane	74.0	68.0	68.0	**70.0**
trans-Nonachlor	66.0	59.0	61.0	**62.0**
o,p'-DDE	95.0	91.0	91.0	**92.0**
cis-Chlordane	70.0	66.0	64.0	**67.0**
Endosulfan	66.0	64.0	60.0	**63.0**
p,p'-DDE	100	89.0	94.0	**96.0**
Dieldrin	70.0	79.0	73.0	**74.0**
o,p'-DDD	57.0	47.0	48.0	**51.0**
Endrin	36.0	33.0	31.0	**33.0**
cis-Nonachlor	71.0	64.0	68.0	**67.0**
o,p'-DDT	77.0	72.0	72.0	**74.0**
p,p'-DDD	72.0	65.0	68.0	**68.0**
Endosulfan-II	72.0	65.0	68.0	**68.0**
p,p'-DDT	72.0	77.0	73.0	**74.0**
Endosulfan Sulfate	70.0	72.0	75.0	**73.0**
Methoxychlor	89.0	83.0	87.0	**86.0**
Mirex	92.0	83.0	87.0	**87.0**
cis-Permethrin	69.0	91.0	81.0	**80.0**
trans-Permethrin	70.0	83.0	98.0	**84.0**
			OCP Mean =	**75.0**
TOTAL PCBs	98.0	63.0	72.0	**78.0**

Table VI

Elution Order of Targeted Analytes During

Gas Chromatographic Analysis*

OC-Pesticides (on DB-35 MS)	Retention Time Min.	PAHs (on DB-5)	Retention Time Min.
Trifluralin	8.83	Naphthalene	5.39
HCB	11.41	Acenaphthylene	9.80
PCA	11.57	Acenaphthene	10.84
α-BHC	11.97	Fluorene	14.37
Diazinon	13.08	D_{10}-Phenanthrene (PRC)	21.16
Lindane	13.90	Phenanthrene	21.31
β-BHC	15.57	Anthracene	21.66
Heptachlor	15.76	Fluoranthene	30.40
δ-BHC	17.06	Pyrene	31.84
Dacthal	18.97	D_{14}-4-Terphenyl as Internal Std	34.78
Chlorpyrifos	19.14	Benz[a]anthracene	41.44
Oxychlordane	20.33	Chrysene	41.69
Heptachlor Epoxide	21.05	Benzo[b]fluoranthene	52.77
trans-Chlordane	22.62	Benzo[k]fluoranthene	53.15
trans-Nonachlor	22.86	Benzo[a]pyrene	56.04
o,p'-DDE	23.00	Indeno[1,2,3-cd]pyrene	64.18
cis-Chlordane	23.25	Dibenz[a,h]anthracene	64.66
Endosulfan	23.41	Benzo[g,h,i]perylene	65.38
p,p'-DDE	25.17		
Dieldrin	25.36		
o,p'-DDD	26.46		
Endrin	27.38		
cis-Nonachlor	28.10		
o,p'-DDT	28.25		
p,p'-DDD	29.18		
Endosulfan-II	29.43		
p,p'-DDT	30.98		
Endosulfan Sulfate	32.58		
Methoxychlor	36.19		
Mirex	36.86		
cis-Pennethrin	41.05		
trans-Permethrin	41.67		
OCN as Internal Std.	45.87		
Total PCBs	10.00 to 42.00		

* NOTE: Slight variations in retention times were noted on a run by run basis. Retention times as given reflect the example provided in Figures I-III.

Table VII

Results of the GC-PID Analysis of Site # 2 Samples

	Canister # 1 µg/gram	Canister # 2 µg/gram	Canister # 3 µg/gram	Mean µg/gram
Naphthalene	<MQL	<MQL	<MQL	**<MQL**
Acenaphthylene	<MDL	<MDL	<MDL	**<MDL**
Acenaphthene	<MQL	<MQL	<MQL	**<MQL**
Fluorene	<MDL	<MDL	<MDL	**<MDL**
Phenanthrene	<MDL	<MDL	<MQL	**<MQL**
Anthracene	<MDL	<MDL	<MQL	**<MQL**
Fluoranthene	0.16	0.17	0.16	**0.16**
Pyrene	0.11	0.12	0.12	**0.11**
Benz[a]anthracene	0.08	0.07	0.08	**0.07**
Chrysene	0.08	0.08	0.09	**0.09**
Benzo[b]fluoranthene	0.13	0.12	0.12	**0.12**
Benzo[k]fluoranthene	<MDL	<MDL	<MDL	**<MDL**
Benzo[a]pyrene	<MQL	<MQL	<MQL	**<MQL**
Indeno[1,2,3-cd]pyrene	<MQL	<MQL	<MQL	**<MQL**
Dibenz[a,h]anthracene	<MDL	<MDL	<MDL	**<MDL**
Benzo[g,h,i]perylene	<MQL	<MQL	<MQL	**<MQL**
			SUM =	**0.55**

* Note: Contaminant levels reported have been background corrected using the GC responses from the field blank sample.

Table VIII

Results of the GC-PID Analysis of Site # 3 Samples

	Canister # 1 μg/gram	Canister # 2 μg/gram	Canister # 3 μg/gram	Mean μg/gram
Naphthalene	<MQL	<MQL	<MQL	<MQL
Acenaphthylene	<MQL	<MDL	0.12	<MQL
Acenaphthene	0.07	0.07	0.07	**0.07**
Fluorene	0.08	0.08	0.08	**0.08**
Phenanthrene	0.10	0.10	0.08	**0.09**
Anthracene	0.11	0.11	0.07	**0.09**
Fluoranthene	1.40	1.40	1.40	**1.40**
Pyrene	1.10	1.20	1.20	**1.20**
Benz[a]anthracene	0.35	0.37	0.34	**0.35**
Chrysene	0.45	0.47	0.45	**0.46**
Benzo[b]fluoranthene	0.62	0.63	0.65	**0.63**
Benzo[k]fluoranthene	0.15	0.16	0.16	**0.16**
Benzo[a]pyrene	0.28	0.23	0.28	**0.26**
Indeno[1,2,3-cd]pyrene	<MQL	<MQL	<MQL	<MQL
Dibenz[a,h]anthracene	<MQL	<MQL	<MQL	<MQL
Benzo[g,h,i]perylene	0.10	0.10	0.10	**0.10**
			SUM =	**2.30**

* Note: Contaminant levels reported have been background corrected using the GC responses from the field blank sample.

Table IX

Results of the GC-PID Analysis of Site # 4 Samples

	Canister # 1 μg/gram	Canister # 2 μg/gram	Canister # 3 μg/gram	Mean μg/gram
Naphthalene	<MQL	<MQL	<MQL	<MQL
Acenaphthylene	0.07	0.10	<MQL	**0.08**
Acenaphthene	0.07	0.07	0.07	**0.07**
Fluorene	0.08	0.08	0.08	**0.08**
Phenanthrene	<MQL	<MQL	<MQL	<MQL
Anthracene	0.15	0.19	0.14	**0.16**
Fluoranthene	0.88	0.82	0.79	**0.83**
Pyrene	0.62	0.63	0.58	**0.61**
Benz[a]anthracene	0.21	0.22	0.21	**0.21**
Chrysene	0.28	0.32	0.30	**0.30**
Benzo[b]fluoranthene	0.28	0.27	0.24	**0.26**
Benzo[k]fluoranthene	<MDL	<MDL	<MDL	<MDL
Benzo[a]pyrene	0.11	0.11	0.09	**0.11**
Indeno[1,2,3-cd]pyrene	<MQL	<MQL	<MQL	<MQL
Dibenz[a,h]anthracene	<MQL	<MQL	<MQL	<MQL
Benzo[g,h,i]perylene	<MQL	<MQL	<MQL	<MQL
			SUM =	**2.70**

* Note: Contaminant levels reported have been background corrected using the GC responses from the field blank sample.

Table X

Results of the GC-PID Analysis of Site # 6 Samples

	Canister # 2 μg/gram	Canister # 3 μg/gram	Mean μg/gram
Naphthalene	<MQL	<MQL	<MQL
Acenaphthylene	<MQL	<MDL	<MQL
Acenaphthene	<MQL	<MQL	<MQL
Fluorene	0.07	0.07	**0.07**
Phenanthrene	<MQL	<MQL	<MQL
Anthracene	0.07	0.08	**0.08**
Fluoranthene	0.22	0.23	**0.22**
Pyrene	0.18	0.20	**0.19**
Benz[a]anthracene	<MQL	<MQL	<MQL
Chrysene	<MDL	<MQL	<MQL
Benzo[b]fluoranthene	<MDL	<MDL	<MDL
Benzo[k]fluoranthene	<MDL	<MDL	<MDL
Benzo[a]pyrene	<MDL	<MDL	<MDL
Indeno[1,2,3-cd]pyrene	<MDL	<MDL	<MDL
Dibenz[a,h]anthracene	<MDL	<MDL	<MDL
Benzo[g,h,i]perylene	<MDL	<MDL	<MDL
		SUM =	**0.56**

* Note: Contaminant levels reported have been background corrected using the GC responses from the field blank sample.

Table XI

Results of the GC-PID Analysis of Site # 7 Samples

	Canister # 1 µg/gram	Canister # 2 µg/gram	Canister # 3 µg/gram	Mean µg/gram
Naphthalene	<MQL	<MQL	<MQL	<MQL
Acenaphthylene	0.08	0.08	<MDL	**0.06**
Acenaphthene	<MQL	0.07	<MQL	<MQL
Fluorene	0.07	0.09	0.08	**0.08**
Phenanthrene	<MQL	<MQL	0.07	<MQL
Anthracene	0.09	0.18	0.09	**0.12**
Fluoranthene	0.39	0.48	0.63	**0.50**
Pyrene	0.32	0.42	0.57	**0.44**
Benz[a]anthracene	<MQL	0.07	0.09	**0.07**
Chrysene	0.09	0.12	0.16	**0.12**
Benzo[b]fluoranthene	<MQL	<MQL	<MQL	<MQL
Benzo[k]fluoranthene	<MDL	<MDL	<MDL	<MDL
Benzo[a]pyrene	<MDL	<MDL	<MDL	<MDL
Indeno[1,2,3-cd]pyrene	<MDL	<MDL	<MDL	<MDL
Dibenz[a,h]anthracene	<MDL	<MDL	<MDL	<MDL
Benzo[g,h,i]perylene	<MDL	<MDL	<MDL	<MDL
			SUM =	**1.40**

* Note: Contaminant levels reported have been background corrected using the GC responses from the field blank sample.

Table XII

Results of the GC-PID Analysis of Site # 8 Samples

	Canister # 1 µg/gram	Canister # 2 µg/gram	Canister # 3 µg/gram	Mean µg/gram
Naphthalene	<MDL	<MQL	<MQL	<MQL
Acenaphthylene	<MDL	<MDL	<MDL	<MDL
Acenaphthene	<MQL	<MQL	<MQL	<MQL
Fluorene	0.08	0.07	0.07	**0.07**
Phenanthrene	<MQL	<MQL	<MQL	<MQL
Anthracene	0.12	0.11	0.09	**0.11**
Fluoranthene	0.24	0.22	0.28	**0.25**
Pyrene	0.18	0.17	0.21	**0.19**
Benz[a]anthracene	<MDL	<MDL	<MQL	<MQL
Chrysene	<MDL	<MDL	<MQL	<MQL
Benzo[b]fluoranthene	<MDL	<MDL	<MDL	<MDL
Benzo[k]fluoranthene	<MDL	<MDL	<MDL	<MDL
Benzo[a]pyrene	<MDL	<MDL	<MDL	<MDL
Indeno[1,2,3-cd]pyrene	<MDL	<MQL	<MDL	<MQL
Dibenz[a,h]anthracene	<MDL	<MDL	<MDL	<MDL
Benzo[g,h,i]perylene	<MDL	<MDL	<MDL	<MDL
			SUM =	**0.62**

* Note: Contaminant levels reported have been background corrected using the GC responses from the field blank sample.

Table XIII

Results of the GC-ECD Analysis of Site # 2 Samples

	Canister # 1 ng/gram	Canister # 2 ng/gram	Canister # 3 ng/gram	Mean ng/gram
Trifluralin	0.22	0.24	0.23	**0.23**
HCB	0.93	1.20	0.67	**0.93**
PCA	5.10	5.80	5.50	**5.50**
α-BHC	<MQL	0.16	<MQL	**0.15**
Diazinon	2.40	2.80	2.90	**2.70**
Lindane	0.22	<MQL	0.81	**0.34**
β-BHC	<MQL	0.31	0.26	**0.24**
Heptachlor	1.70	3.70	3.10	**2.80**
δ-BHC	0.86	0.76	0.99	**0.87**
Dacthal	1.20	1.10	0.68	**0.98**
Chlorpyrifos	8.00	8.80	5.90	**7.50**
Oxychlordane	<MQL	<MQL	<MQL	<MQL
Heptachlor Epoxide	1.40	1.10	1.20	**1.20**
trans-Chlordane	4.40	4.10	4.20	**4.30**
trans-Nonachlor	6.90	6.60	6.40	**6.60**
o,p'-DDE	<MDL	<MDL	<MDL	**<MDL**
cis-Chlordane	7.80	6.50	7.10	**7.10**
Endosulfan	2.00	1.20	1.60	**1.60**
p,p'-DDE	6.30	6.10	6.50	**6.30**
Dieldrin	4.80	5.50	5.20	**5.20**
o,p'-DDD	1.30	3.10	2.60	**2.30**
Endrin	5.30	8.30	7.60	**7.00**
cis-Nonachlor	1.40	1.80	1.70	**1.70**
o,p'-DDT	1.50	1.70	1.80	**1.60**
p,p'-DDD	5.90	7.40	6.70	**6.70**
Endosulfan-II	0.66	1.30	1.20	**1.10**
p,p'-DDT	<MQL	<MQL	<MQL	<MQL
Endosulfan Sulfate	0.69	0.65	0.80	**0.73**
Methoxychlor	1.20	1.30	1.60	**1.40**
Mirex	<MDL	<MDL	<MDL	**<MDL**
cis-Permethrin	<MDL	<MQL	2.40	**<MQL**
trans-Permethrin	<MDL	<MQL	<MQL	**<MQL**
TOTAL PCBs	22.0	31.0	27.0	**27.0**
			SUM =	**100**

* Note: Contaminant levels reported have been background corrected using the GC responses from the field blank sample.

Table XIV

Results of the GC-ECD Analysis of Site # 3 Samples

	Canister # 1 ng/gram	Canister # 2 ng/gram	Canister # 3 ng/gram	Mean ng/gram
Trifluralin	0.39	<MQL	0.48	**0.32**
HCB	1.30	1.10	1.30	**1.20**
PCA	5.90	5.60	6.00	**5.90**
α-BHC	0.17	0.16	0.18	**0.17**
Diazinon	6.40	5.90	6.30	**6.20**
Lindane	0.19	<MDL	0.30	**0.16**
β-BHC	<MDL	<MQL	0.33	**0.13**
Heptachlor	2.80	0.48	1.00	**1.40**
δ-BHC	0.51	0.62	0.74	**0.62**
Dacthal	1.00	0.96	1.00	**0.99**
Chlorpyrifos	5.60	5.40	5.70	**5.60**
Oxychlordane	<MDL	<MDL	<MQL	**<MQL**
Heptachlor Epoxide	1.80	0.98	1.70	**1.50**
trans-Chlordane	4.10	4.20	3.90	**4.00**
trans-Nonachlor	4.60	4.70	5.30	**4.90**
o,p'-DDE	0.16	0.19	<MQL	**0.12**
cis-Chlordane	4.90	5.90	4.70	**5.10**
Endosulfan	1.60	1.70	1.60	**1.60**
p,p'-DDE	9.00	7.90	8.50	**8.50**
Dieldrin	5.40	5.30	5.10	**5.30**
o,p'-DDD	3.60	3.70	3.10	**3.50**
Endrin	6.40	6.90	7.00	**6.80**
cis-Nonachlor	1.50	1.80	1.40	**1.60**
o,p'-DDT	1.30	1.60	1.10	**1.30**
p,p'-DDD	8.90	8.90	8.20	**8.70**
Endosulfan-II	0.77	0.82	0.79	**0.79**
p,p'-DDT	1.20	1.40	<MQL	**1.20**
Endosulfan Sulfate	0.30	0.32	<MQL	**0.22**
Methoxychlor	<MDL	<MDL	<MDL	**<MDL**
Mirex	<MDL	<MDL	<MDL	**<MDL**
cis-Permethrin	**	**	**	**
trans-Permethrin	**	**	**	**
TOTAL PCBs	48.0	39.0	44.0	**44.0**
			SUM =	**130**

* Note: Contaminant levels reported have been background corrected using the GC responses from the field blank sample.
** See Table 3, which gives GC-MS confirmation data for selected analytes.

Table XV

Results of the GC-ECD Analysis of Site # 4 Samples

	Canister # 1 ng/gram	Canister # 2 ng/gram	Canister # 3 ng/gram	Mean ng/gram
Trifluralin	0.35	0.36	0.28	**0.33**
HCB	0.90	0.84	0.88	**0.87**
PCA	5.20	6.00	5.20	**5.4**
α-BHC	0.15	0.19	0.17	**0.17**
Diazinon	2.80	2.80	<MDL	**1.90**
Lindane	0.42	0.45	<MQL	**0.33**
β-BHC	<MDL	<MDL	<MDL	**<MDL**
Heptachlor	<MQL	<MQL	<MDL	**<MQL**
δ-BHC	0.66	0.75	0.58	**0.66**
Dacthal	0.71	0.99	0.89	**0.86**
Chlorpyrifos	3.50	4.40	3.80	**3.90**
Oxychlordane	<MQL	<MQL	<MQL	**<MQL**
Heptachlor Epoxide	0.82	0.75	1.00	**0.87**
trans-Chlordane	2.90	2.70	3.00	**2.90**
trans-Nonachlor	3.60	3.50	3.60	**3.60**
o,p'-DDE	1.40	1.10	1.40	**1.30**
cis-Chlordane	3.40	3.40	3.50	**3.40**
Endosulfan	1.00	0.69	1.20	**0.99**
p,p'-DDE	4.70	4.20	4.40	**4.40**
Dieldrin	4.60	4.50	4.50	**4.50**
o,p'-DDD	2.10	1.80	2.00	**1.90**
Endrin	8.60	8.90	9.00	**8.80**
cis-Nonachlor	0.96	1.00	0.98	**0.99**
o,p'-DDT	0.75	0.84	0.79	**0.80**
p,p'-DDD	5.80	5.70	5.70	**5.70**
Endosulfan-II	0.55	0.76	0.76	**0.69**
p,p'-DDT	1.60	1.20	1.60	**1.50**
Endosulfan Sulfate	0.51	0.05	0.40	**0.32**
Methoxychlor	2.30	2.00	1.80	**2.00**
Mirex	<MDL	<MDL	<MDL	**<MDL**
cis-Permethrin	**	**	**	**
trans-Permethrin	**	**	**	**
TOTAL PCBs	37.0	34.0	28.0	**33.0**
			SUM =	**110**

*Note: Contaminant levels reported have been background corrected using the GC responses from the field blank sample.
** See Table 3 , which gives GC-MS confirmation data for selected analytes.

Table XVI

Results of the GC-ECD Analysis of Site # 6 Samples

	Canister # 2 ng/gram	Canister # 3 ng/gram	Mean ng/gram
Trifluralin	<MDL	<MDL	**<MDL**
HCB	0.41	0.56	**0.49**
PCA	1.60	1.60	**1.60**
α-BHC	<MQL	<MQL	**<MQL**
Diazinon	<MDL	<MDL	<MDL
Lindane	<MDL	<MDL	<MDL
β-BHC	<MDL	<MDL	<MDL
Heptachlor	<MDL	<MDL	<MDL
δ-BHC	1.10	1.20	**1.10**
Dacthal	0.23	0.46	**0.34**
Chlorpyrifos	4.50	5.00	**4.80**
Oxychlordane	1.10	<MQL	**<MQL**
Heptachlor Epoxide	<MDL	<MDL	<MDL
trans-Chlordane	5.40	5.90	**5.60**
trans-Nonachlor	7.40	6.80	**7.10**
o,p'-DDE	1.60	1.70	**1.60**
cis-Chlordane	28.0	31.0	**30.0**
Endosulfan	1.00	0.98	**1.00**
p,p'-DDE	23.0	22.0	**23.0**
Dieldrin	6.30	7.20	**6.70**
o,p'-DDD	8.4	9.50	**9.00**
Endrin	16.2	23.0	**19.0**
cis-Nonachlor	1.90	2.10	**2.00**
o,p'-DDT	<MDL	<MDL	<MDL
p,p'-DDD	23.0	26.0	**25.0**
Endosulfan-II	0.78	0.45	**0.62**
p,p'-DDT	0.57	0.89	**0.73**
Endosulfan Sulfate	<MDL	<MDL	<MDL
Methoxychlor	0.68	0.86	**0.77**
Mirex	<MDL	<MDL	<MDL
cis-Permethrin	<MDL	<MDL	<MDL
trans-Permethrin	<MDL	<MDL	<MDL
TOTAL PCBs	33.0	37.0	**35.0**
		SUM =	**170**

* Note: Contaminant levels reported have been background corrected using the GC responses from the field blank sample.

Table XVII

Results of the GC-ECD Analysis of Site # 7 Samples

	Canister # 1 ng/gram	Canister # 2 ng/gram	Canister # 3 ng/gram	Mean ng/gram
Trifluralin	<MDL	<MDL	<MQL	**<MQL**
HCB	0.50	0.60	0.75	**0.62**
PCA	3.30	3.80	4.40	**3.80**
α-BHC	0.18	0.19	0.19	**0.19**
Diazinon	<MDL	<MDL	<MDL	**<MDL**
Lindane	0.50	0.69	0.71	**0.64**
β-BHC	<MDL	<MDL	<MDL	**<MDL**
Heptachlor	<MDL	<MDL	<MDL	**<MDL**
δ-BHC	0.82	0.46	0.91	**0.73**
Dacthal	0.73	0.76	1.20	**0.90**
Chlorpyrifos	3.90	4.30	5.80	**4.70**
Oxychlordane	<MDL	<MQL	<MQL	**<MQL**
Heptachlor Epoxide	<MDL	<MDL	0.68	**0.23**
trans-Chlordane	1.60	1.80	2.00	**1.80**
trans-Nonachlor	4.40	4.80	4.40	**4.60**
o,p'-DDE	<MDL	<MDL	<MDL	**<MDL**
cis-Chlordane	5.10	5.40	7.00	**5.80**
Endosulfan	0.63	0.84	0.76	**0.74**
p,p'-DDE	4.80	5.30	6.10	**5.40**
Dieldrin	3.00	3.60	4.80	**3.80**
o,p'-DDD	0.75	0.94	1.30	**0.98**
Endrin	<MDL	<MDL	1.30	**0.42**
cis-Nonachlor	1.20	1.10	1.30	**1.20**
o,p'-DDT	<MDL	<MDL	<MDL	**<MDL**
p,p'-DDD	3.00	3.40	4.60	**3.70**
Endosulfan-II	0.35	0.38	0.50	**0.41**
p,p'-DDT	<MQL	<MQL	<MQL	**<MQL**
Endosulfan Sulfate	<MQL	<MDL	<MDL	**<MQL**
Methoxychlor	1.20	0.88	0.74	**0.94**
Mirex	<MDL	<MDL	<MDL	**<MDL**
cis-Permethrin	<MDL	<MDL	<MDL	**<MDL**
trans-Permethrin	<MDL	<MQL	<MDL	**<MQL**
TOTAL PCBs	23.0	30.0	29.0	**27.0**
			SUM =	**68.0**

* Note: Contaminant levels reported have been background corrected using the GC responses from the field blank sample.

Table XVIII

Results of the GC-ECD Analysis of Site # 8 Samples

	Canister # 1 ng/gram	Canister # 2 ng/gram	Canister # 3 ng/gram	Mean ng/gram
Trifluralin	<MDL	<MDL	<MDL	<MDL
HCB	0.49	0.40	0.52	**0.47**
PCA	2.30	1.90	2.60	**2.30**
α-BHC	0.15	<MDL	0.16	**0.14**
Diazinon	4.00	4.00	6.50	**4.80**
Lindane	0.49	0.50	0.50	**0.50**
β-BHC	<MDL	<MDL	<MDL	<MDL
Heptachlor	<MDL	<MDL	<MDL	<MDL
δ-BHC	0.86	0.73	0.92	**0.84**
Dacthal	0.29	0.57	0.24	**0.37**
Chlorpyrifos	4.00	4.70	5.50	**4.70**
Oxychlordane	<MQL	<MQL	<MQL	**<MQL**
Heptachlor Epoxide	<MDL	<MDL	<MDL	<MDL
trans-Chlordane	1.80	2.40	2.60	**2.20**
trans-Nonachlor	7.00	6.10	6.80	**6.60**
o,p'-DDE	<MDL	<MDL	<MDL	<MDL
cis-Chlordane	9.00	6.70	7.50	**7.80**
Endosulfan	0.72	0.75	0.81	**0.76**
p,p'-DDE	5.50	4.60	4.70	**4.90**
Dieldrin	4.00	4.30	4.80	**4.40**
o,p'-DDD	0.57	0.72	0.83	**0.71**
Endrin	8.10	11.0	12.0	**10.0**
cis-Nonachlor	0.97	0.96	1.10	**1.00**
o,p'-DDT	<MDL	<MDL	<MDL	<MDL
p,p'-DDD	2.70	2.80	3.70	**3.10**
Endosulfan-II	0.36	0.37	0.56	**0.43**
p,p'-DDT	<MDL	<MQL	0.44	**0.16**
Endosulfan Sulfate	0.30	0.30	0.47	**0.35**
Methoxychlor	0.66	<MDL	<MDL	**0.23**
Mirex	<MDL	<MDL	<MDL	<MDL
cis-Permethrin	**	<MQL	**	**1.00**
trans-Permethrin	**	<MQL	**	**3.00**
TOTAL PCBs	28.0	22.0	24.0	**25.0**
			SUM =	**86.0**

* Note: Contaminant levels reported have been background corrected using the GC responses from the field blank sample.
** See Table 3 , which gives GC-MS confirmation data for selected analytes.

Table XIX

Permeability Reference Compound Recovery

QA/QC Sample	µg PRC
Fabrication Blank	9.00
Site # 1 Field Blank	8.00
Site # 2 Field Blank	9.20
Site # 3 Field Blank	5.70
Site # 4 Field Blank	8.00
Site # 6 Field Blank	7.90
Site # 8 Field Blank	7.70
Mean	7.90*

Deployment Site	Canister # 1 µg PRC	Canister # 2 µg PRC	Canister # 3 µg PRC	Mean µg PRC
Site # 2	0.44	0.47	0.47	0.46**
Site # 3	0.51	0.49	0.50	0.50**
Site # 4	Lost	0.69	0.70	0.70**
Site # 6	Lost	1.20	1.20	1.20**
Site # 7	0.52	0.50	0.75	0.59**
Site # 8	1.00	1.40	1.40	1.20**

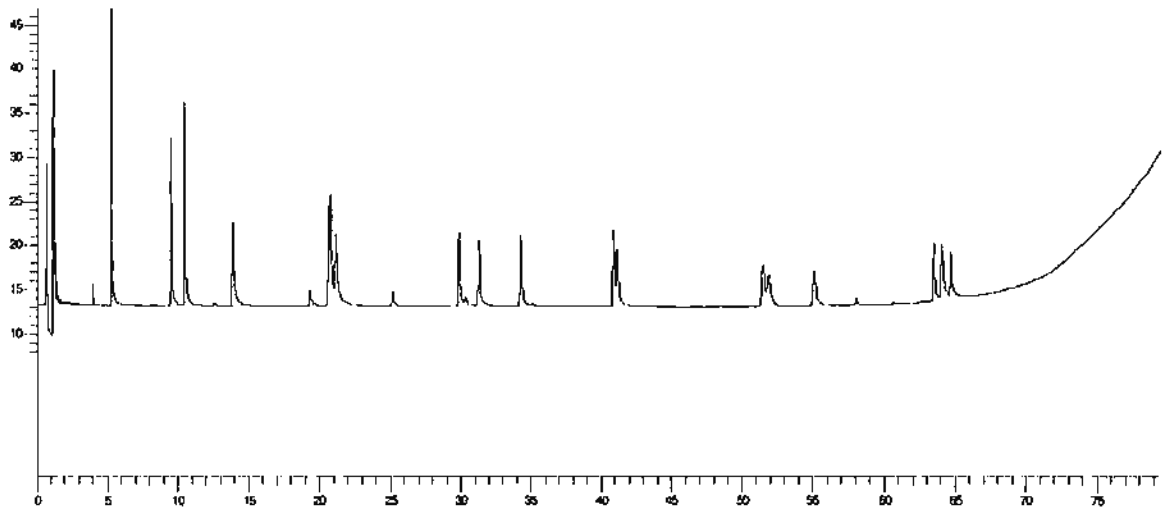
Deployment Site	k_{eprc} (d^{-1})
Site # 2	0.094
Site # 3	0.092
Site # 4	0.081
Site # 6	0.063
Site # 7	0.086
Site # 8	0.062

$$k_{eprc} = \frac{\ln(C_{SPMDo} / C_{SPMD})}{t}$$

* C_{SPMDo}
** C_{SPMD}

Figure I

GC-PID Analysis of PAH Standards

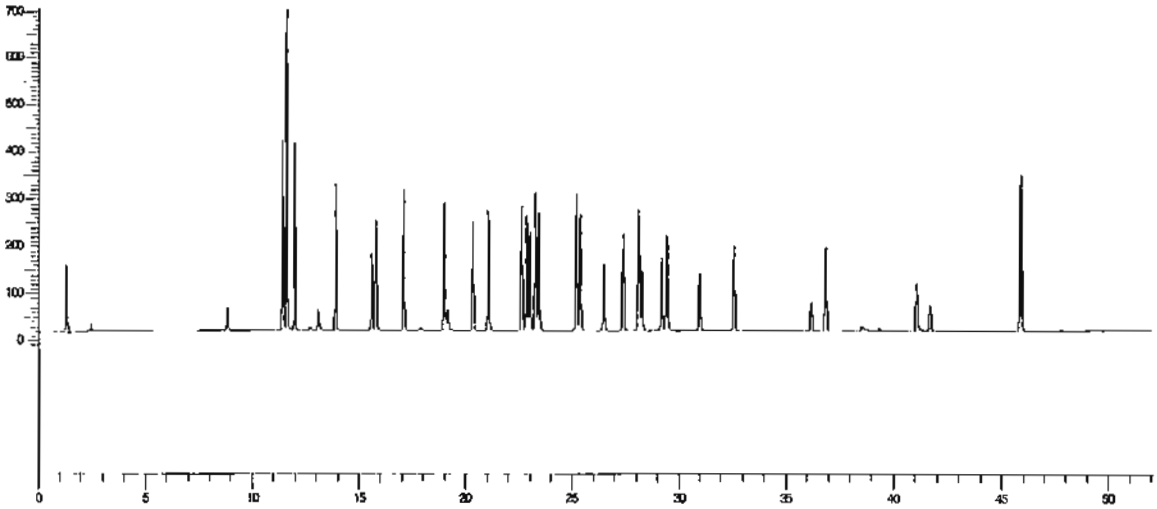


4.0 μg/mL PAH mixed standard. See Table VI for component list and retention times.

Note: Hewlett Packard 5890 series gas chromatograph (GC) equipped with 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 °C, then 15 °C/min to 165 °C, followed by 2.5 °C/min to 250 °C, then 10°C/min to 320 °C and held at 320 °C for 1 min.

Figure II

GC-ECD Analysis of OC-Pesticide Standards

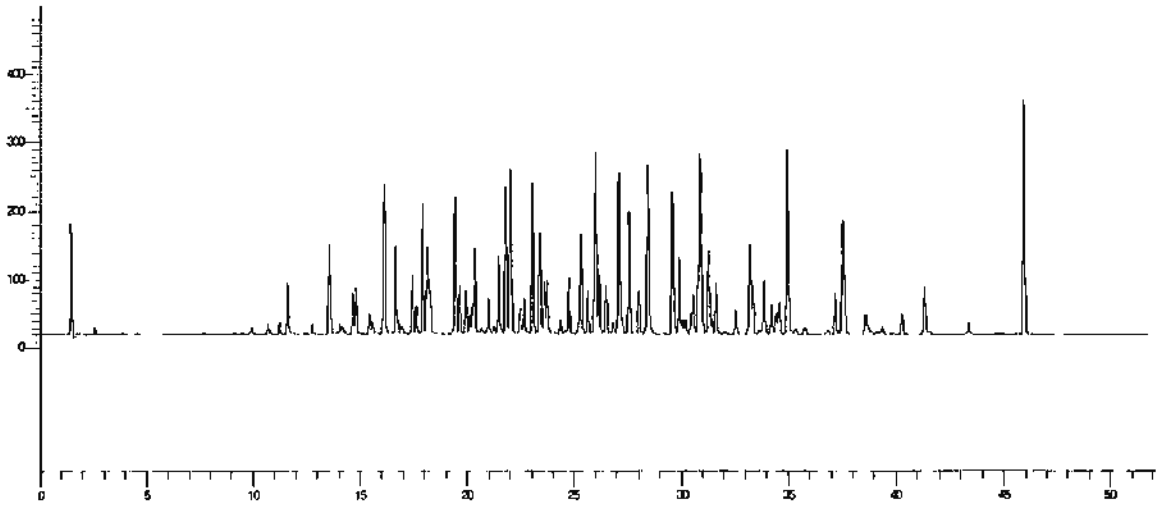


40 ng/mL OC-Pesticide mixed standard. See Table VI for component list and retention times.

Note: Hewlett Packard 5890 series gas chromatograph (GC) equipped with a DB-35MS (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 90 °C; then 15 °C/min to 165 °C; followed by 2.5 °C/min to 250 °C; then at 10 °C/min to 320 °C. The electron capture detector (ECD) was maintained at 330 °C (Hewlett Packard, Inc., Palo Alto, CA).

Figure III

GC-ECD Analysis of PCB Standard



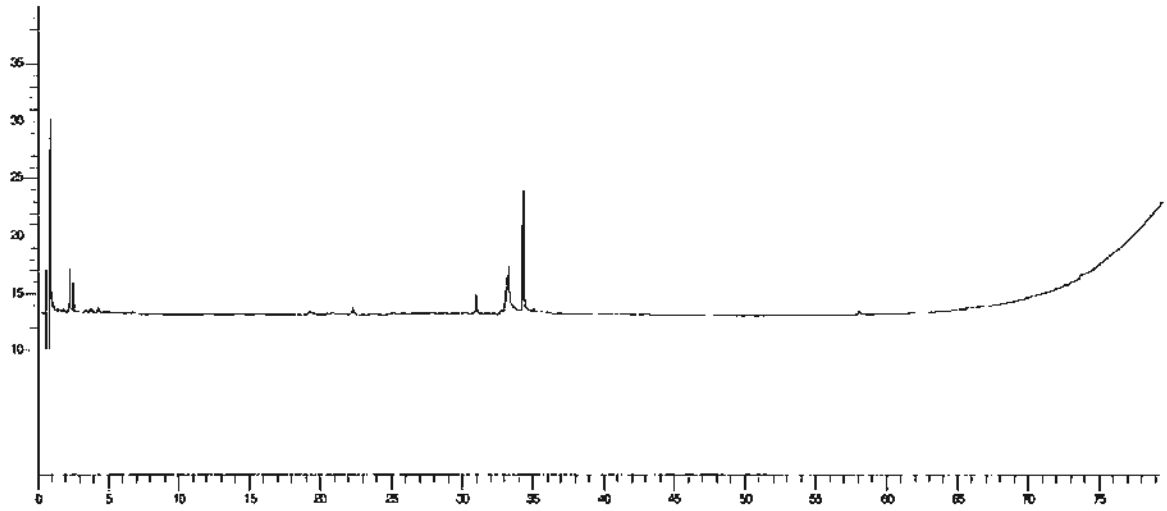
400 total ng/mL 1:1:1:1 mixture of Aroclor® (1242:1248:1254:1260) standard. See Table VI for component list and retention times.

Note: Hewlett Packard 5890 series gas chromatograph (GC) equipped with a DB-35MS (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 90 °C; then 15 °C/min to 165 °C; followed by 2.5 °C/min to 250 °C; then at 10 °C/min to 320 °C. The electron capture detector (ECD) was maintained at 330 °C (Hewlett Packard, Inc., Palo Alto, CA).

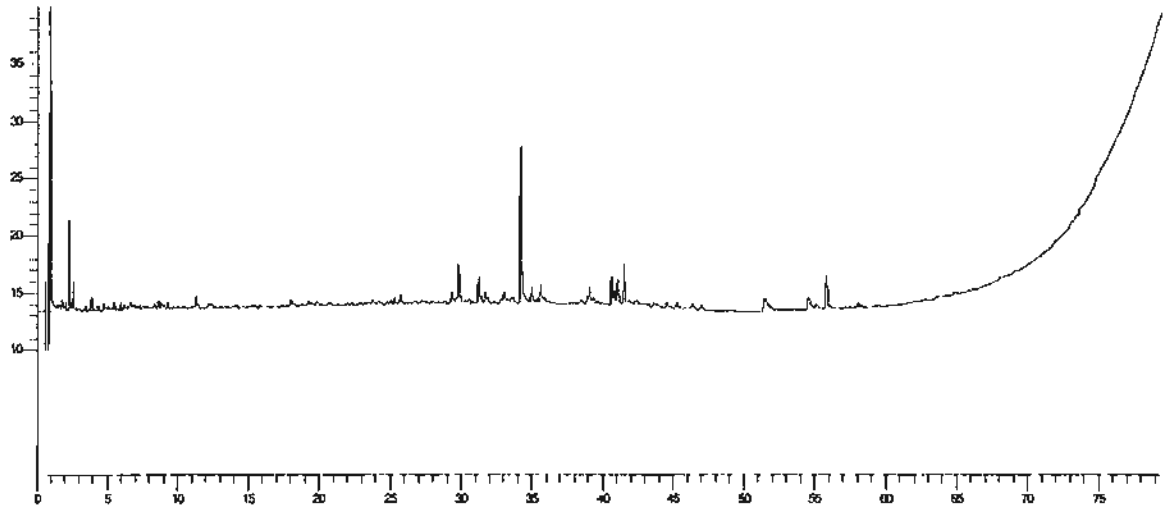
Figure IV

GC-PID Analysis of "PAH" Fractions

Site # 2



Field Blank SPMD

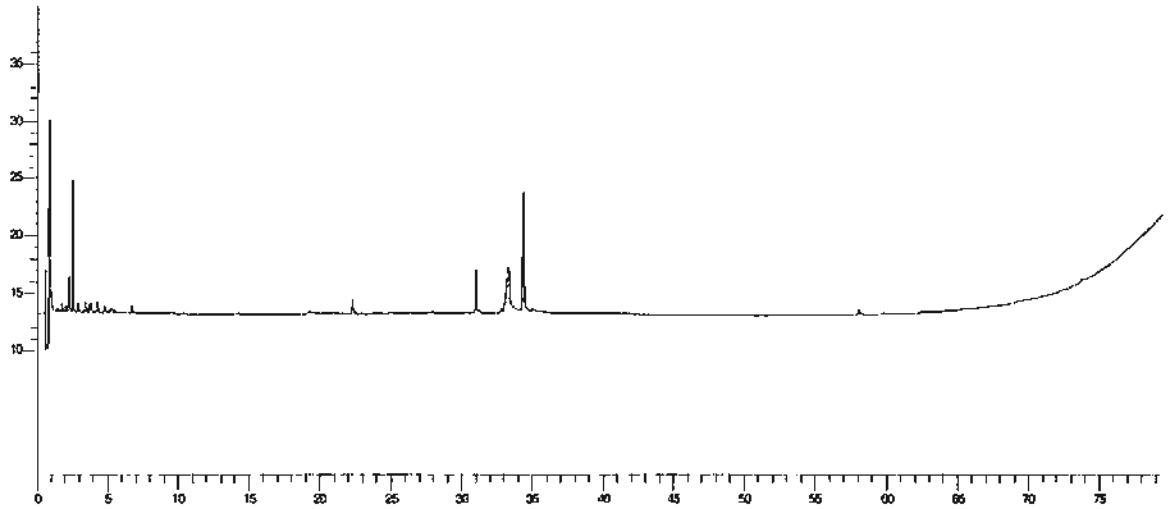


Canister # 2 SPMD Sample

Figure V

GC-PID Analysis of "PAH" Fractions

Site # 3



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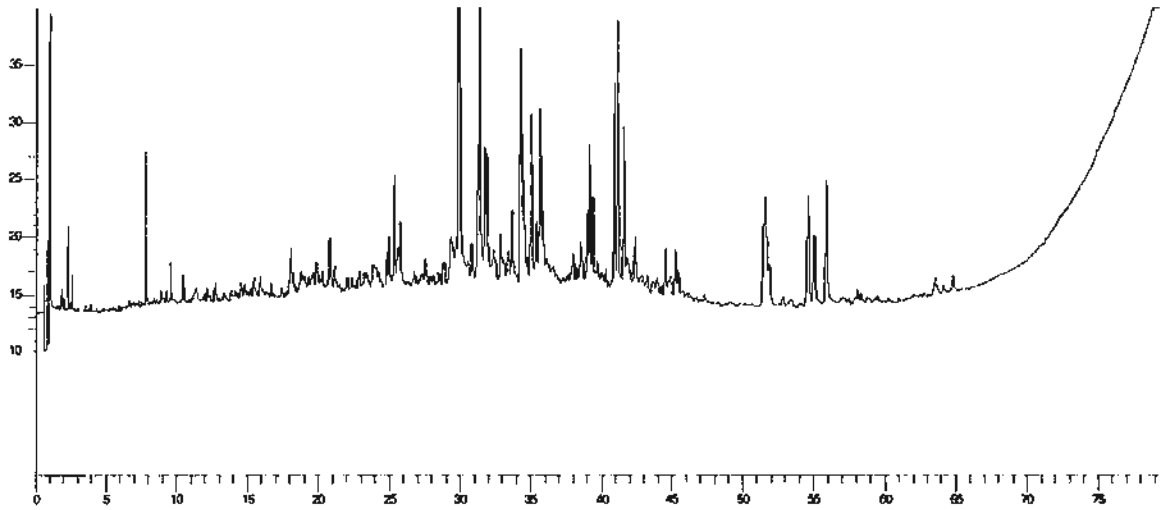
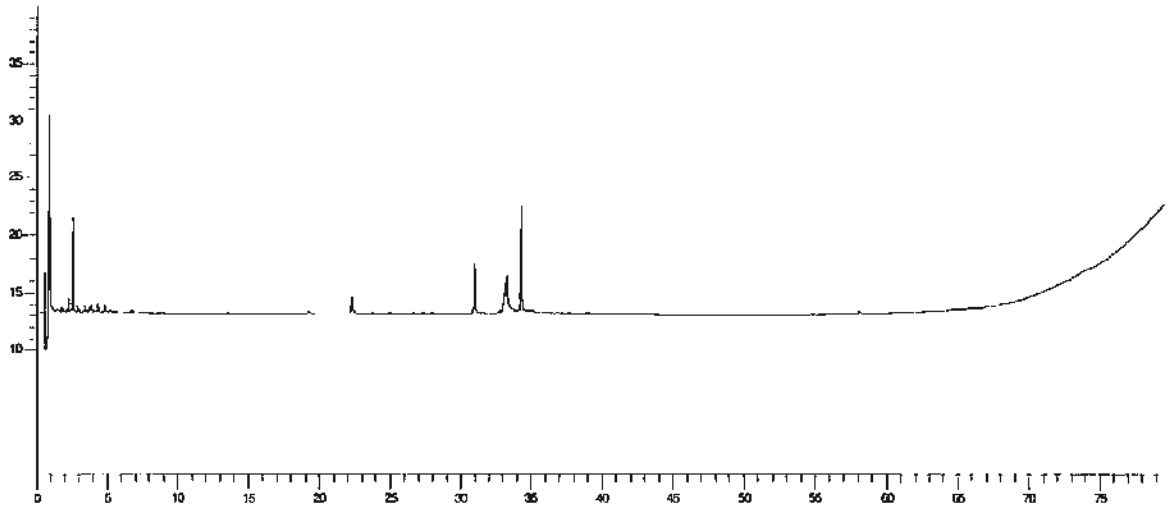


Canister # 2 SPMD Sample

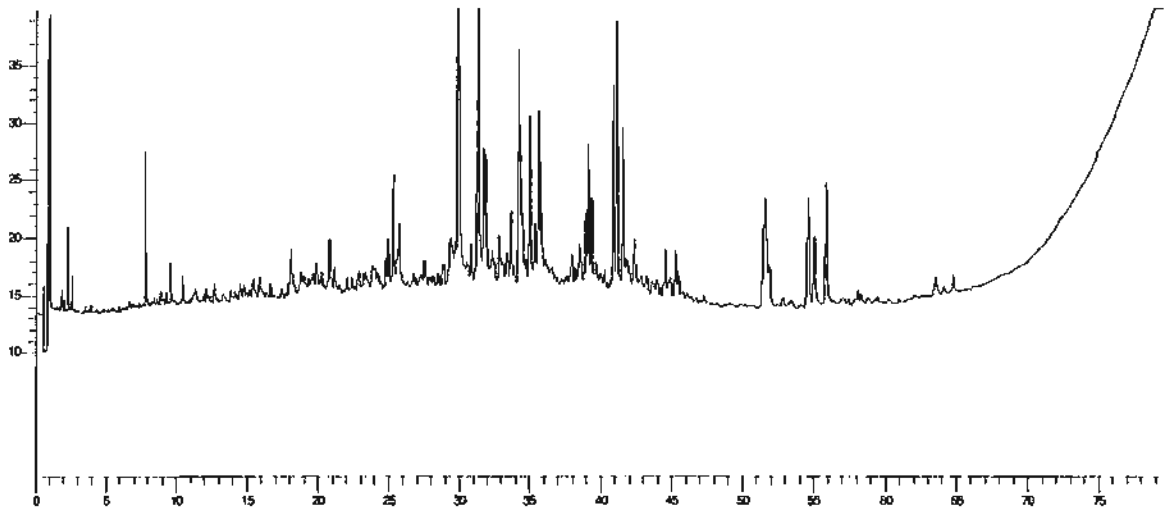
Figure VI

GC-PID Analysis of "PAH" Fractions

Site # 4



Field Blank SPMD

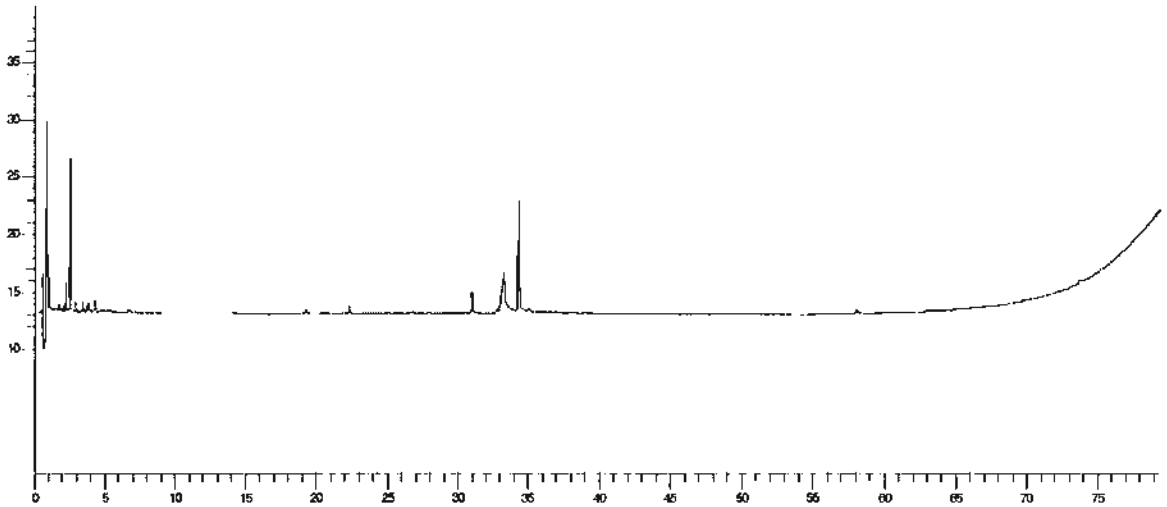


Canister # 2 SPMD Sample

Figure VII

GC-PID Analysis of "PAH" Fractions

Site # 6



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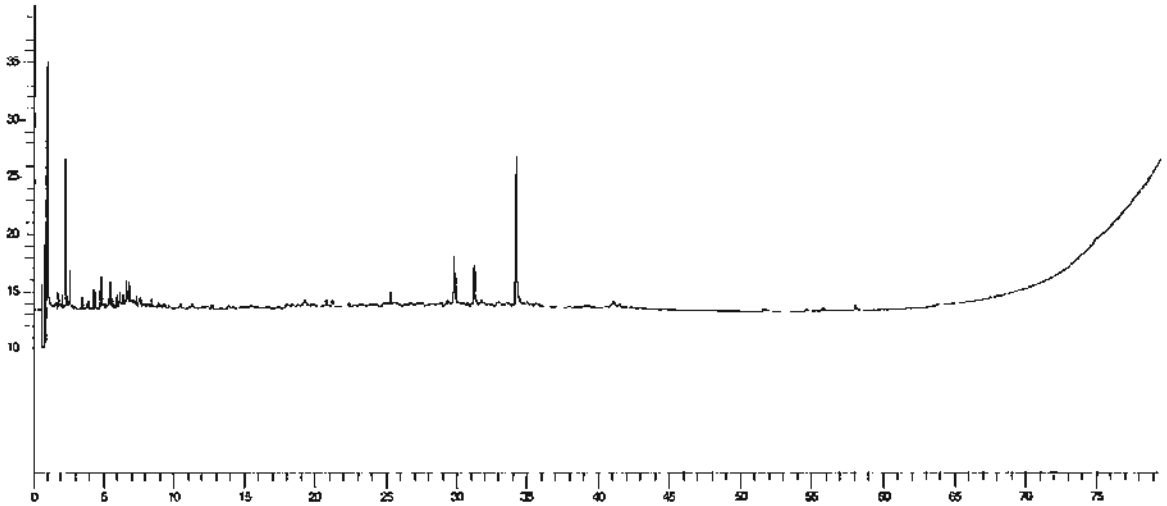
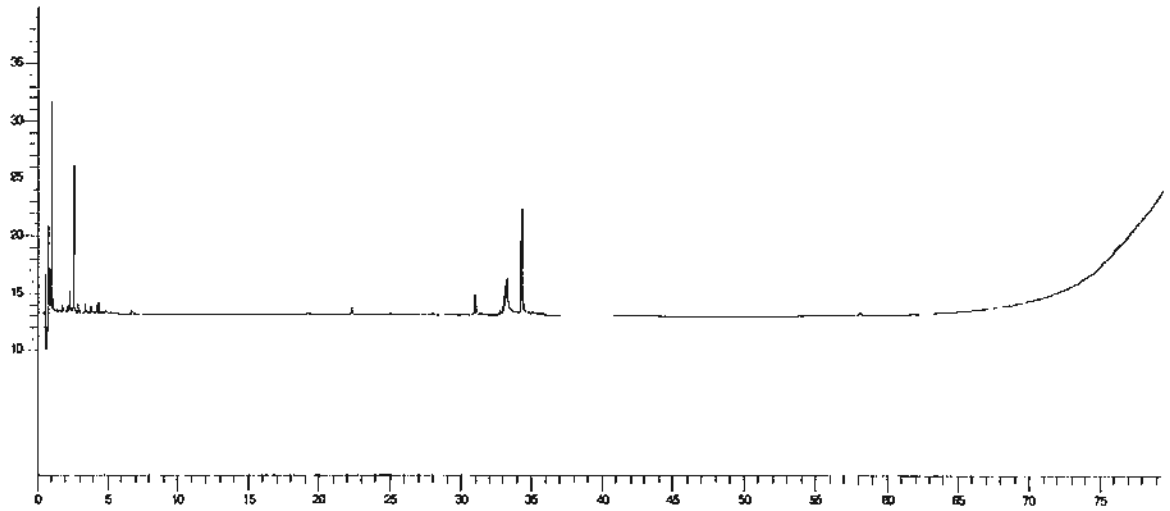


Canister # 2 SPMD Sample

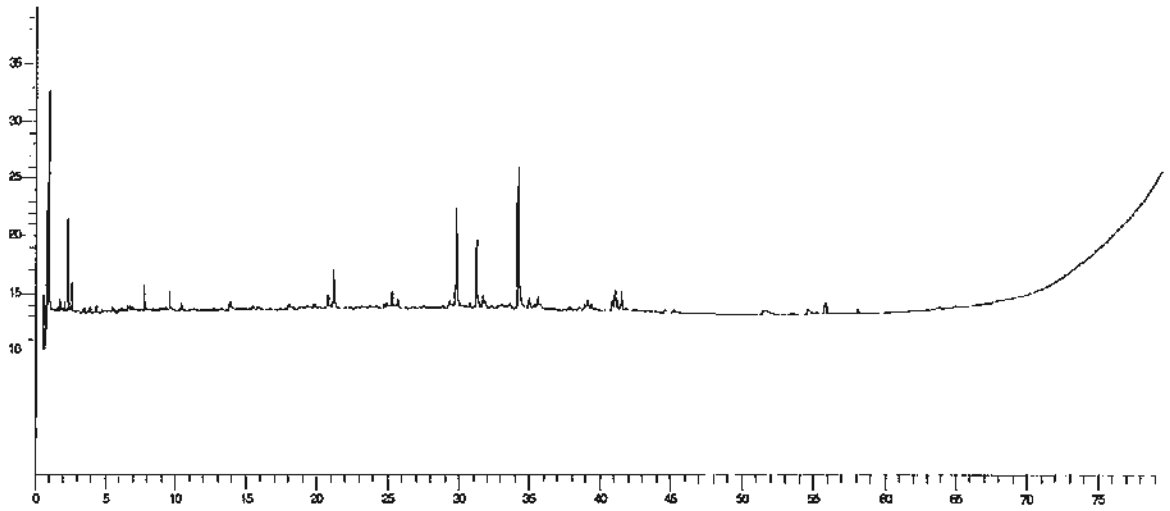
Figure VIII

GC-PID Analysis of "PAH" Fractions

Site # 7



Field Blank SPMD

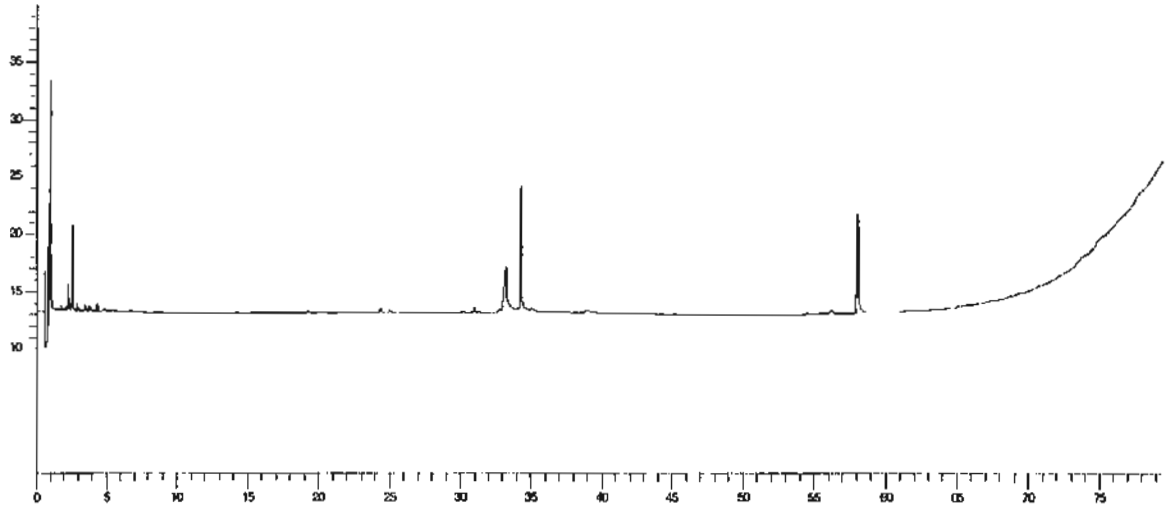


Canister # 2 SPMD Sample

Figure IX

GC-PID Analysis of "PAH" Fractions

Site # 8



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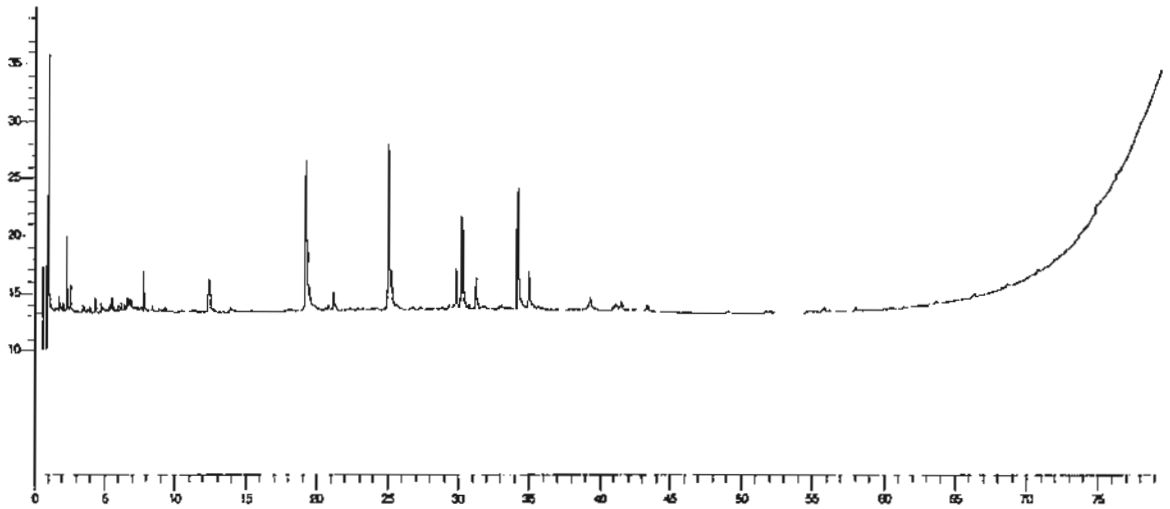
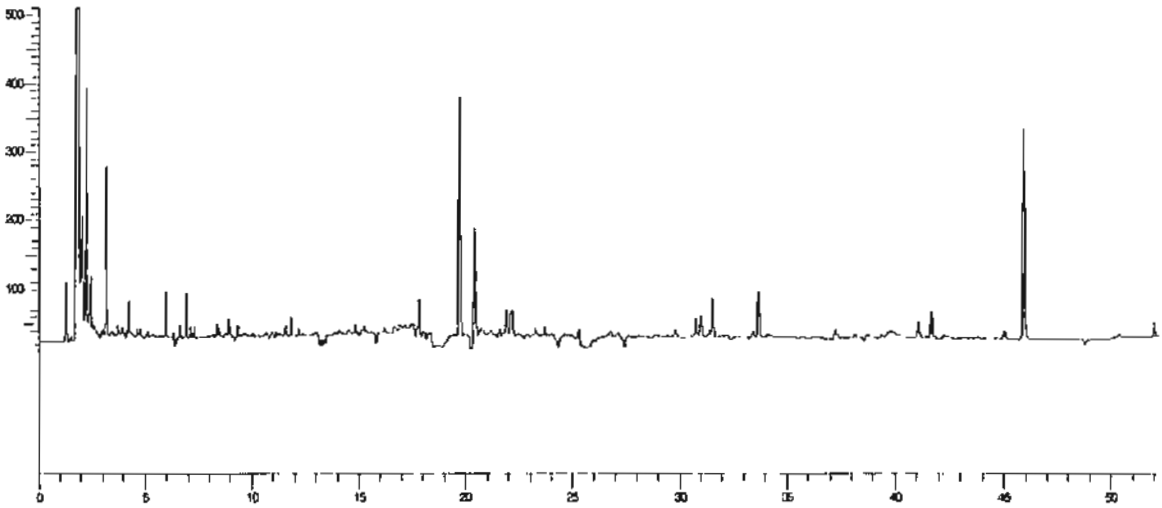


Canister # 2 SPMD Sample

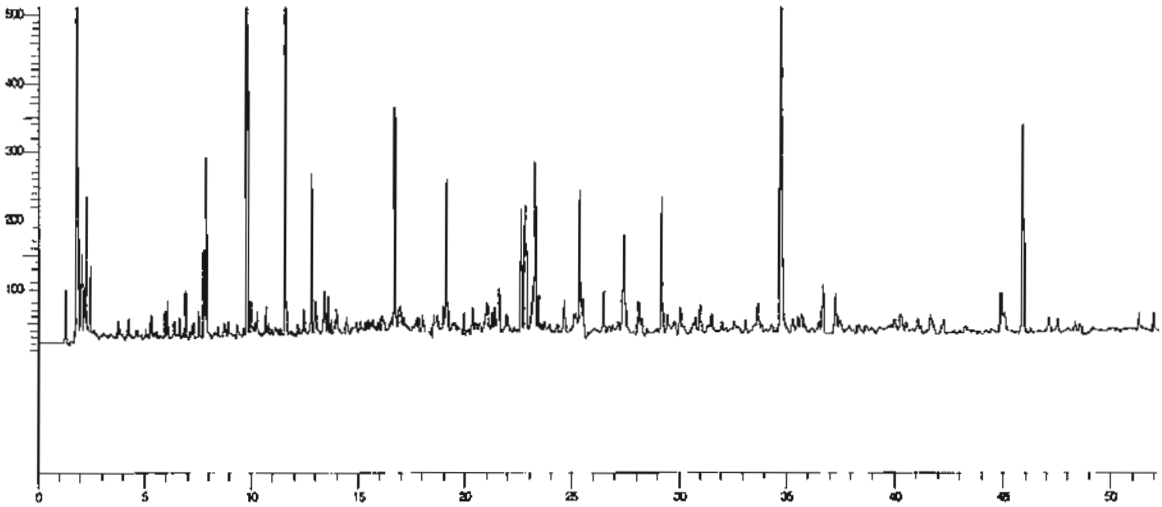
Figure X

GC-ECD Analysis of "SG2" Fractions (i.e. OC-Pesticides)

Site # 2



Field Blank SPMD

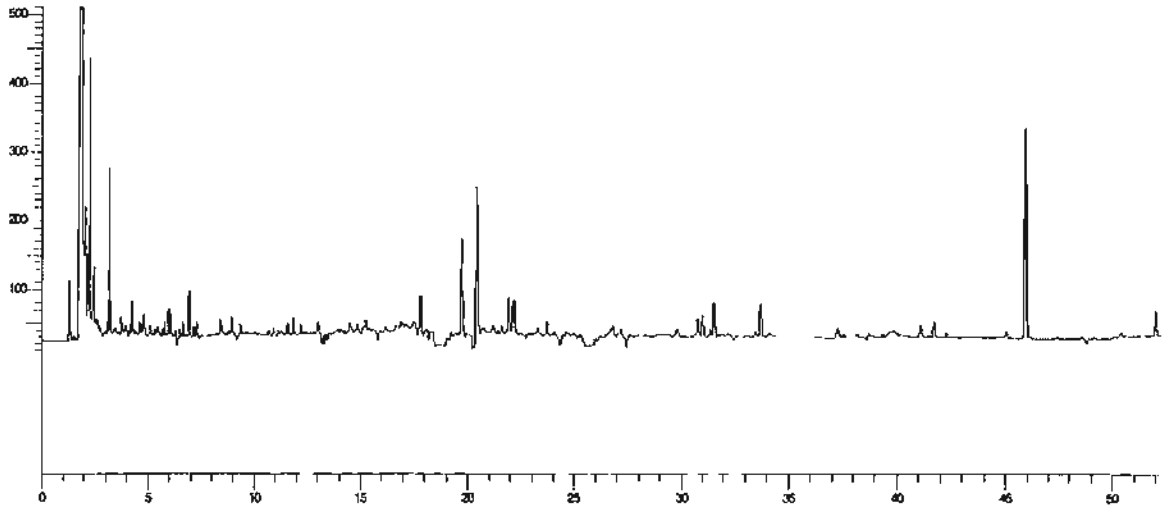


Canister # 2 SPMD Sample

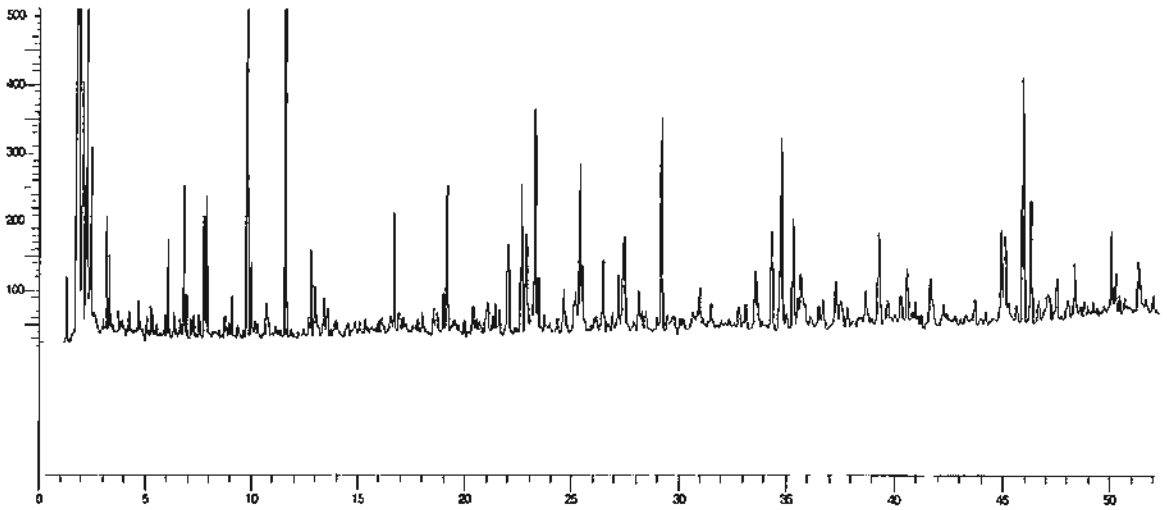
Figure XI

GC-ECD Analysis of "SG2" Fractions (i.e. OC-Pesticides)

Site # 3



Field Blank SPMD

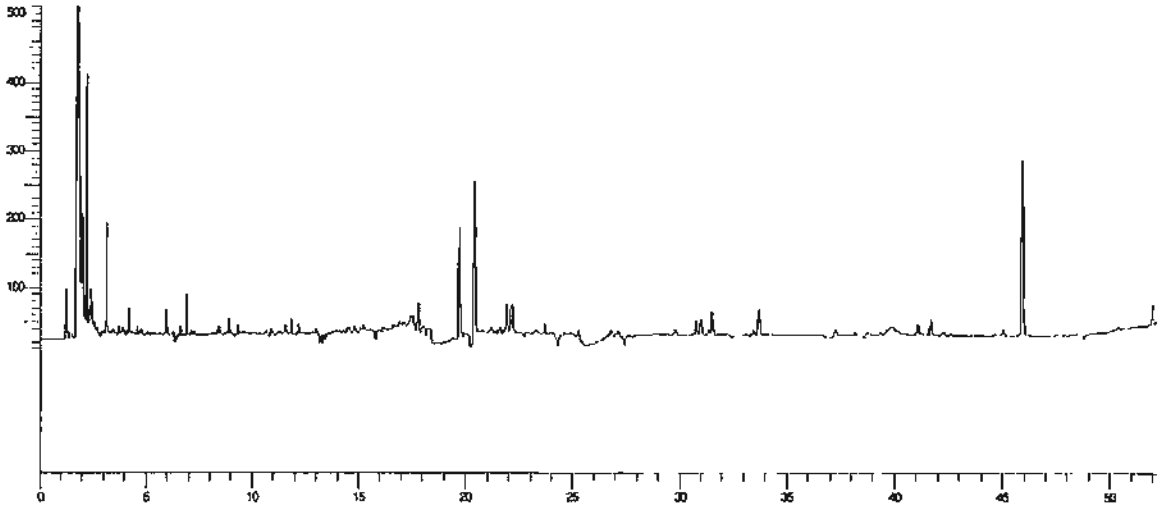


Canister # 2 SPMD Sample

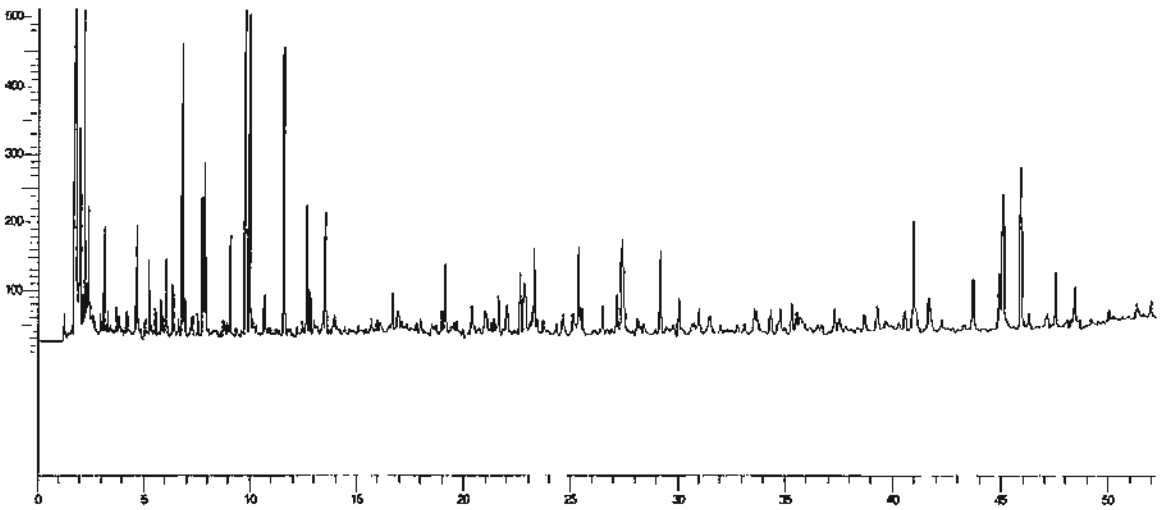
Figure XII

GC-ECD Analysis of "SG2" Fractions (i.e. OC-Pesticides)

Site # 4



Field Blank SPMD

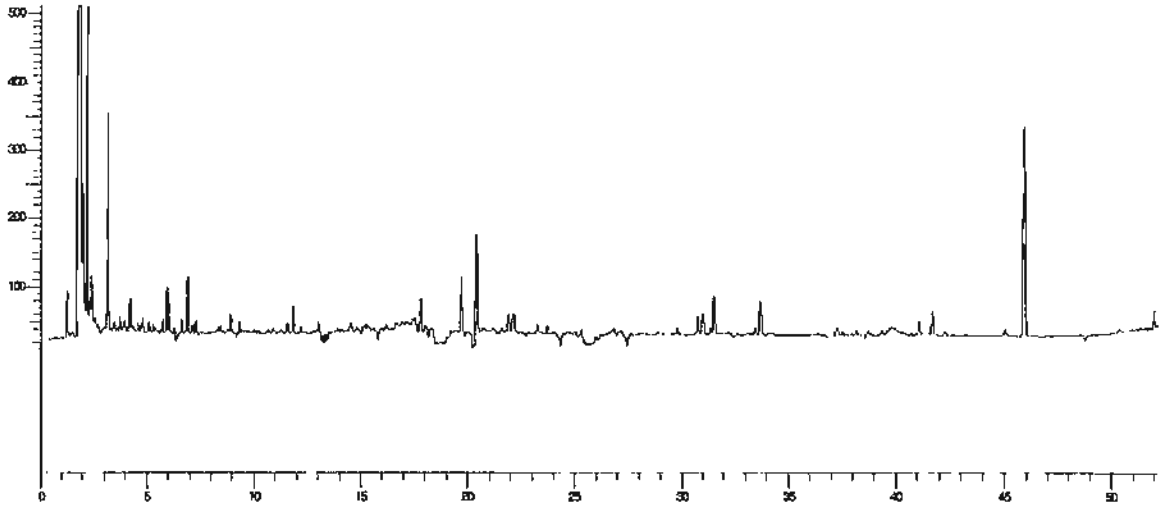


Canister # 2 SPMD Sample

Figure XIII

GC-ECD Analysis of "SG2" Fractions (i.e. OC-Pesticides)

Site # 6



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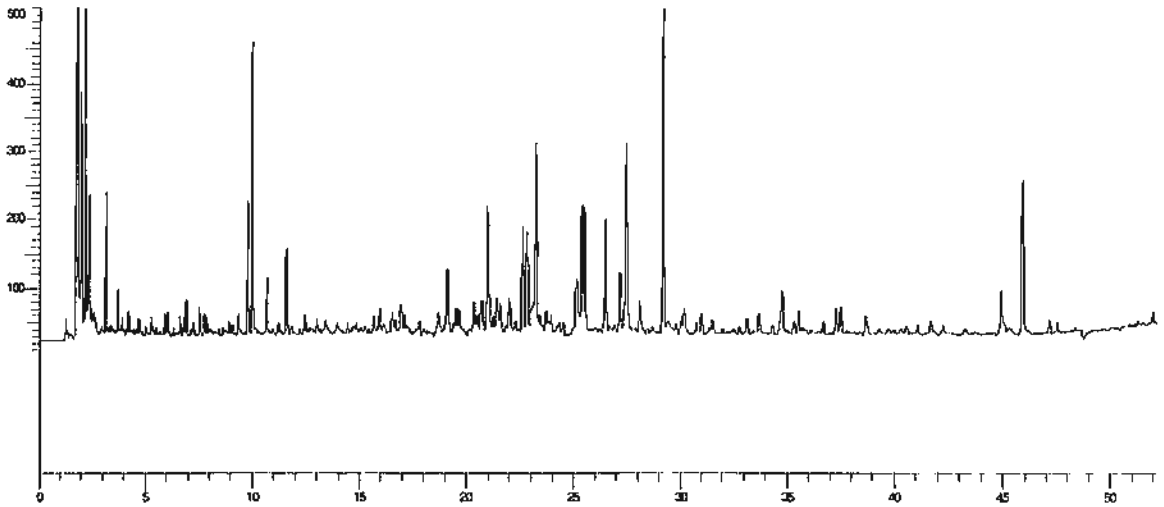
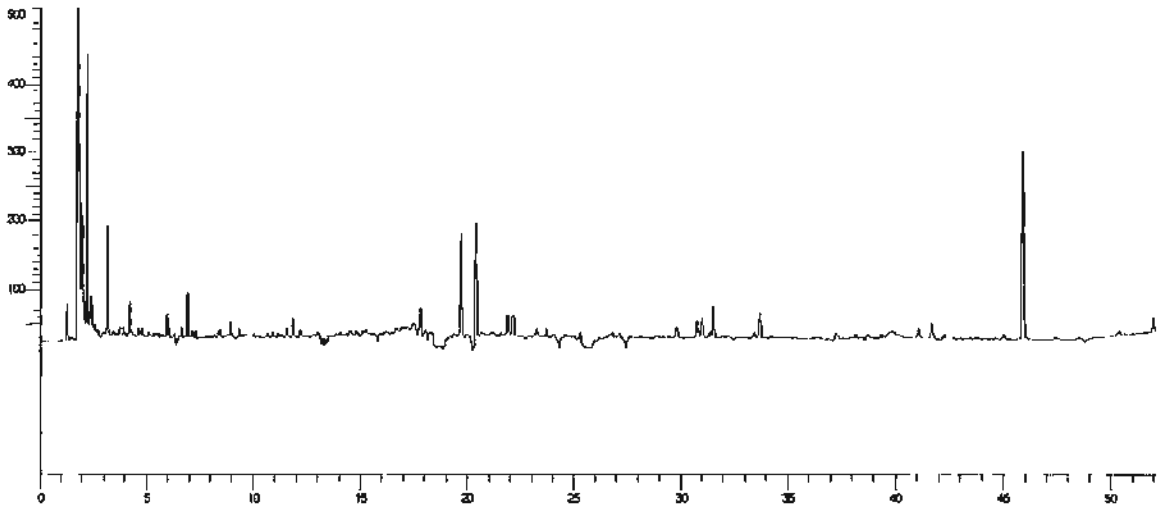


Canister # 2 SPMD Sample

Figure XIV

GC-ECD Analysis of "SG2" Fractions (i.e. OC-Pesticides)

Site # 7



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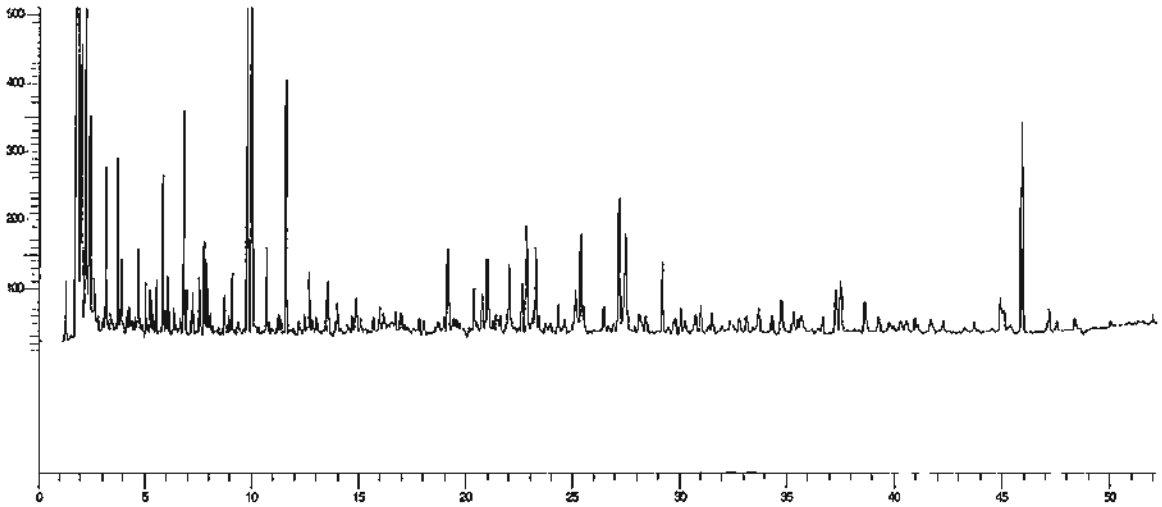
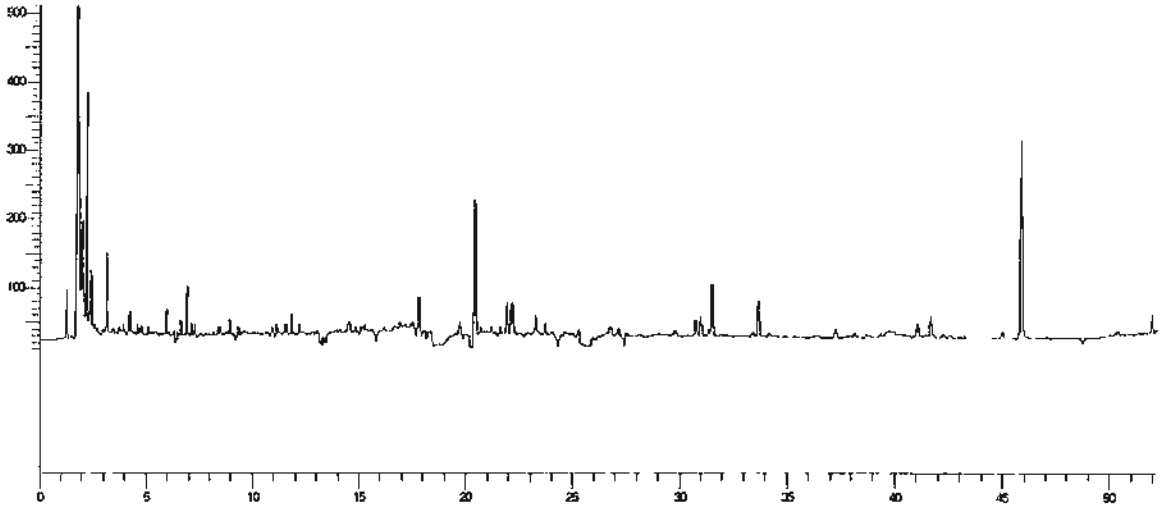


Canister # 2 SPMD Sample

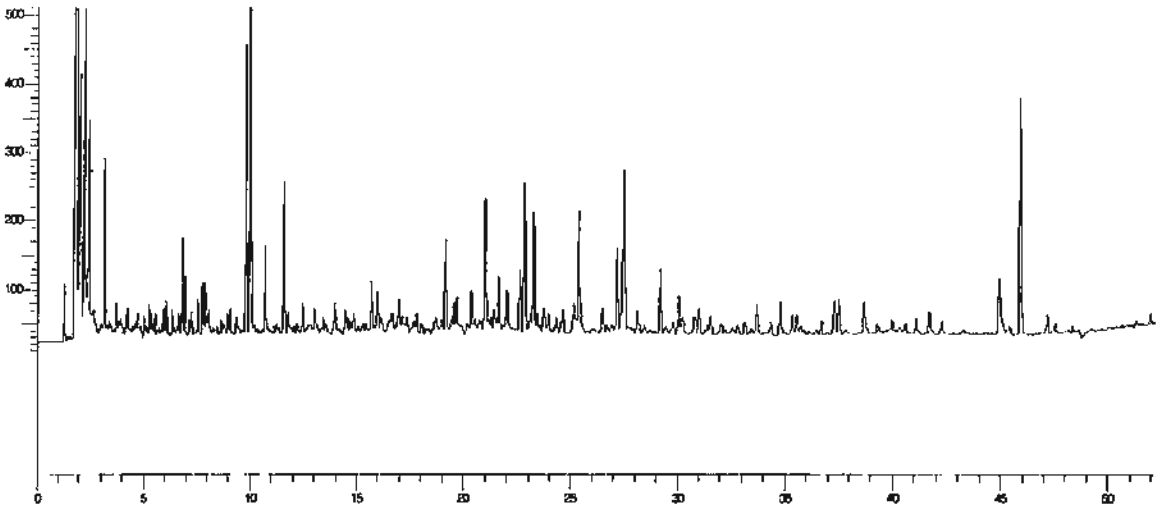
Figure XV

GC-ECD Analysis of "SG2" Fractions (i.e. OC-Pesticides)

Site # 8



Field Blank SPMD

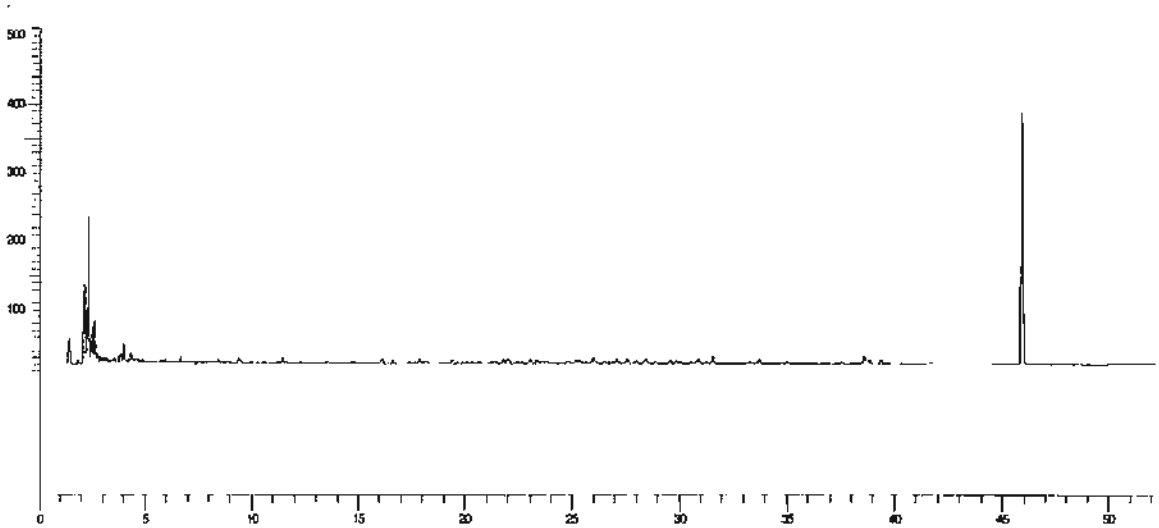


Canister # 2 SPMD Sample

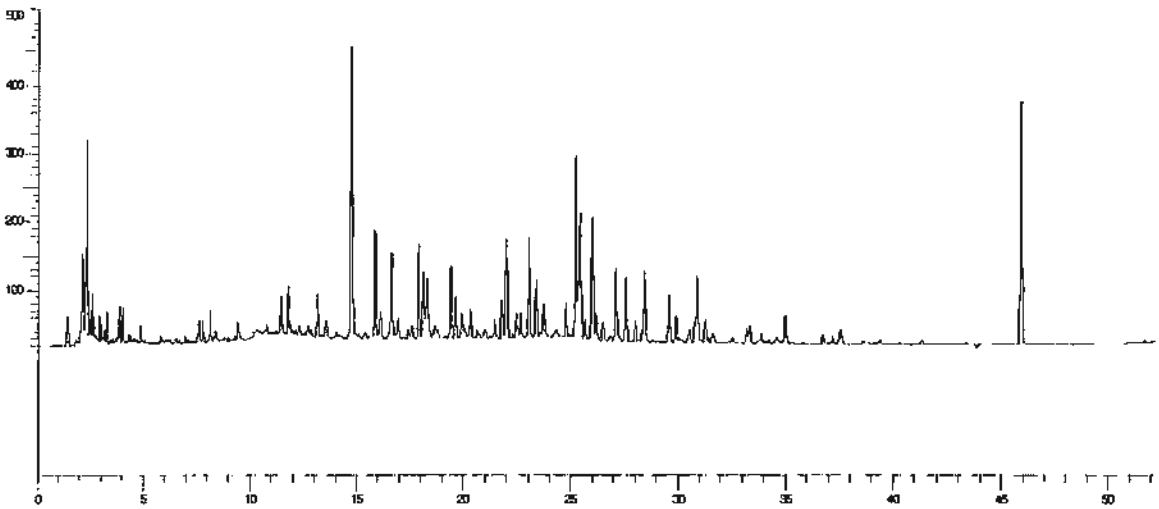
Figure XVI

GC-ECD Analysis of "SG1" Fractions (i.e. PCBs)

Site # 2



Field Blank SPMD

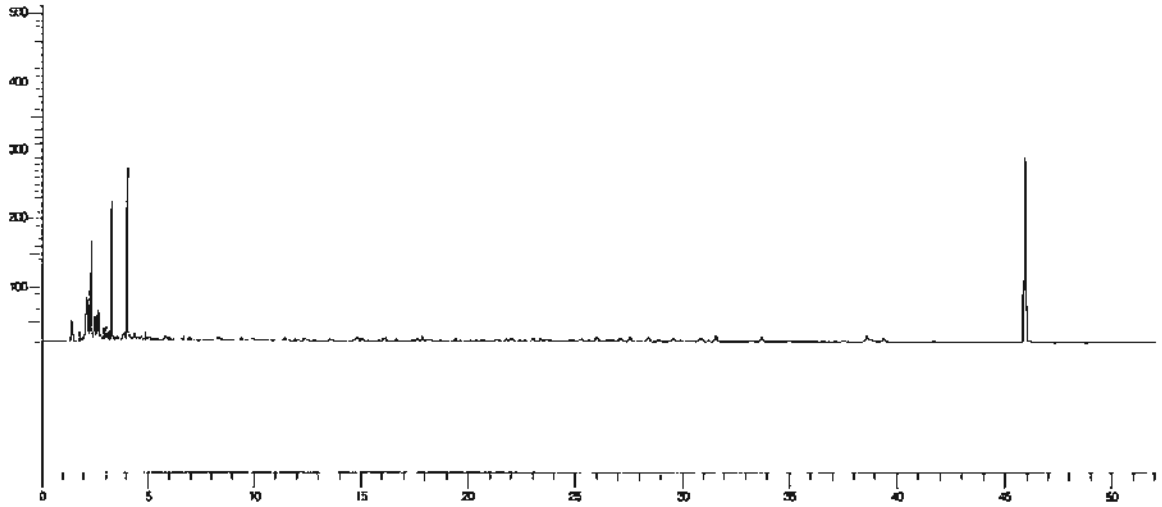


Canister # 2 SPMD Sample

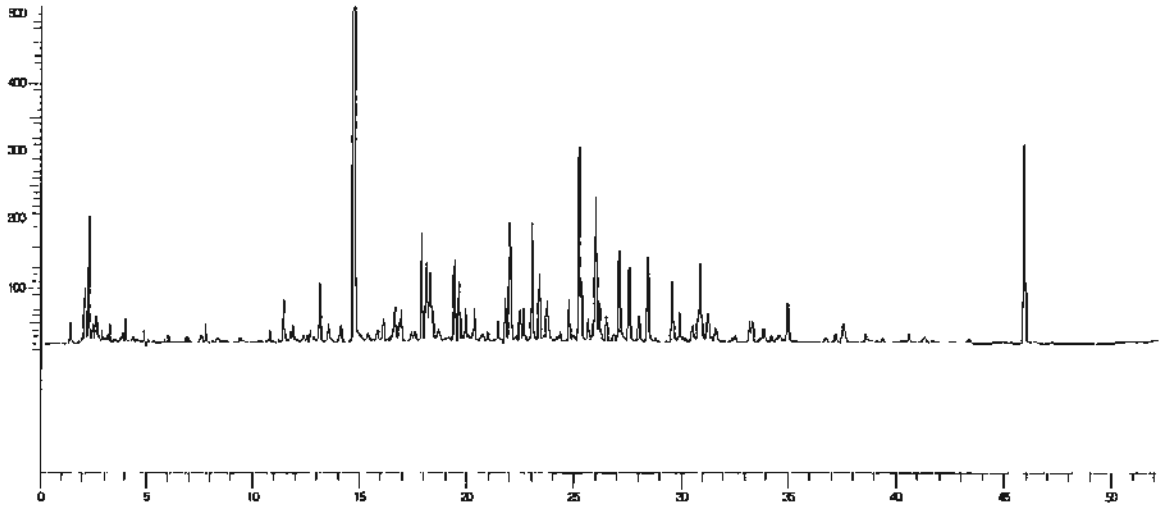
Figure XVII

GC-ECD Analysis of "SG1" Fractions (i.e. PCBs)

Site # 3



Field Blank SPMD

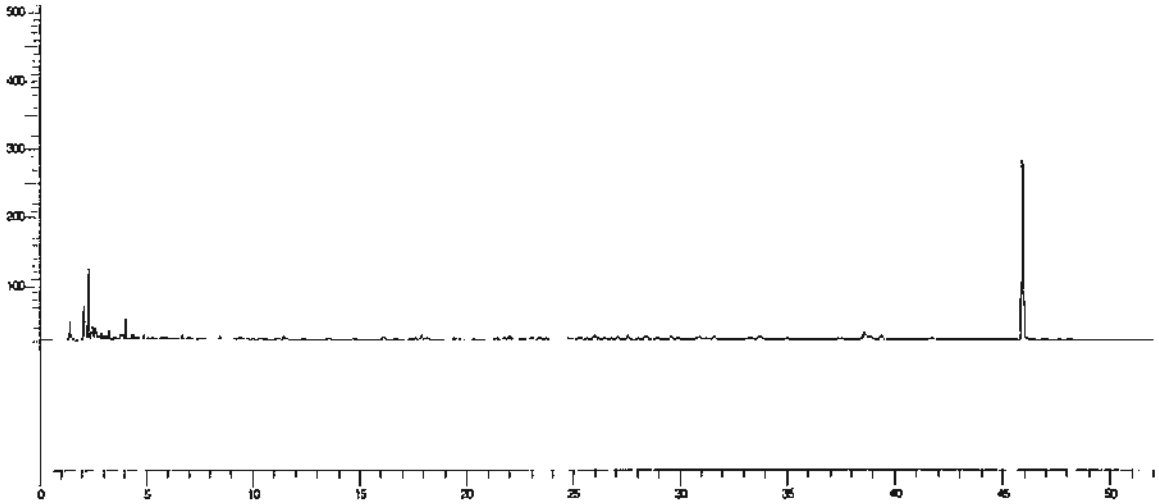


Canister # 2 SPMD Sample

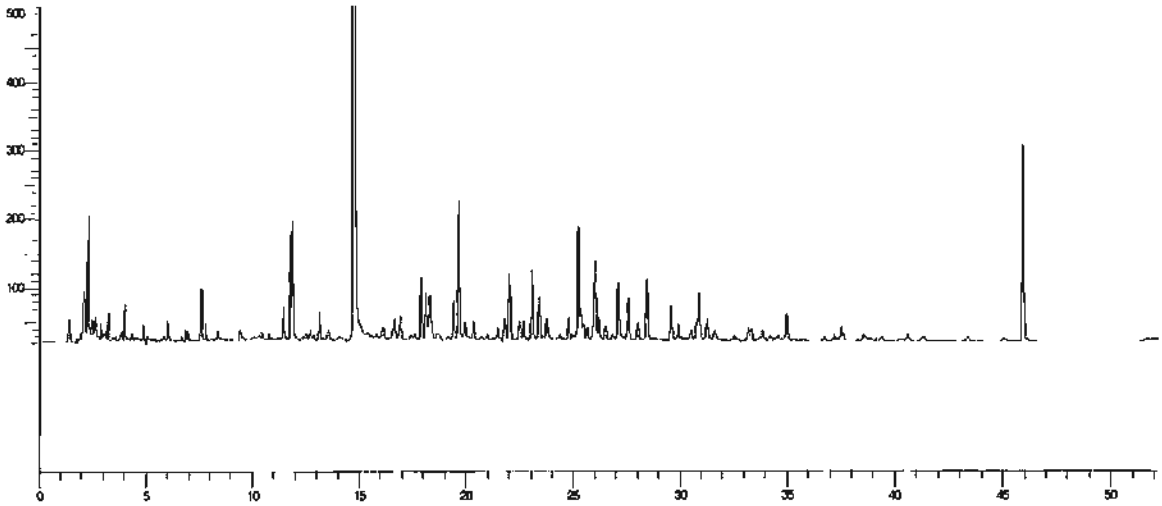
Figure XVIII

GC-ECD Analysis of "SG1" Fractions (i.e. PCBs)

Site # 4



Field Blank SPMD

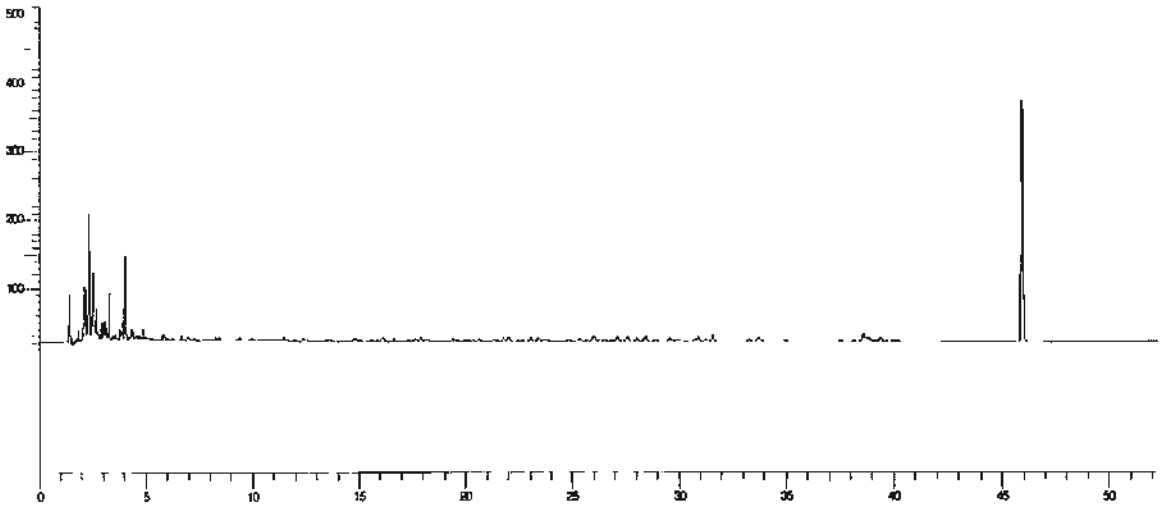


Canister # 2 SPMD Sample

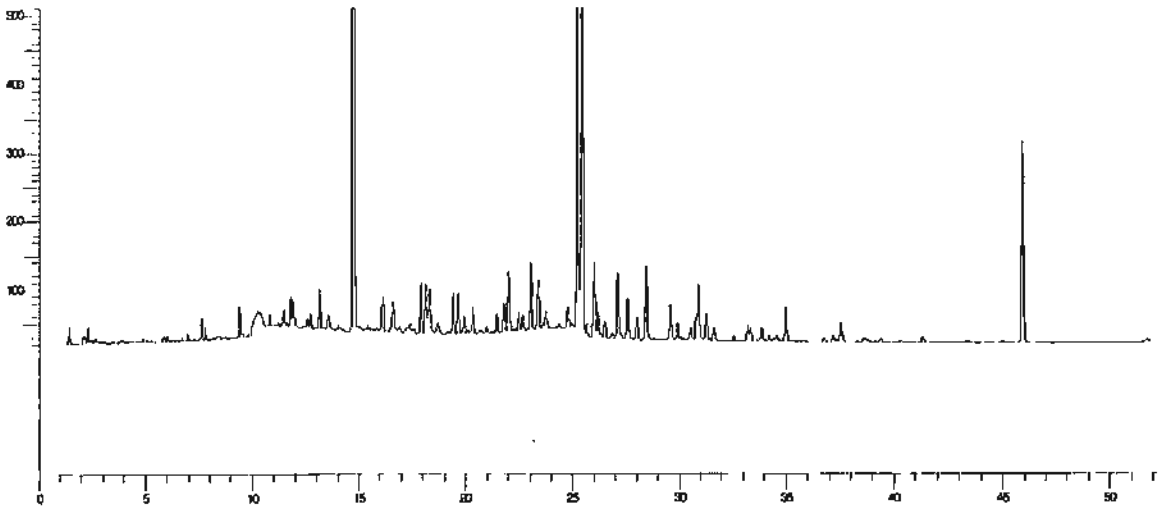
Figure XIX

GC-ECD Analysis of "SG1" Fractions (i.e. PCBs)

Site # 6



Field Blank SPMD

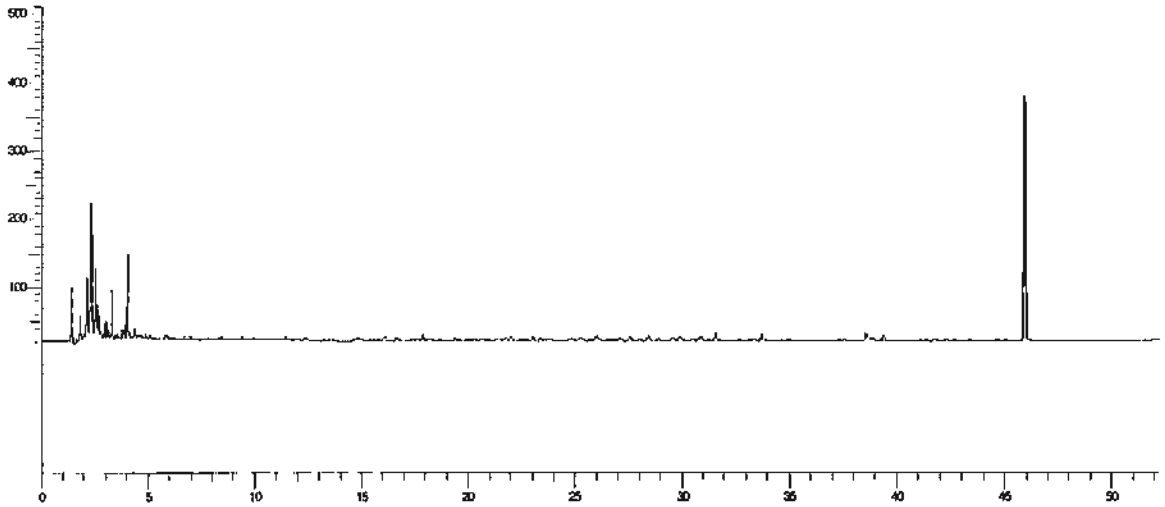


Canister # 2 SPMD Sample

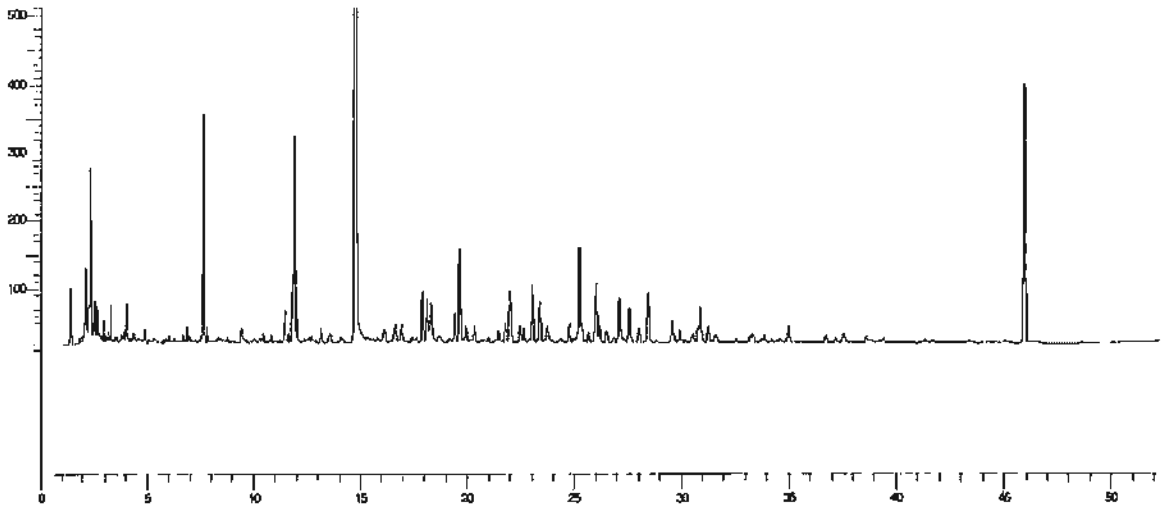
FigureXX

GC-ECD Analysis of "SG1" Fractions (i.e. PCBs)

Site # 7



Field Blank SPMD

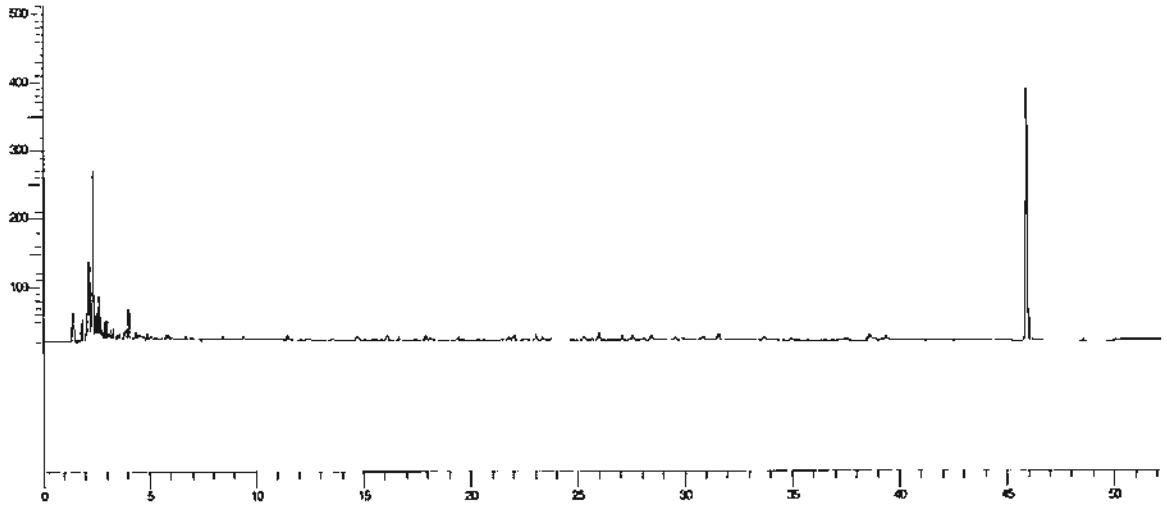


Canister # 2 SPMD Sample

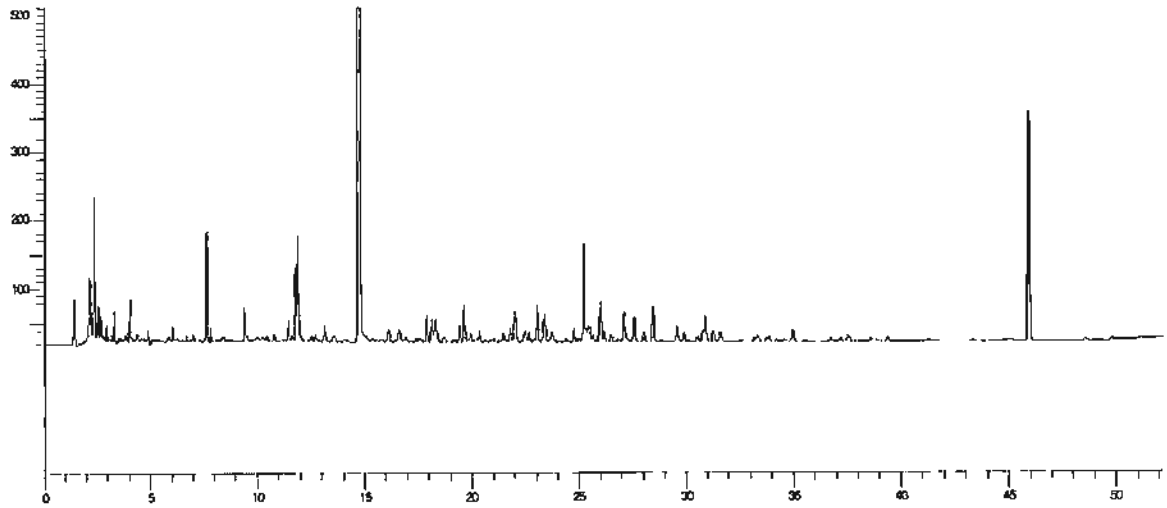
Figure XXI

GC-ECD Analysis of "SG1" Fractions (i.e. PCBs)

Site # 8



Field Blank SPMD



Canister # 2 SPMD Sample