ASSESSMENT OF ORGANIC CONTAMINANTS IN INTEGRATIVE SAMPLERS FROM CHESAPEAKE BAY TRIBUTARIES

By

David A. Alvarez
Walter L. Cranor
James N. Huckins
Randal C. Clark
And
Stephanie D. Perkins

USGS/Columbia Environmental Research Center
4200 New Haven Road
Columbia, MO 65201

Prepared For:

Fred Pinkney
Environmental Contaminants Specialists
U.S. Fish and Wildlife Service
Annapolis, MD 21401

Final Report

March 1, 2004

Prepared by:

_____

David Alvarez
Research Chemist

Prepared by:

_____

Walter Cranor
Chemist

Reviewed by:

_____

Thomas May
Research Chemist

Reviewed by:

_____

Paul Heine
CERC Quality Assurance Officer

Reviewed by:

_____

William Brumbaugh
Research Chemist

Approved by:

_____

Carl Orazio, Chief
Environmental Chemistry Branch

Approved by:

_____

Michael Mac, Center Director
Columbia Environmental Research Center

Table of Contents

EXECUTIVE SUMMARY

This work was conducted as the final phase of a three year collaborative effort between the U.S. Geological Survey's Columbia Environmental Research Center (CERC) and the U.S. Fish and Wildlife Service to provide baseline knowledge on the presence of selected chemicals in several rivers and their tributaries in the Chesapeake Bay region. SPMDs and POCIS were successfully deployed at 5 sites for 40 to 42 days.

SPMD samples from all five study sites had measurable levels of a wide variety of organochlorine (OC) pesticides. Elk River and Buck Creek showed the highest levels of sequestered OC-pesticide contaminants with totals at ~ 300 and ~250 total ng per SPMD. Sequestered levels of OC-pesticide contaminants from the remaining three sites were similar to each other and ranged from 116 to 126 total ng per SPMD. Specific contaminants which were observed at all five sites included the chlordanes, DDD, dieldrin, the nonachlors, dacthal, PCA, and the current use pesticides acetochlor and chlorpyrifos. SPMD samples from all five study sites also had measurable levels of PAHs. Only Buck Creek showed elevated levels of sequestered PAH contaminants with ~ 1000 to 13000 pg/L of fluoranthene, pyrene, and chrysene. The ubiquitous PAHs fluoranthene and pyrene were observed at low levels (~ 400 to 900 pg/L) at each site.

Only the POCIS samples from Station 3 of the Northeast River had measurable levels of the targeted hormone 17β-estradiol at ~ 4 ng/L. No other targeted hormones were detected in any of the POCIS samples from the study sites. Various tetracycline antibiotics were identified in POCIS extracts from three of the sites. Chlortetracycline was isolated in samples from Station 5 of the Northeast River and oxytetracycline was measured at Station 3 of the Northeast River. POCIS samples from Buck Creek contained all three antibiotics, ocytetracycline, tetracycline, and chlortetracycline.

Elucidation of the potential biological effects from exposure to complex mixtures of chemicals requires further research. The water concentrations of select contaminants observed in this study would appear to be of some concern. This would be especially true for Elk River and Buck Creek and to a lesser extent the remaining three sites. Since information describing the location of the sites was not provided, it is impossible for CERC scientists to make any conclusions on the potential sources of the identified contaminants.

INTRODUCTION

Input of bioconcentratable toxic organic contaminants such as organochlorine pesticides (OCs), polychlorinated biphenyls (PCBs), etc., are of continuing concern. Also, more polar organic chemicals such as hormones and antibiotics, widely used in concentrated animal feeding operations (CAFO) animal husbandry, are increasingly being recognized as emerging contaminants of concern (1,2,3). A majority of these "emerging contaminants" do not bioconcentrate and in fact have historically been viewed as being benign (e.g. antibiotics).

Assessing the potential detrimental impacts of the complex mixture of contaminants present in aquatic systems requires a holistic approach. Unfortunately, nearly all currently employed contaminant assessment approaches are based on single point in time sampling techniques. Scientists at the USGS's Columbia Environmental Research Center (CERC) have an ongoing research program designed to develop a holistic assessment approach for addressing the presence and potential toxicological consequences of organism exposure to a wide variety of environmental contaminants.

CERC scientists have developed a semipermeable membrane device (SPMD) for passive integrative monitoring of aquatic contaminants. (4,5,6,7,8) The SPMD consists of layflat polyethylene (PE) tubing containing a thin film of a high molecular weight ($\geq$ 600 Da) neutral lipid such as triolein. Other sequestration phases such as high molecular weight silicone fluids, adsorbents, etc., may also be used. The polymeric membrane used in the SPMD sampler functions by allowing the readily bioavailable contaminant molecules to pass through transient membrane cavities approaching 10 Δ in cross sectional diameter. Transfer through these polymeric cavities appears to be very similar to the transport of contaminants through biomembranes (9). Phenomenologically, the SPMD appears to mimic key aspects of uptake of dissolved chemicals by aquatic organisms. Uptake generally involves active transport to a biomembrane surface, diffusion through the exterior mucosal layer and the biomembrane, and in the case of bioconcentratable contaminants, export away from the membrane's inner surface to lipid containing tissues. Although contaminant uptake is complex, the process can be simplified to its passive elements which include diffusion of organic chemicals through thin liquid phase layers, then the nonpolar regions of the biomembranes and finally into the organism's lipid pool. The SPMD has been employed as a passive integrative sampler (5) and appears to simulate these key portions of uptake of chemicals by a broad array of species.

By using a combination of integrative samplers developed at CERC, a more complete assessment of waterborne anthropogenic contaminants is possible. Of particular concern are the more water-soluble chemicals and current use pesticides for which no time weighted assessment technique is widely available. Scientists at CERC have recently developed an integrative sampler for polar organic compounds, the polar organic chemical sampler or POCIS (10), which functions to address the more polar waterborne contaminants.

During 2003, the third year of the current project, scientists at CERC continued in joint research efforts with U.S Fish and Wildlife scientists to assess the potential impacts of anthropogenic contaminants potentially impacting selected aquatic systems in the Chesapeake Bay region. The Delmarva Peninsula, which consists of eastern Maryland, most of Delaware and the part of Virginia east of Chesapeake Bay, is one of the largest poultry CAFO areas in the United States, producing more than 600 million chickens worth in excess of 2 billion dollars annually (USDA, 1992). Swine operations and to a lesser extent dairy farms, are also present in this heavily agricultural area. In addition to the agricultural use of the peninsula, six national wildlife refuges, a national seashore, significant breeding sites for various duck species, rookeries for herons, and bald eagle nesting sites are located there.

Presented herein are the results of the analyses of the SPMD and POCIS integrative samplers for a broad spectrum of organic contaminants.

EXPERIMENTAL

Materials and Reagents: Analytical standards of all targeted analytes (Table I), were obtained from AccuStandard Inc., New Haven, CT, ChemService Inc., West Chester, PA, Crescent Chemical, Islandia, NY, or Sigma Aldrich, St. Louis, MO. All laboratory chemicals were ACS Reagent grade and organic solvents were Optima grade from Fisher Scientific Co., Pittsburgh, PA. Florisil® (60-100 mesh) is obtained from Fisher Scientific Company, Pittsburgh, PA. The Florisil® was first heated at 475°C for 8 hours, then blended with 5 % (W:W) of deionized water and equilibrated at 130°C for 48 hours. The Florisil® was subsequently stored at room temperature over P_2O_5 as a desiccant. Silica gel (SG-60, 70-230 mesh) was obtained from Thomas Scientific, Swedesboro, NJ. The silica gel was first washed with 40:60 methyl tert-butyl ether:hexane (V:V) followed by 100% hexane. The silica gel was then activated at 130°C for a minimum of 72 hours before use and stored at room temperature over P_2O_5 as a desiccant. Phosphoric acid/silica gel (PASG) was made by combining ACS reagent grade phosphoric acid and the silica gel described above in a 40:60 (W:W) ratio, blending to achieve homogeneity, and subsequently storing at room temperature over P_2O_5 as a desiccant. Potassium silicate (KS, a sorbent developed and used at CERC) was made by combining a methanolic solution of ACS reagent grade potassium hydroxide with the silica gel described above in the ratio of 250 mL of methanol to 56 grams of potassium hydroxide to 100 grams of silica gel. After mixing for 1.5 hours and solvent removal, the potassium silicate was activated at 130°C for 48 hours before use and subsequently stored at room temperature over P_2O_5 as a desiccant. Low density polyethylene (PE) layflat tubing was purchased from Environmental Sampling Technologies, 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. Polyethersulfone membrane disks (47 mm diameter, 0.1 µm d_p) were purchased from Pall Gelman Sciences, Inc. (Ann Arbor, MI). Isolute® ENV+ solid resin was purchased from Jones Chromatography (Lakewood, CA). Ambersorb® 1500 was obtained from Rohm and Haas (Philadelphia, PA). S-X3 Bio-Beads (200-400 mesh) were purchased from Bio-Rad Laboratories (Hercules, CA). The stainless steel materials used in construction of POCIS

were purchased from McMaster-Carr (Elmhurst, IL). The Oasis® HLB SPE cartridges (200 mg of sorbent, 6 mL capacity) were obtained from Waters Corp., Milford, MA. Polypropylene centrifuge tubes (50mL, 30 x 115 mm style) were purchased from Becton Dickinson Labware, Franklin Lakes, NJ.

Instrumentation: A Perkin-Elmer Series 410 HPLC (Perkin-Elmer, Inc., Norwalk, CN), was employed as the solvent delivery system for size exclusion chromatography (SEC) cleanup. This HPLC unit was equipped with a ThermoFinnigan AS3000 autosampler (ThermoFinnigan, San Jose, CA). The SEC column was a 300-mm X 21.2-mm i.d. (10-µm d_p, 100 Δ pore size) Phenogel column (Phenomenex, Inc., Torrance, CA), equipped with a 50-mm X 7.5-mm i.d. Phenogel guard column. The SEC system was completed with a D-Star DFW-20 fixed wavelength ultra violet (UV) detector (D-Star Instruments, Manassas, VA) and an Isco Foxy 200 fraction collector (Isco, Inc., Lincoln, NE).

Gas chromatographic analyses for PAHs (Table I) were conducted on an Agilent 6890 GC equipped with an Agilent 7683 autosampler (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 with the following temperature program: injection at 50 °C, held for 2 min, then ramped at 25 °C/min to 130 °C, held for 1 min, followed by 6 °C/min ramp to 310 °C and held at 310 °C for 5 min. Detection was performed with a 5973 mass selective detector (Agilent Technologies, Inc., Palo Alto, CA) in the selected ion mode (SIM). 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 internal calibration. Calibration standard concentrations were 0.02, 0.05, 0.10, 0.50, 1.0, 2.0, and 4.0 µg/mL for each of the analytes with the internal standards, 2-methylnaphthalene-d_{10} and benzo[e]pyrene-d_{12}, maintained at 0.250 µg/mL.

Gas chromatographic analyses, for all analytes excluding PAHs, hormones and antibiotics (Table I), were conducted using Hewlett Packard 5890 series gas chromatographs (GC) equipped with a Hewlett Packard 7673A autosamplers (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 were performed using DB-35MS (30 m x 0.25 mm i.d. x 0.25 µm film thickness) capillary columns (J&W Scientific, Folsom, CA) with the following temperature program: injection at 90 ^{o}C; then ramped at 15 ^{o}C/min to 165 ^{o}C; followed by 2.5 ^{o}C/min ramp to 250 ^{o}C; and finally ramped at 10 ^{o}C/min to 320 ^{o}C. The electron capture detector (ECD, Hewlett Packard, Inc., Palo Alto, CA) was maintained at 330 ^{o}C. Quantitation of organochlorine pesticides (OCs) was accomplished using a six-point curve with PCB congener I-30 as retention time reference compound and PCB congener I-207 as the instrumental internal standard (IIS). The levels of the OC standards spanned an 80-fold range of concentration for each compound. Quantitation of total PCBs 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 PCB congener I-30 as retention time reference

compound and PCB congener I-207 as IIS. The levels of the PCB standards spanned a 20-fold concentration range from 50 to1,000 total ng/mL.

The HPLC system used in the analysis of the hormones and antibiotics (Table I) consisted of a Hewlett Packard 1090 Series II Liquid Chromatograph with a diode array detector (Hewlett Packard, Palo Alto, CA) with the ChemStation for LC software package revision A.08.03 (Agilent Technologies, Inc., Palo Alto, CA). A Supelco (Supelco, Bellefonte, PA) Discovery® C_8 analytical column (150 x 4.6 mm, 5 µm d_p), a Phenomenex Security Guard C_8 cartridge was used for both the hormone and antibiotics analysis. A mobile phase of 65:35 water:acetonitrile with a flow rate of 1 mL/min were used during hormone analysis. Antibiotic analysis utilized a mobile phase of 25 mM KH_2PO_4 (pH 3) buffer:acetonitrile 80:20 with a flow rate of 1 mL/min. Detection of the hormones and antibiotics occurred at 281 and 365 nm respectively. Peak purity/confirmation was performed by observing the UV spectra profiles of the analytes. Multi-point calibration curves (10, 25, 50, 100, 200, 300, 400, and 500 ng of each hormone and each antibiotic injected on column) were run on a daily basis. All samples and standards were dissolved in the appropriate mobile phase prior to analysis. Analytical standards for the tetracycline antibiotics were kept cool, protected from light and made fresh daily once placed in mobile phase due to potential degradation of the analytes.

Analytical Standard Solutions: When available, certified stock solutions were purchased directly from the supplier at appropriate concentration levels. Primary stock solutions of analytical standards were made by serial dilution of the commercially available solutions or by accurately weighing portions of the neat materials (weights corrected for assayed purity) and diluting with an appropriate volume of suitable solvent to make final concentrations at 500 ng/mL to 200 µg/mL. Solutions were protected from light, stored at either -20°C or room temperature as appropriate for the individual chemical, and prepared fresh every six months or more often as necessary. Working solutions of mixed standards were prepared by transferring predetermined amounts of each stock solution into a volumetric flask and making to volume. These solutions were made fresh as needed.

Sample Storage and Custody: The SPMDs and POCIS for this study were prepared at CERC between April 16 and April 18 of 2003. These were stored in a laboratory freezer at -15 °C from fabrication until time of their shipment to the USF&WS Chesapeake Bay Field Office on Monday, April 21 of 2003. Following field deployment and receipt of the samples at CERC on Thursday, June 12, 2003, the samples were stored, as received, in a laboratory freezer at -15 °C until needed for processing.

SPMD Preparation, Deployment, Processing, and Analyses for PAHs, PCBs and OC-Pesticides

SPMD Preparation: The SPMDs for the project were constructed at CERC using 86 cm lengths of LDPE tubing with 1.0 mL (0.91 g) of triolein (Nu-Check Prep Inc. Elysian, MN, this 99% triolein, Lot T-235-05-L was further purified at CERC (11) on 11-19-01)

being added to each SPMD. The active surface area of the finished device was ~ 440 cm^2. Each of the four deployed SPMDs (for each site) and the two SPMDs used as Field Blanks (for each site) were spiked with 4.0 µg of Phenanthrene-d_{10} (permeability reference compound [PRC]). Four SPMDs were loaded onto deployment devices (for each of seven deployment sites). These were placed into labeled, solvent rinsed cans which were then flushed with argon and sealed. The Field Blank SPMDs were placed into labeled, solvent rinsed pint cans (two per can). These cans were also flushed with argon and sealed. All cans were then shipped to the USF&WS Chesapeake Bay Field Office for deployment by US FWS personnel.

SPMD Deployment: Samplers at study Sites # 3 and # 7 were lost during deployment. The deployment dates and site descriptions for the remaining five study sites were identified on the USF&WS "Chain of Custody Record" as follows;

Station No.	Deployment	Retrieval	Station Location
Site # 1	4/28/03	6/9/03	"ELR2"- Elk River # 2
Site # 2	4/28/03	6/9/03	"BOR2"-Bohemia River # 2
Site # 4	4/28/03	6/9/03	"NER5"-Northeast River # 5
Site # 5	4/28/03	6/9/03	"NER3"-Northeast River # 3
Site # 6	4/29/03	6/8/03	"SER5"- Buck Creek

SPMD Processing and Residue Enrichment: There was one canister containing four SPMDs at each deployment site. During processing, two SPMDs from each canister were combined to give two 2-SPMD composites. Compositing extracts was performed because it was anticipated that sequestered contaminant concentrations would be too low to be detected in a single SPMD extract. Sample processing was similar to procedures previously described (7), with specific details noted in the following sections

SPMD Cleanup: SPMDs as received from field exposures were subjected to cleanup before dialysis. This cleanup was applied to all SPMDs received from the field as well as to all QA/QC SPMDs generated in conjunction with the analysis sets. The steps associated with the cleanup were applied to each SPMD individually and sequentially, and were as follows. The sealed metal cans containing deployment canisters holding the field deployed SPMDs were opened and the SPMDs were removed from the deployment canisters. The SPMDs were then rinsed by immersion into 100 mL of hexane. Then, the hexane was discarded. The SPMDs were placed individually into a large flat stainless steel pan and washed using running tap water and a clean brush to remove all remaining surface adhering material. 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. SPMDs were air dried by laying the SPMD on a piece of solvent-rinsed aluminum foil. (Note, exposure time was minimized to prevent airborne chemical uptake by the SPMDs)

SPMD Dialysis: 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 165 mL of hexane in each jar and were dialyzed individually at 18 ^{o}C for 18 hours. The hexane was removed and transferred into an evaporation flask. A second volume of 165 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 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 rotoevaporation system, and quantitatively transferred through a pre-rinsed glass fiber filter into appropriately labeled test tubes.

Post-Dialysis Sample Splitting: Because different enrichment techniques were required for the targeted environmental contaminants, the samples were split into two equal portions prior to further fractionation and enrichment. These were identified as the "PAH" fractions and the "OC" fractions. After splitting, the two fractions were each reduced to a volume of ~ 1 mL using high purity N_2 blow-down. The procedures employed to enrich the "OC" and "PAH" fractions are presented separately as follows:

Processing of "PAH" Fractions

The size exclusion chromatography (SEC) system previously described was employed for the initial cleanup step.

SEC Calibration: 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 the calibration solution, in sequence of elution, were diethylhexylphthalate (DEHP; a model compound 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 interfering substance encountered frequently in environmental samples). Elution of these components was monitored at 254 nm using the D-Star DFW-20 fixed wavelength UV detector.

SEC Processing: SEC cleanup 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. The fractions collected were amended with ~ 2 mL of isooctane,

reduced to a volume of ~ 1 mL on a rotoevaporation system, and quantitatively transferred with hexane into appropriately labeled test tubes.

Column Cleanup: The post-SEC "PAH" fractions were then processed using open column chromatography. The "PAH" fractions, at ~ 0.5 mL in hexane, were treated using a tri-adsorbent column consisting of from 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) MTBE:Hexane. This procedure resulted in a solution suitable for GC analysis of PAH residues. The fractions collected were amended with ~2 mL of isooctane, reduced to a volume of ~ 0.5 mL on a rotoevaporation system, and quantitatively transferred with hexane into labeled GC vials. Following addition of an appropriate amount of IIS, sample volumes were adjusted to 1.0 mL. These samples were then ready for GC-MSD analysis for PAHs. Gas chromatographic analyses were conducted using the systems previously described.

Processing of "OC" Fractions

SEC of "OC" Fractions: This procedure was as previously described for the processing of "PAH" fractions with the following modification. 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. 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.

Preliminary Column Cleanup of "OC" Fractions: The post-SEC "OC" fractions were then processed using open column chromatography. The "OC" fractions, at 1.0 mL in hexane, were applied to Florisil columns (5 g) and subsequently eluted with 60 mL of 75:25 (V:V) MTBE:Hexane giving a fraction identified as FL1. Each column was then eluted with a 70 mL portion of acetone giving a fraction identified as FL2. Each fraction collected was amended with ~ 2 mL of isooctane, reduced to a volume of ~ 1 mL on a rotoevaporation system, and quantitatively transferred with hexane into an appropriately labeled test tube.

Secondary Column Cleanup of "FL1" and "FL2" Fractions: Both type of "OC" fractions (i.e. FL1 & FL2) were processed using open column chromatography. These (FL1 And FL2), at ~1 mL in isooctane, were applied to silica gel columns (5 g). Two fractions were eluted; fraction SG1 (46 mL of hexane) and SG2 (75 mL of 40:60 (V:V) MTBE:Hexane). The SG1 and SG2 fractions from the FL1 fractions were both retained and were identified as "SG1" and "SG2" respectively. The SG1 fractions from the FL2 fractions were discarded. The SG2 fractions from the FL2 samples were retained and identified as "FL2" All fractions were then reduced to a volume of ~ 0.5 mL and quantitatively transferred with hexane into labeled GC vials. Samples were amended with appropriate IIS and the volumes adjusted to 1.0 mL using hexane and high purity N_2 blow-down. These samples, identified as "SG1" "SG2" and "FL2," were then ready for GC-ECD analysis for PCBs, OC-pesticides, and the highly polar targeted analytes (i.e.

Alochlor, Acetochlor, and Metolachlor) respectively. Gas chromatographic analyses were conducted using the systems previously described.

POCIS Analysis for Hormones and Antibiotics

POCIS Description: There were two canisters containing POCIS at each deployment site. In each canister, there were two POCIS constructed using the sorbent admixture of 80:20 (w/w) Isolute ENV+:S-X3 dispersed Ambersorb 1500 for sampling the hormones and two POCIS constructed using the Oasis HLB sorbent for sampling the antibiotics. During processing, the two POCIS with similar sorbents from each canister were combined to give a sample equivalent to two devices. Compositing extracts is performed in cases where it is suspected that contaminant concentrations may be too low to be detected in a single extract. This task resulted in replicate two-POCIS composites from each site.

POCIS Cleaning and Extraction (i.e., Recovery of Analytes) for Hormones: Each POCIS was removed from its deployment canister and rinsed with water to remove any debris. The contents of the POCIS were then transferred with methanol into 1 cm (i.d.) glass chromatography columns fitted with a glass wool plug. Solvent extraction (elution) of sequestered analytes was achieved with the addition of 50 mL of 1:1:8 (V:V:V) MeOH:toluene:DCM. The collected eluate was evaporated by rotary evaporation to 2-3 mL, 20 mL of MeOH was added to the flask and evaporated again to approximately 1 mL. The additional MeOH was necessary to form an azeotrope to facilitate the removal of the toluene from the sample. The sample was then quantitatively transferred through a pre-rinsed glass fiber filter into appropriately labeled test tubes with acetone and subsequently evaporated under high purity N_2 to 0.5 mL.

Processing of Extracted POCIS Hormone Fractions: Each filtered POCIS extract designated for hormone analysis, was divided between two vials for injection on SEC using the 30% window as previously described. The post-SEC samples were evaporated and transferred into GC vials with acetone, taken to near dryness under high purity N_2, and reconstituted with 0.5 mL of 50:50 Hexane:dichloromethane. The samples were applied to KS columns for further cleanup and fractionation. Gravity flow glass chromatography columns (1 cm i.d.) containing 3 g of KS were rinsed with 25 mL methanol followed by 25 mL 75% dichloromethane/Hexane prior to sample application. The sample was applied in ~ 0.5 mL dichloromethane to the KS with 3 rinses of 75% dichloromethane /Hexane. A total of 25 mL of 75% dichloromethane /Hexane was used to wash the column following sample application. Analyte elution was accomplished using 20 mL of 2:49:49 (V:V:V) methanol: dichloromethane:hexane. The hormone containing fractions from KS were evaporated, transferred into vials, taken to dryness under high purity N_2, redissolved in 0.5 mL 1:1 water:acetonitrile and analyzed by HPLC.

POCIS Cleaning and Extraction (i.e., Recovery of Analytes) for Antibiotics: The POCIS were cleaned and the sorbent was transferred into columns as described previously. Elution of the antibiotics occurred by the addition of 40 mL of methanol to the sorbent.

The eluate was evaporated by rotary evaporation to 1-2 mL and quantitatively transferred through a pre-rinsed glass fiber filter into appropriately labeled test tubes with 3 rinses of methanol. The filtered samples were then evaporated under high purity N_2 to 0.5 mL.

Processing of Extracted POCIS Antibiotic Fractions: The filtered POCIS sample extracts to be analyzed for antibiotics, underwent subsequent cleanup by application to Oasis SPE cartridges. The extracts at 0.5 mL of methanol were diluted to 10 mL with McIlvaine-EDTA buffer solution. The Oasis cartridge was conditioned prior to sample application with successive rinses of 3 mL methanol, 2 mL RO water, and 2 mL McIlvaine-EDTA buffer solution. The sample was then applied to the cartridge followed by washing of the cartridge with 2 mL of 5% methanol/water. The tetracyclines were eluted with the addition of 3 mL methanol. The post-Oasis samples were taken to dryness and then re-dissolved in 1.0 mL of 25 mM KH_2PO_4 buffer (pH 3). The samples were filtered into vials and analyzed by HPLC.

RESULTS AND DISCUSSIONS

Quality Control: Field blank SPMDs and POCIS accompanied the SPMDs and POCIS during deployment, retrieval, and transportation to CERC. These field blanks were processed and analyzed exactly as the deployed samples. Analysis of the field blank samples gave no coincident GC or HPLC peaks at levels significantly higher than those associated with the laboratory control SPMDs and POCIS and indicated a successful deployment and retrieval. A series of control SPMD and POCIS samples were processed and analyzed exactly as the study samples. The method detection limit (MDL) and method quantitation limit (MQL) for analysis of the study specific SPMD and POCIS samples were determined for each analyte by measuring the values of coincident GC-MSD, GC-ECD, and HPLC peaks for each compound in these control samples. The MDL was defined as the mean plus three standard deviations of values so determined (12). The MQL was defined as the mean plus 10 standard deviations of values so determined (12). For individual analytes having no coincident chromatographic peak, an assumed value equal to the low sample reject for the method was used to calculate the mean. In the cases where the MQLs were below the level of the calibration curve employed, the MQLs were set at the value of the lowest level of the calibration curve in quantifying the analyte levels. The MDLs and MQLs for analysis of the study samples for all targeted analytes in SPMDs and POCIS are presented in Table II.

QC checks were employed to demonstrate an acceptable outcome of sample analyses. These checks included; 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 about 48,000 disintegrations per minute) and measuring recovery through the system ; 2) evaluation of the combined dialysis and SEC process for SPMDs. This ^{14}C-SPMD spike was prepared by fortifying a blank SPMD with approximately 161,000 disintegrations per minute of ^{14}C-Dibenz[a,h]anthracene and measuring recovery through the combined dialysis and SEC processing steps; and 3) monitoring the recoveries of all analytes of interest through the entire extraction, dialysis, SEC, chromatographic fractionation and enrichment

procedures by using spiked control matrix blanks. These matrix spikes were prepared by fortifying an individual blank matrix (i.e., SPMDs and POCIS) with targeted analytes (Table I). The spiking levels were intended to approximate levels near the method quantitation limit (MQL) and were intended to be representative of levels found in environmental samples. Recovery of ^{14}C-TCB through the SEC system averaged 96.9% (n=2). For the ^{14}C-SPMD spike, post-SEC recovery was 89.9 %. For the SPMD spike (Table III), recoveries of PAHs and OCs were consistent with recovery levels reported in conjunction with analytical method validation conducted concurrently with the first years work on this joint USF&WS / USGS project. Recovery of total PCBs was 74.3%. Recovery of targeted analytes from the POCIS were unexpectedly lower than studies with 36 to 71% recovered. It is unknown what caused the loss in recovery. Values from the analyses of SPMD and POCIS extracts are given in Tables IV through IX.

Derivation of Water Concentrations from SPMD Residues (Modeling): SPMD uptake kinetic data are required to accurately estimate aquatic concentrations of environmental contaminants. Using models previously developed (4), data from the analysis of the PRC levels (Table IX), and data from uptake kinetic studies, the aquatic concentrations of selected contaminants present in SPMDs exposed during this study were estimated for the 30-day exposure (Table X).

An example of the overall estimation procedure is as follows. The analyte sampling rate (R_{sw}) is determined from laboratory exposures conducted under about the same conditions (i.e., water temperature and exposure duration) as the field study. The linear SPMD uptake of OCs from water was described by Huckins, et al. (4) as follows:

$$C_L = C_W k_o K_{mW} A t / V_L \quad (1)$$

substituting R_{sw} for $k_o K_{mW} A$ in equation 2 gives

$$C_L = C_W R_{sw} t / V_L \quad (2)$$

where C_L is the concentration of the analyte in the lipid, C_W is the concentration of the analyte in the water, t is the exposure time in days, and V_L is the volume of the lipid. Rearranging equation 3 results in

$$C_W = C_L V_L / R_{sw} t \quad (3)$$

Because the analytes present in the membrane were also recovered during the dialysis procedure, equation 4 can be rewritten as

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

where C_{SPMD} is the concentration of the individual analyte in the SPMD and M_{SPMD} is the mass of the SPMD. In the present case we use the uptake rate constant (k_{uw}) defined as L/dg (Liters per day per gram) of SPMD (membrane + lipid).

$$C_W = C_{SPMD} / (R_{sw} / M_{SPMD})\, t \quad (5)$$

$$C_W = C_{SPMD} / k_{uw}\ t \quad (6)$$

SPMD sampling rates can change due to changes in temperature, flow velocity of the surrounding water, 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 exposure R_{SW} values. PRCs are noninterfering (analytically) compounds, such as perdeuterated (all hydrogen atom replaced by deuterium atoms) PAHs with moderate to fairly high fugacity (escaping tendency), added to the SPMD's triolein prior to deployment (4). Measuring the PRC loss over the exposure period provides in situ k_e values which when compared to the calibration k_e values can serve as an indicator to differences in the environmental conditions. If large differences exist between the k_e calibration and exposure values, adjustments can be made to the laboratory calibration data to better reflect actual sampling rates. The k_{eprc} values are derived as follows

$$C_{SPMD} = C_{SPMDo} \exp(-k_{eprc}\ t) \quad (7)$$

$$k_{eprc} = \ln(C_{SPMDo} / C_{SPMD}) / t \quad (8)$$

where C_{SPMDo} is the initial 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

$$k_{ec} = R_s / K_{SPMD}\ V_{SPMD}\ d_{SPMD} \quad (9)$$

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

$$R_{sf} = (k_{eprc} / k_{ec})\ R_{sc} \quad (10)$$

The estimated bioavailable waterborne concentration of selected contaminants present at the sampling sites are presented in Table X. These values were generated using an average R_{sc} for a temperature of 18°C.

Derivation of Water Concentrations from POCIS Residues (Modeling): The POCIS and SPMD integrative samplers share similar functional attributes allowing models derived for the SPMD to be applied. Contaminant sampling models have been discussed in detail (13). From these models, the following equation is derived

$$C_W = C_{POCIS} / (R_s \cdot t) \quad (11)$$

where C_W is the estimated water concentration, C_{POCIS} is the total mass of the analyte in the POCIS sample extract, R_s is the sampling rate in L/d, and t is the deployment time in

days. R_s data has been determined in the laboratory for select chemicals under various flow conditions (14). Due to a lack of information on the specific conditions at each deployment site, R_s values for highly turbulent systems were used in the calculations to serve as a worst case scenario. The results are given in Table XI. The biological consequence of organism exposure to these levels of waterborne polar organic chemicals is unknown.

Observations and Findings: All study samples were processed concurrently with the above referenced quality control samples. Therefore, the results obtained from processing and analyses conducted on these samples are taken to be similar to the observed results for the quality control samples described. During the chromatographic analysis of study sample fractions, conditions were optimized to give sufficient resolution for quantitation of the targeted analytes (Table XII and Figures 1,2,3,4,5).

The results of the GC and HPLC analyses are given for all targeted analytes and are presented in Tables IV through VIII with representative chromatograms given in Figures 1, 4, 5, 6, 7, & 8. Estimated water concentrations of selected analytes are presented in Tables X and XI.

SPMD samples from all five study sites had measurable levels of a wide variety of OC pesticides (Tables IV through VIII). Site # 1 and site # 6 (Elk River and Buck Creek respectively) showed the highest levels of sequestered OC-pesticide contaminants with totals at ~ 300 and ~250 total ng per SPMD respectively. Sequestered levels of OC-pesticide contaminants from the remaining three sites were similar to each other and ranged from 116 to 126 total ng per SPMD. These values are in sharp contrast to levels of contaminants observed using SPMDs during the first year of this three year study where only a very few contaminants were observed and then only at much lower levels than reported here (15). Specific contaminants which were observed at all five sites at levels well above the MQLs were 1) Chlordanes, 2) DDD, 3) Dieldrin, 4) Nonachlors, 5) Dacthal, 6) PCA, and the current use pesticides Acetochlor and Chlorpyrifos. It should be noted that many chlorinated pesticides have been banned – some for nearly 20 years (16). The apparent longevity of these chlorinated contaminants may result in a continued reduction in habitat quality. For instance, Dieldrin, the DDT complex, and the Chlordane components along with a much larger set of diverse environmental contaminants have been reported to cause endocrine-disruption in some organisms (17).

SPMD samples from all five study sites also had measurable levels of PAHs (Tables IV through VIII). Only site # 6 (Buck Creek) showed elevated levels of sequestered PAH contaminants. The ubiquitous PAHs Fluoranthene and Pyrene were observed at low levels (~ 100 to 400 ng per SPMD) for sites # 1, # 2, # 4, and # 5. For site # 6, µg quantities of Fluoranthene, Pyrene, and Chrysene were observed with numerous PAHs present in the ~ 100 to 400 ng per SPMD range (Table VIII).

Only the POCIS samples from Site # 5 (Northeast River) had measurable levels of the targeted hormone 17β-estradiol. No other targeted hormones were detected in any of the POCIS samples from the study sites (Tables IV to VII). The concentration of 17β-

estradiol of Site # 5 water was calculated to be ~ 4 ng/L (Table XI). The hormone 17β-estradiol is readily leached from chicken litter into aquatic systems via surface run-off following initial land application (1,18,19). Hormone residues are less likely to found in areas containing aged litter. Aquatic organisms, livestock and human inputs can also add to the 17β-estradiol loading making identification of a point source difficult.

The analytical methods for these POCIS sample analyses were developed at CERC from previously reported work (20,21). Various tetracycline antibiotics were identified in POCIS extracts from three of the sites. Chlortetracycline was isolated in samples from Station 5 of the Northeast River and oxytetracycline was measured at Station 3 of the Northeast River. POCIS samples from Buck Creek contained all three antibiotics, ocytetracycline, tetracycline, and chlortetracycline.

Elucidation of the potential biological effects from exposure to complex mixtures of chemicals requires further research. The water concentrations of select contaminants (Table X) observed in this study would appear to be of some concern. This would be especially true for Site # 1 and Site # 6, Elk River and Buck Creek respectively, and to a lesser extent the remaining three sites.

SUMMARY

Scientists at the U.S. Geological Survey working with members of the U.S. Fish and Wildlife Service have entered the third year of a holistic assessment of the presence and potential impacts of anthropogenic contaminants on the water resources of the Chesapeake Bay region. Analysis of the SPMDs indicated that Buck Creek and Elk River were significantly more contaminated than the remaining sites. The hormone 17β-estradiol was only identified in POCIS samples from Station 5 of the Northeast River. Various tetracycline antibiotics were found in three of the study sites. However, information on the location of the sites was not available, therefore, any conclusions on the sources of identified chemicals can not be made.

ACKNOWLEDGEMENTS

We gratefully acknowledge the funding of the U.S. Fish and Wildlife Service. Also, the efforts of personnel involved in the collection of and shipment of study samples to CERC for processing and analysis are greatly appreciated.

LITERATURE CITED

1. Nichols, D.J.; Daniel, T.C.; Moore, P.A.; Edwards, D.R., Pote, D.H. 1997. *J. Environ. Qual.*, 26, 1002-1006.
2. Miller, C.V., Foster, G.D., Huff, T.B. Organic Compounds and Trace Elements in the Pocomoke River and Tributaries, Maryland. 1999. *U.S. Geological Survey Open-File Report 99-57, Baltimore, MD.*

3. Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., Buxton, H.T. 2002. *Environ. Sci. Technol.*, 36, 1202-1211.
4. Huckins, J.N., Manuweera, G.K., Petty, J.D., MacKay, D., Lebo, J.A. 1993. Environ. Sci. Technol., 27, 2489-2496.
5. Petty, J.D., Huckins, J.N., and Zajicek, J.L. 1993. Chemosphere, 27, 1609-1624.
6. Petty, J.D., Huckins, J.N., Orazio, C.E., Lebo, J.A., Poulton, B.C., Gale, R.W., Charbonneau, C.S., Kaiser, E.M. 1995. Environ. Sci. Technol., 29, 2561-2566.
7. Lebo, J.A., Gale, R.W., Petty, J.D., Huckins, J.N., Echols, K.R., Schroeder, D.J., Inmon, L.E. 1995. Environ. Sci. Technol., 29, 2886-2892.
8. Huckins, J.N., Tubergen, M.W., Manuweera, G.K. 1990. Chemosphere, 20, 533-553.
9. Oppenhuizen, A., Velde, E.W., Gobas, F.A.P., Leim, D.A.K., Steen, J.M.D. 1985. Chemosphere, 14, 1871-1896
10. Petty, J.D., Huckins, J.N., Alvarez, D.A. A device for the sequestration and concentration of polar organic chemicals from water. U.S. Patent Number 6,478,691, November 12, 2002.
11. Lebo, J.A., Almeida, F.V., Cranor, W.L., Petty, J.D., Huckins, J.N., Rastall, A.C., Alvarez, D.A., Mogensen, B.B., Johnson, B.T. 2004. Chemosphere, 54, 1217-1224
12. Keith, L.H. 1991 Environmental Sampling and Analysis: A Practical Guide, CRC Press, Inc.; Boca Raton, FL, pp 101-113.
13. Alvarez, D.A., Doctoral Thesis, University of Missouri-Columbia, Columbia, MO, 1999.
14. Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P., Manahan, S.E. 2004. Environ. Tox. Chem. *in press*.
15. Petty, J.D.; Huckins, J.N.; Cranor, W.L.; Alvarez, D.A.; Lebo, J.A.; and Clark, R.C. *Assessment of Waterborne Bioavailable Organic Contaminants Originating From Concentrated Animal Feeding Operations.* March 31, 2001, USGS report prepared for B.L. McGee, US F&WS, Annapolis, MD.
16. Colborn, T., Vom Saal, F.S., Soto, A.M. 1993. Environ. Health Perspect., 101, 378-384
17. Davis, W.P., Bortone, S.A. In "Chemically Induced Alterations in Sexual and Functional Development: The Wildlife/Human Connection", Colborn, T., Clement, C. Eds., Princeton Scientific Publishing: Princeton, NJ, 1992, pp 113-127
18. Shore, L.S., Correll, D.L., Chakraborty, P.K. Relationship of fertilization with chicken manure and concentrations of estrogens in small streams. In, *Animal Waste and the Land-Water Interface*, Steele, K., ed., CRC Press, Boca Raton, FL. 1995, pp. 155-162.
19. Furhacker, M., Breithofer, A., Jungbauer, A. 1999. *Chemosphere*, 39, 1903-1909.
20. AOAC Official Methods of Analysis. Official Method 995.09 Chlortetracycline, Oxytetracycline, and Tetracycline in Edible Animal Tissues. Chapter 23, p 20 (2000).
21. Rogstad, A.; Hormazabal, V.; Yndestad, M. 1988. *J. Liq. Chromatogr.* 11, 2337-2347.

Table I. Organic Contaminants Targeted for Analysis at CERC

PCBs (SPMDs)
Total PCBs

Pesticides (SPMDs)

Trifluralin
HCB*
PCA**
α-BHC***
Diazinon
Atrazine
Lindane
β-BHC***
Heptachlor
Acetochlor
Alachlor
δ-BHC***
Metolachlor
Dacthal
Chlorpyrifos
Oxychlordane
Heptachlor Epoxide
trans-Chlordane
trans-Nonachlor
o,p'-DDE
cis-Chlordane
Endosulfan
p,p'-DDE
Dieldrin
o,p'-DDD
Endrin
cis-Nonachlor
o,p'-DDT
p,p'-DDD
Endosulfan-II
p,p'-DDT
Endosulfan Sulfate
Methoxychlor
Mirex
8-Cyhalothrin
cis-Permethrin
trans-Permethrin

PAHs (SPMDs)
Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benz[a]anthracene
Chrysene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[a]pyrene
Indeno[1,2,3-cd]pyrene
Dibenz[a,h]anthracene
Benzo[g,h,i]perylene

Benzo[b]thiophene
2-methylnaphthalene
1-methylnaphthalene
Biphenyl
1-ethylnaphthalene
1,2-dimethylnaphthalene
4-methylbiphenyl
2,3,5-trimethylnaphthalene
1-methylfluorene
Dibenzothiophene
2-methylphenanthrene
9-methylanthracene
3,6-dimethylphenanthrene
2-methylfluoranthene
Benzo[b]naphtho[2,1-
Benzo[e]pyrene
Perylene
3-methylcholanthrene

Hormones (POCIS)
17β-Estradiol
Estrone

Antibiotics (POCIS)
Oxytetracycline
Tetracycline
Chlortetracycline

* Hexachlorobenzene
** Pentachloroanisole
*** Benzenehexachloride

Table II. MDL and MQL Values For Targeted Analytes in SPMDs and POCIS

PCBs (SPMDs)	MDL ng/SPMD	MQL ng/SPMD
TOTAL PCBs	10	50
Pesticides (SPMDs)		
Trifluralin	0.05	0.25
HCB	0.20	1.00
PCA	0.20	1.00
α-BHC	0.20	1.00
Diazinon	0.25	1.25
Atrazine	20.0	100
Lindane	0.20	1.00
β-BHC	0.20	1.00
Heptachlor	0.20	1.00
Acetochlor	0.25	1.25
Alachlor	0.25	1.25
δ-BHC	0.20	1.00
Metolachlor	1.00	5.00
Dacthal	0.20	1.00
Chlorpyrifos	0.25	0.25
Oxychlordane	0.20	1.00
Heptachlor Epoxide	0.20	1.00
Trans-Chlordane	0.20	1.00
Trans-Nonachlor	0.20	1.00
o,p'-DDE	0.20	1.00
cis-Chlordane	0.20	1.00
Endosulfan	0.20	1.00
p,p'-DDE	0.20	1.00
Dieldrin	0.20	1.00
o,p'-DDD	0.20	1.00
Endrin	0.20	1.00
cis-Nonachlor	0.20	1.00
o,p'-DDT	0.20	1.00
p,p'-DDD	0.20	1.00
Endosulfan-II	0.20	1.00
p,p'-DDT	0.20	1.00
Endosulfan Sulfate	0.20	1.00
Methoxychlor	0.20	1.00
Mirex	0.20	1.00
8-Cyhalothrin	0.10	0.50
cis-Permethrin	0.60	3.00
Trans-Permethrin	0.40	2.00

PAHs (SPMDs)	MDL ng/SPMD	MQL ng/SPMD
Naphthalene	76	160
Acenaphthylene	5	20
Acenaphthene	5	20
Fluorene	5	20
Phenanthrene	49	140
Anthracene	5	20
Fluoranthene	24	73
Pyrene	12	37
Benz[a]anthracene	5	20
Chrysene	74	170
Benzo[b]fluoranthene	5	20
Benzo[k]fluoranthene	5	20
Benzo[a]pyrene	5	20
Indeno[1,2,3-cd]pyrene	5	20
Dibenz[a,h]anthracene	5	20
Benzo[g,h,i]perylene	5	20
Benzo[b]thiophene	5	20
2-methylnaphthalene	44	50
1-methylnaphthalene	19	44
Biphenyl	5	20
1-ethylnaphthalene	5	20
1,2-dimethylnaphthalene	5	20
4-methylbiphenyl	5	20
2,3,5-trimethylnaphthalene	5	20
1-methylfluorene	5	20
Dibenzothiophene	5	20
2-methylphenanthrene	5	20
9-methylanthracene	5	20
3,6-dimethylphenanthrene	5	20
2-methylfluoranthene	5	20
Benzo[b]naphtho[2,1-d]thiophene	5	20
Benzo[e]pyrene	5	20
Perylene	5	20
3-methylcholanthrene	5	20

Hormones (POCIS)	ng/POCIS	ng/POCIS
17β-Estradiol	5.0	25
Estrone	5.0	25

Antibiotics (POCIS)	ng/POCIS	ng/POCIS
Oxytetracycline	5.0	25
Tetracycline	5.0	25
Chlortetracycline	5.0	25

Table III. Recovery of PAHs, OC-Pesticides and PCBs From SPMD Spike

	Percent Recovery		Percent Recovery
Total PCBs	74.3	Naphthalene	19.0
		Acenaphthylene	33.4
Trifluralin	11.1	Acenaphthene	37.5
HCB	66.3	Fluorene	48.4
PCA	94.7	Phenanthrene	64.4
α-BHC	24.8	Anthracene	66.1
Diazinon	4.8	Fluoranthene	74.1
Atrazine	35.5	Pyrene	73.7
Lindane	80.3	Benz[a]anthracene	80.7
β-BHC	57.6	Chrysene	75.3
Heptachlor	51.8	Benzo[b]fluoranthene	82.5
Acetochlor	6.4	Benzo[k]fluoranthene	77.0
Alachlor	6.0	Benzo[a]pyrene	82.3
δ-BHC	51.2	Indeno[1,2,3-cd]pyrene	82.9
Metolachlor	4.1	Dibenz[a,h]anthracene	81.9
Dacthal	48.3	Benzo[g,h,i]perylene	79.1
Chlorpyrifos	32.5		
Oxychlordane	67.3		
Heptachlor Epoxide	71.5		
trans-Chlordane	61.2		
trans-Nonachlor	54.1		
O,p'-DDE	74.7		
cis-Chlordane	61.1		
Endosulfan	72.9		
P,p'-DDE	30.9		
Dieldrin	70.6		
O,p'-DDD	70.6		
Endrin	38.0		
cis-Nonachlor	44.2		
O,p'-DDT	69.6		
P,p'-DDD	62.4		
Endosulfan-II	60.7		
P,p'-DDT	99.2		
Endosulfan Sulfate	51.4		
Methoxychlor	103		
Mirex	60.6		
8-Cyhalothrin	12.0		
cis-Permethrin	6.8		
trans-Permethrin	9.1		

Table IV. Site 1 (Elk River station #2) chemical analyses from SPMDs and POCIS (corrected for background). Results expressed as ng/SPMD or ng/POCIS.

	Rep. #1	Rep. #2
PCBs (SPMDs)	ng/SPMD	ng/SPMD
TOTAL PCBs	<MQL	<MQL
Pesticides (SPMDs)	ng/SPMD	ng/SPMD
Trifluralin	<MDL	<MDL
HCB	<MDL	<MDL
PCA	13.2	14.4
α-BHC	<MQL	<MQL
Diazinon	<MQL	<MDL
Atrazine	<MDL	<MDL
Lindane	6.47	6.80
β-BHC	<MQL	<MQL
Heptachlor	<MDL	<MDL
Acetochlor	93.2	93.3
Alachlor	4.08	3.67
δ-BHC	2.26	2.26
Metolachlor	<MDL	<MQL
Dacthal	4.26	3.38
Chlorpyrifos	8.56	7.62
Oxychlordane	1.59	<MDL
Heptachlor Epoxide	10.1	6.76
Trans-Chlordane	12.3	12.4
Trans-Nonachlor	7.47	7.21
o,p'-DDE	12.7	12.5
cis-Chlordane	30.3	30.8
Endosulfan	<MDL	<MDL
p,p'-DDE	4.88	6.65
Dieldrin	33.5	35.4
o,p'-DDD	20.7	22.0
Endrin	<MDL	1.72
cis-Nonachlor	1.92	2.39
o,p'-DDT	3.08	3.74
p,p'-DDD	51.0	55.4
Endosulfan-II	2.17	4.33
p,p'-DDT	5.65	6.06
Endosulfan Sulfate	<MQL	<MQL
Methoxychlor	<MDL	<MDL
Mirex	<MDL	<MDL
8-Cyhalothrin	<MDL	<MDL
cis-Permethrin	<MDL	<MDL
Trans-Permethrin	<MDL	<MDL

	Rep. #1	Rep. #2
PAHs (SPMDs)	ng/SPMD	ng/SPMD
Naphthalene	<MDL	<MDL
Acenaphthylene	<MDL	<MDL
Acenaphthene	<MDL	<MDL
Fluorene	<MDL	<MDL
Phenanthrene	<MDL	<MDL
Anthracene	<MDL	<MDL
Fluoranthene	160	130
Pyrene	430	360
Benz[a]anthracene	<MQL	<MQL
Chrysene	110	90
Benzo[b]fluoranthene	30	20
Benzo[k]fluoranthene	20	20
Benzo[a]pyrene	<MQL	<MQL
Indeno[1,2,3-cd]pyrene	<MQL	<MDL
Dibenz[a,h]anthracene	<MDL	<MDL
Benzo[g,h,i]perylene	<MQL	<MQL
Benzo[b]thiophene	<MDL	<MDL
2-methylnaphthalene	<MDL	<MDL
1-methylnaphthalene	<MDL	<MDL
Biphenyl	<MDL	<MDL
1-ethylnaphthalene	<MDL	<MDL
1,2-dimethylnaphthalene	<MDL	<MDL
4-methylbiphenyl	<MDL	<MDL
2,3,5-trimethylnaphthalene	<MDL	<MDL
1-methylfluorene	<MDL	<MDL
Dibenzothiophene	<MDL	<MDL
2-methylphenanthrene	<MQL	<MQL
9-methylanthracene	<MDL	<MDL
3,6-dimethylphenanthrene	<MDL	<MDL
2-methylfluoranthene	<MDL	<MDL
Benzo[b]naphtho[2,1-d]thiophene	<MDL	<MDL
Benzo[e]pyrene	40	30
Perylene	70	60
3-methylcholanthrene	<MDL	<MDL
Hormones (POCIS)	ng/POCIS	ng/POCIS
17β-Estradiol	<MDL	<MDL
Estrone	<MDL	<MDL
Antibiotics (POCIS)	ng/POCIS	ng/POCIS
Oxytetracycline	<MDL	<MDL
Tetracycline	<MDL	<MDL
Chlortetracycline	<MDL	<MDL

Table V. Site 2 (Bohema River station #2) chemical analyses from SPMDs and POCIS (corrected for background). Results expressed as ng/SPMD or ng/POCIS.

	Rep. #1	Rep. #2
PCBs (SPMDs)	ng/SPMD	ng/SPMD
TOTAL PCBs	<MDL	<MDL
Pesticides (SPMDs)	ng/SPMD	ng/SPMD
Trifluralin	<MDL	<MDL
HCB	<MDL	<MDL
PCA	10.8	9.10
α-BHC	<MQL	<MQL
Diazinon	<MQL	<MDL
Atrazine	<MDL	<MDL
Lindane	5.61	4.22
β-BHC	3.31	3.21
Heptachlor	<MDL	<MDL
Acetochlor	36.9	30.0
Alachlor	<MQL	2.06
δ-BHC	2.82	1.29
Metolachlor	<MDL	4.02
Dacthal	3.67	1.42
Chlorpyrifos	7.35	5.53
Oxychlordane	1.67	<MDL
Heptachlor Epoxide	10.2	7.82
Trans-Chlordane	4.58	3.72
Trans-Nonachlor	3.36	2.99
o,p'-DDE	<MDL	<MDL
cis-Chlordane	13.1	12.3
Endosulfan	<MDL	<MDL
p,p'-DDE	<MDL	<MDL
Dieldrin	17.2	17.7
o,p'-DDD	5.55	5.78
Endrin	<MQL	<MQL
cis-Nonachlor	<MDL	<MDL
o,p'-DDT	<MQL	<MQL
p,p'-DDD	13.9	13.7
Endosulfan-II	1.61	<MQL
p,p'-DDT	<MQL	<MQL
Endosulfan Sulfate	<MQL	<MQL
Methoxychlor	<MDL	<MDL
Mirex	<MDL	<MDL
8-Cyhalothrin	<MDL	<MDL
cis-Permethrin	<MDL	<MDL
Trans-Permethrin	<MDL	<MDL

	Rep. #1	Rep. #2
PAHs (SPMDs)	ng/SPMD	ng/SPMD
Naphthalene	<MDL	<MDL
Acenaphthylene	<MDL	<MDL
Acenaphthene	<MDL	<MDL
Fluorene	<MDL	<MQL
Phenanthrene	<MDL	<MDL
Anthracene	<MDL	<MDL
Fluoranthene	<MQL	<MQL
Pyrene	70	80
Benz[a]anthracene	<MDL	<MDL
Chrysene	<MDL	<MDL
Benzo[b]fluoranthene	<MQL	<MQL
Benzo[k]fluoranthene	<MQL	<MQL
Benzo[a]pyrene	<MDL	<MDL
Indeno[1,2,3-cd]pyrene	<MDL	<MDL
Dibenz[a,h]anthracene	<MDL	<MDL
Benzo[g,h,i]perylene	<MDL	<MDL
Benzo[b]thiophene	<MDL	<MDL
2-methylnaphthalene	<MDL	<MDL
1-methylnaphthalene	<MDL	<MDL
Biphenyl	<MDL	<MDL
1-ethylnaphthalene	<MDL	<MDL
1,2-dimethylnaphthalene	<MDL	<MDL
4-methylbiphenyl	<MDL	<MDL
2,3,5-trimethylnaphthalene	<MDL	<MDL
1-methylfluorene	<MDL	<MDL
Dibenzothiophene	<MDL	<MDL
2-methylphenanthrene	<MDL	<MDL
9-methylanthracene	<MDL	<MDL
3,6-dimethylphenanthrene	<MDL	<MDL
2-methylfluoranthene	<MDL	<MDL
Benzo[b]naphtho[2,1-d]thiophene	<MDL	<MDL
Benzo[e]pyrene	<MQL	<MQL
Perylene	30	40
3-methylcholanthrene	<MDL	<MDL
Hormones (POCIS)	ng/POCIS	ng/POCIS
17β-Estradiol	<MDL	<MDL
Estrone	<MDL	<MDL
Antibiotics (POCIS)	ng/POCIS	ng/POCIS
Oxytetracycline	<MDL	<MDL
Tetracycline	<MDL	<MDL
Chlortetracycline	<MDL	<MDL

Table VI. Site 4 (Northeast River station #5) chemical analyses from SPMDs and POCIS (corrected for background). Results expressed as ng/SPMD or ng/POCIS.

	Rep. #1	Rep. #2
PCBs (SPMDs)	ng/SPMD	ng/SPMD
TOTAL PCBs	<MDL	<MDL
Pesticides (SPMDs)	ng/SPMD	ng/SPMD
Trifluralin	2.44	2.80
HCB	<MDL	<MDL
PCA	18.1	17.4
α-BHC	<MDL	<MQL
Diazinon	<MQL	<MQL
Atrazine	<MDL	<MDL
Lindane	2.32	2.65
β-BHC	<MDL	<MDL
Heptachlor	<MDL	<MDL
Acetochlor	45.6	34.4
Alachlor	1.39	<MQL
δ-BHC	<MDL	<MDL
Metolachlor	<MQL	<MQL
Dacthal	1.82	1.74
Chlorpyrifos	12.5	12.4
Oxychlordane	<MDL	<MDL
Heptachlor Epoxide	4.85	4.72
Trans-Chlordane	4.43	4.74
Trans-Nonachlor	2.14	2.12
o,p'-DDE	<MDL	<MDL
cis-Chlordane	6.32	6.26
Endosulfan	3.28	3.18
p,p'-DDE	<MDL	<MDL
Dieldrin	14.6	15.1
o,p'-DDD	4.08	4.09
Endrin	2.35	2.44
cis-Nonachlor	<MQL	<MQL
o,p'-DDT	<MDL	1.14
p,p'-DDD	8.52	7.30
Endosulfan-II	2.02	1.11
p,p'-DDT	1.70	1.09
Endosulfan Sulfate	<MQL	<MQL
Methoxychlor	<MDL	<MDL
Mirex	<MDL	<MDL
8-Cyhalothrin	<MDL	<MDL
cis-Permethrin	<MDL	<MDL
Trans-Permethrin	<MDL	<MDL

	Rep. #1	Rep. #2
PAHs (SPMDs)	ng/SPMD	ng/SPMD
Naphthalene	<MDL	<MDL
Acenaphthylene	<MDL	<MDL
Acenaphthene	<MQL	<MQL
Fluorene	<MQL	<MQL
Phenanthrene	<MQL	<MQL
Anthracene	<MQL	<MQL
Fluoranthene	300	300
Pyrene	310	310
Benz[a]anthracene	<MQL	<MQL
Chrysene	<MQL	<MQL
Benzo[b]fluoranthene	<MQL	20
Benzo[k]fluoranthene	<MQL	<MQL
Benzo[a]pyrene	<MQL	<MQL
Indeno[1,2,3-cd]pyrene	<MDL	<MDL
Dibenz[a,h]anthracene	<MDL	<MDL
Benzo[g,h,i]perylene	<MQL	<MQL
Benzo[b]thiophene	<MDL	<MDL
2-methylnaphthalene	<MQL	<MQL
1-methylnaphthalene	<MQL	<MQL
Biphenyl	<MDL	<MDL
1-ethylnaphthalene	<MDL	<MDL
1,2-dimethylnaphthalene	<MDL	<MDL
4-methylbiphenyl	<MDL	<MDL
2,3,5-trimethylnaphthalene	<MDL	<MDL
1-methylfluorene	20	<MDL
Dibenzothiophene	20	<MDL
2-methylphenanthrene	20	20
9-methylanthracene	<MDL	<MDL
3,6-dimethylphenanthrene	<MDL	<MDL
2-methylfluoranthene	<MDL	<MDL
Benzo[b]naphtho[2,1-d]thiophene	<MDL	<MDL
Benzo[e]pyrene	20	20
Perylene	150	170
3-methylcholanthrene	<MDL	<MDL
Hormones (POCIS)	ng/POCIS	ng/POCIS
17β-Estradiol	<MDL	<MDL
Estrone	<MDL	<MDL
Antibiotics (POCIS)	ng/POCIS	ng/POCIS
Oxytetracycline	<MDL	<MDL
Tetracycline	<MDL	<MDL
Chlortetracycline	160	180

Table VII. Site 5 (Northeast River station #3) chemical analyses from SPMDs and POCIS (corrected for background). Results expressed as ng/SPMD or ng/POCIS.

	Rep. #1	Rep. #2
PCBs (SPMDs)	ng/SPMD	ng/SPMD
TOTAL PCBs	<MDL	<MDL
Pesticides (SPMDs)	ng/SPMD	ng/SPMD
Trifluralin	1.76	1.70
HCB	<MDL	<MDL
PCA	28.3	27.2
α-BHC	1.61	1.55
Diazinon	3.43	14.15
Atrazine	<MDL	<MDL
Lindane	6.79	8.51
β-BHC	<MDL	<MDL
Heptachlor	<MDL	<MDL
Acetochlor	18.0	17.3
Alachlor	<MQL	<MQL
δ-BHC	<MDL	<MDL
Metolachlor	5.96	<MQL
Dacthal	1.87	1.84
Chlorpyrifos	10.7	9.74
Oxychlordane	<MDL	<MQL
Heptachlor Epoxide	5.12	7.27
Trans-Chlordane	4.47	8.17
Trans-Nonachlor	2.45	4.78
o,p'-DDE	<MDL	<MDL
cis-Chlordane	6.82	8.32
Endosulfan	5.12	6.24
p,p'-DDE	<MDL	<MDL
Dieldrin	15.6	15.1
o,p'-DDD	3.46	<MQL
Endrin	<MDL	<MQL
cis-Nonachlor	<MQL	<MQL
o,p'-DDT	<MDL	<MQL
p,p'-DDD	5.98	6.35
Endosulfan-II	2.15	2.05
p,p'-DDT	1.38	1.72
Endosulfan Sulfate	<MDL	<MQL
Methoxychlor	<MDL	<MDL
Mirex	<MDL	<MDL
8-Cyhalothrin	<MDL	<MDL
cis-Permethrin	<MDL	<MDL
Trans-Permethrin	<MDL	<MDL

	Rep. #1	Rep. #2
PAHs (SPMDs)	ng/SPMD	ng/SPMD
Naphthalene	<MDL	<MDL
Acenaphthylene	<MDL	<MDL
Acenaphthene	<MDL	<MDL
Fluorene	<MQL	<MQL
Phenanthrene	<MDL	<MDL
Anthracene	<MQL	<MQL
Fluoranthene	220	220
Pyrene	320	310
Benz[a]anthracene	<MQL	<MQL
Chrysene	<MDL	<MDL
Benzo[b]fluoranthene	20	20
Benzo[k]fluoranthene	<MQL	<MQL
Benzo[a]pyrene	<MQL	<MQL
Indeno[1,2,3-cd]pyrene	<MDL	<MDL
Dibenz[a,h]anthracene	<MDL	<MDL
Benzo[g,h,i]perylene	<MQL	<MQL
Benzo[b]thiophene	<MDL	<MDL
2-methylnaphthalene	<MDL	<MDL
1-methylnaphthalene	<MDL	<MDL
Biphenyl	<MDL	<MDL
1-ethylnaphthalene	<MDL	<MDL
1,2-dimethylnaphthalene	<MDL	<MDL
4-methylbiphenyl	<MDL	<MDL
2,3,5-trimethylnaphthalene	<MDL	<MDL
1-methylfluorene	<MDL	<MDL
Dibenzothiophene	<MDL	<MDL
2-methylphenanthrene	20	20
9-methylanthracene	<MDL	<MDL
3,6-dimethylphenanthrene	<MDL	<MDL
2-methylfluoranthene	<MDL	<MDL
Benzo[b]naphtho[2,1-d]thiophene	<MDL	<MDL
Benzo[e]pyrene	20	20
Perylene	160	220
3-methylcholanthrene	<MDL	<MDL
Hormones (POCIS)	ng/POCIS	ng/POCIS
17β-Estradiol	94	110
Estrone	<MDL	<MDL
Antibiotics (POCIS)	ng/POCIS	ng/POCIS
Oxytetracycline	140	210
Tetracycline	<MDL	<MDL
Chlortetracycline	<MDL	<MDL

Table VIII. Site 6 (Buck Creek) chemical analyses from SPMDs and POCIS (corrected for background). Results expressed as ng/SPMD or ng/POCIS.

	Rep. #1	Rep. #2
PCBs (SPMDs)	ng/SPMD	ng/SPMD
TOTAL PCBs	<MQL	<MQL
Pesticides (SPMDs)	ng/SPMD	ng/SPMD
Trifluralin	<MDL	<MDL
HCB	<MDL	<MDL
PCA	55.1	65.9
α-BHC	<MDL	<MDL
Diazinon	5.15	20.9
Atrazine	<MDL	<MDL
Lindane	<MDL	<MDL
β-BHC	4.90	3.47
Heptachlor	<MDL	<MDL
Acetochlor	23.8	19.8
Alachlor	<MQL	<MQL
δ-BHC	7.34	5.70
Metolachlor	9.92	<MQL
Dacthal	3.10	2.24
Chlorpyrifos	9.64	8.77
Oxychlordane	<MQL	<MQL
Heptachlor Epoxide	27.5	24.9
Trans-Chlordane	14.7	15.7
Trans-Nonachlor	9.69	11.5
o,p'-DDE	<MDL	<MDL
cis-Chlordane	25.3	25.9
Endosulfan	<MDL	<MDL
p,p'-DDE	<MDL	<MDL
Dieldrin	55.1	55.9
o,p'-DDD	2.50	4.45
Endrin	1.97	4.46
cis-Nonachlor	3.78	5.87
o,p'-DDT	4.73	6.95
p,p'-DDD	3.46	8.87
Endosulfan-II	3.63	10.2
p,p'-DDT	<MDL	7.11
Endosulfan Sulfate	<MDL	<MDL
Methoxychlor	<MDL	<MDL
Mirex	<MDL	<MDL
8-Cyhalothrin	<MDL	<MDL
cis-Permethrin	5.48	<MDL
Trans-Permethrin	<MDL	<MDL

	Rep. #1	Rep. #2
PAHs (SPMDs)	ng/SPMD	ng/SPMD
Naphthalene	<MDL	<MDL
Acenaphthylene	<MDL	<MDL
Acenaphthene	60	80
Fluorene	90	100
Phenanthrene	240	240
Anthracene	40	50
Fluoranthene	5420	5660
Pyrene	3340	3520
Benz[a]anthracene	160	180
Chrysene	990	1090
Benzo[b]fluoranthene	350	430
Benzo[k]fluoranthene	180	240
Benzo[a]pyrene	60	70
Indeno[1,2,3-cd]pyrene	50	60
Dibenz[a,h]anthracene	<MQL	<MQL
Benzo[g,h,i]perylene	50	60
Benzo[b]thiophene	<MDL	<MDL
2-methylnaphthalene	<MDL	60
1-methylnaphthalene	<MDL	<MQL
Biphenyl	<MDL	<MQL
1-ethylnaphthalene	<MDL	<MDL
1,2-dimethylnaphthalene	<MQL	20
4-methylbiphenyl	<MDL	<MDL
2,3,5-trimethylnaphthalene	<MDL	140
1-methylfluorene	200	200
Dibenzothiophene	20	20
2-methylphenanthrene	150	150
9-methylanthracene	<MDL	<MDL
3,6-dimethylphenanthrene	140	140
2-methylfluoranthene	130	130
Benzo[b]naphtho[2,1-d]thiophene	120	130
Benzo[e]pyrene	210	240
Perylene	20	20
3-methylcholanthrene	<MDL	<MDL
Hormones (POCIS)	ng/POCIS	ng/POCIS
17β-Estradiol	<MDL	<MDL
Estrone	<MDL	<MDL
Antibiotics (POCIS)	ng/POCIS	ng/POCIS
Oxytetracycline	<MDL	160
Tetracycline	210	200
Chlortetracycline	<MDL	170

Table IX. Permeability Reference Compound (Phenanthrene-d_{10}) Recovery

QA/QC Sample	µg PRC
Field Blank, Site # 1	5.44*
Field Blank, Site # 2	5.47*
Field Blank, Site # 4	5.33*
Field Blank, Site # 5	5.76*
Field Blank, Site # 6	5.53*
Mean	5.51*

Exposure Site	µg PRC
Site # 1	0.23**
Site # 2	1.05**
Site # 4	0.64**
Site # 5	0.87**
Site # 6	0.64**

Exposure Site	k_{eprc} (d^{-1})
Site # 1	0.076
Site # 2	0.039
Site # 4	0.051
Site # 5	0.044
Site # 6	0.054

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

* $\mathbf{C_{SPMDso}}$

** C_{SPMD}

Table X. Estimated Aqueous Concentrations of Select Contaminants Sequestered in Deployed SPMDs

	Site # 1 pg/L	Site # 2 pg/L	Site # 4 pg/L	Site # 5 pg/L	Site # 6 pg/L
α-BHC	N.A.	N.A.	N.A.	67	N.A
PCA	22	11	23	33	79
Lindane	400	290	150	460	N.A.
Endrin	7.3	N.A.	20	N.A.	27
Oxychlordane	0.9	4.5	N.A.	N.A.	N.A.
Dacthal	14	41	31	33	47
Chlorpyrifos	420	29	60	47	44
Diazinon	N.A.	N.A.	N.A.	1500	2140
Heptachlor Epoxide	90	96	51	66	280
trans-Chlordane	19	17	5.7	23	19
cis-Chlordane	46	58	22	31	89
cis-Nonachlor	4.7	N.A.	N.A.	N.A.	16
trans-Nonachlor	17	15	7.5	15	37
Dieldrin	310	160	130	140	500
o,p'-DDT	4.0	N.A.	1.0	N.A.	5.4
p,p'-DDT	10	N.A.	2.0	2.0	10
o,p'-DDD	43	22	12	12	10
p,p'-DDD	41	47	20	19	16
o,p'-DDE	15	N.A.	N.A.	N.A.	N.A.
p,p'-DDE	5.5	N.A.	N.A.	N.A.	N.A.
Acenaphthene	N.A.	N.A.	N.A.	N.A.	1340
Fluorene	N.A.	N.A.	N.A.	N.A.	1190
Phenanthrene	N.A.	N.A.	N.A.	N.A.	2820
Anthracene	N.A.	N.A.	N.A.	N.A.	450
Fluoranthene	420	N.A.	720	490	13300
Pyrene	940	130	630	320	6940
Benz[a]anthracene	N.A.	N.A.	N.A.	N.A.	460
Chrysene	120	N.A.	N.A.	N.A.	1030
Benzo[b]fluoranthene	N.A.	N.A.	58	67	1120
Benzo[k]fluoranthene	33	N.A.	N.A.	N.A.	510
Benzo[a]pyrene	N.A.	N.A.	N.A.	N.A.	150
Indeno[1,2,3-cd]pyrene	N.A.	N.A.	N.A.	N.A.	130
Benzo[g,h,I]perylene	N.A.	N.A.	N.A.	N.A.	220

NOTE: N.A. = Not Applicable

* Estimated using extrapolated value for PRC corrected Rs

Table XI. Estimated Aqueous Concentrations of Select Contaminants Sequestered in Deployed POCIS

	Site # 1 pg/L	Site # 2 pg/L	Site # 4 pg/L	Site # 5 pg/L	Site # 6 pg/L
17β-Estradiol	N.A.	N.A.	N.A.	4000	N.A.

NOTE: N.A. = Not Applicable

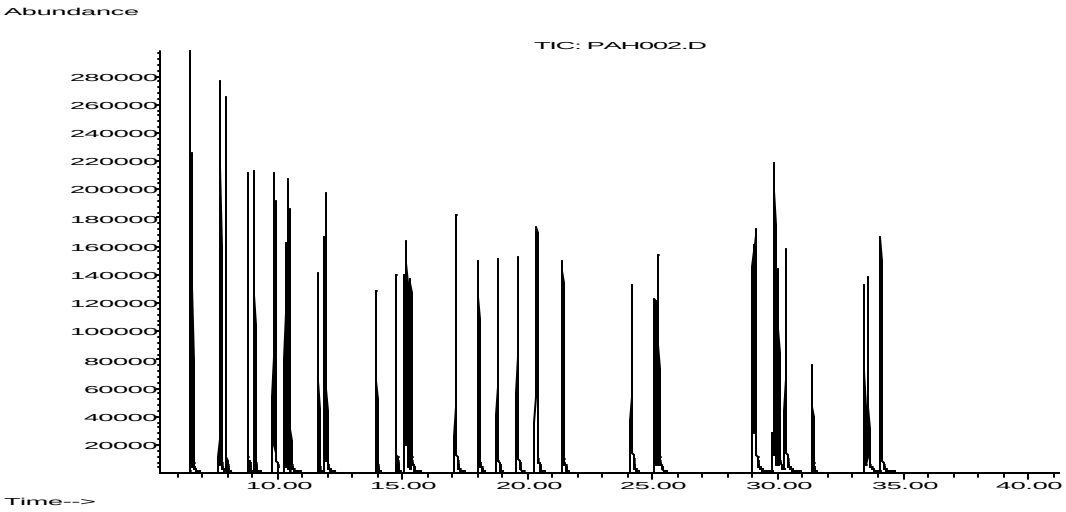
Table XII. Elution Order of Targeted Analytes During Instrumental Analysis*

	Retention Time Min.		Retention Time min.
PCBs (GC-ECD)		**PAHs (GC-MSD)**	
TOTAL PCBs	8.80 – 44.50	Naphthalene	6.52
		Acenaphthylene	9.87
Pesticides (GC-ECD)		Acenaphthene	10.40
		Fluorene	11.95
Trifluralin	8.16	Phenanthrene	15.18
HCB	10.49	Anthracene	15.33
PCA	10.66	Fluoranthene	19.59
α-BHC	11.02	Pyrene	20.37
Diazinon	12.14	Benz[a]anthracene	25.08
Atrazine	12.35	Chrysene	25.21
Lindane	12.90	Benzo[b]fluoranthene	28.99
β-BHC	14.57	Benzo[k]fluoranthene	29.08
Heptachlor	14.71	Benzo[a]pyrene	30.01
Acetochlor	14.95	Indeno[1,2,3-cd]pyrene	33.44
Alachlor	15.59	Dibenz[a,h]anthracene	33.57
δ-BHC	16.02	Benzo[g,h,i]perylene	34.09
Metolachlor	17.61		
Dacthal	17.98	Benzo[b]thiophene	6.60
Chlorpyrifos	18.17	2-methylnaphthalene	7.73
Oxychlordane	19.31	1-methylnaphthalene	7.95
Heptachlor Epoxide	20.05	Biphenyl	8.81
trans-Chlordane	21.67	1-ethylnaphthalene	9.09
trans-Nonachlor	21.92	1,2-dimethylnaphthalene	9.94
o,p'-DDE	22.10	4-methylbiphenyl	10.51
cis-Chlordane	22.33	2,3,5-trimethylnaphthalene	11.64
Endosulfan	22.46	1-methylfluorene	13.96
p,p'-DDE	24.37	Dibenzothiophene	14.73
Dieldrin	24.49	2-methylphenanthrene	17.12
o,p'-DDD	25.71	9-methylanthracene	18.04
Endrin	26.59	3,6-dimethylphenanthrene	18.79
cis-Nonachlor	27.39	2-methylfluoranthene	21.40
o,p'-DDT	27.58	Benzo[b]naphtho[2,1-d]thiophene	24.14
p,p'-DDD	28.59	Benzo[e]pyrene	29.86
Endosulfan-II	28.76	Perylene	30.29
p,p'-DDT	30.49	3-methylcholanthrene	31.36
Endosulfan Sulfate	32.13		
Methoxychlor	36.08	**Hormones (HPLC)**	
Mirex	36.51	17β-Estradiol	10.14
8-Cyhalothrin	37.30	Estrone	14.25
cis-Permethrin	41.35		
trans-Permethrin	42.02	**Antibiotics (HPLC)**	
		Oxytetracycline	3.49
		Tetracycline	4.15
		Chlortetracycline	7.85

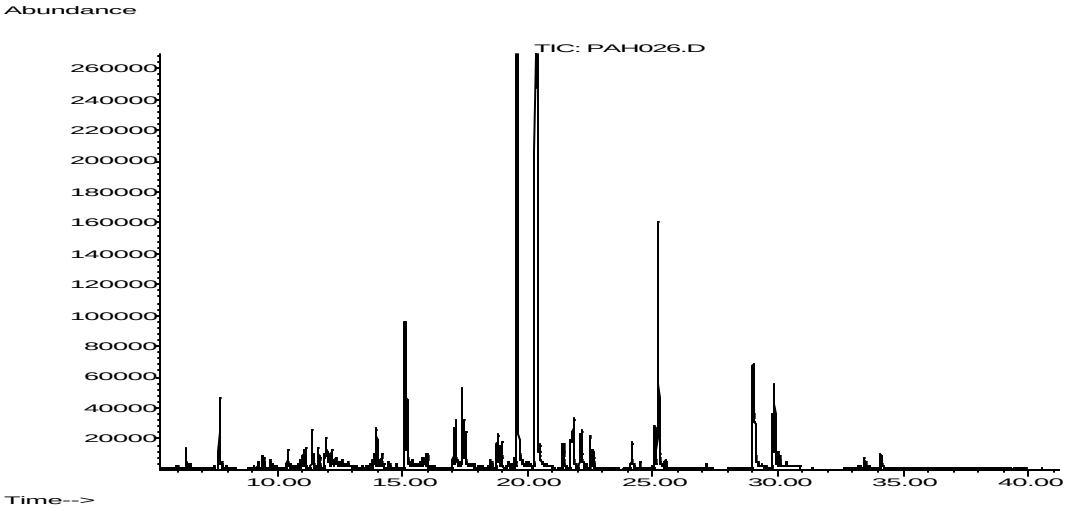
* NOTE: Slight variations in retention times were noted on a run by run basis. Retention times as given reflect the example provided in Figures 1,2, and 3.

Figure 1

GC-MSD Analysis for PAHs



1.0 µg/mL PAH mixed standard. See Table IX for components and retention times.

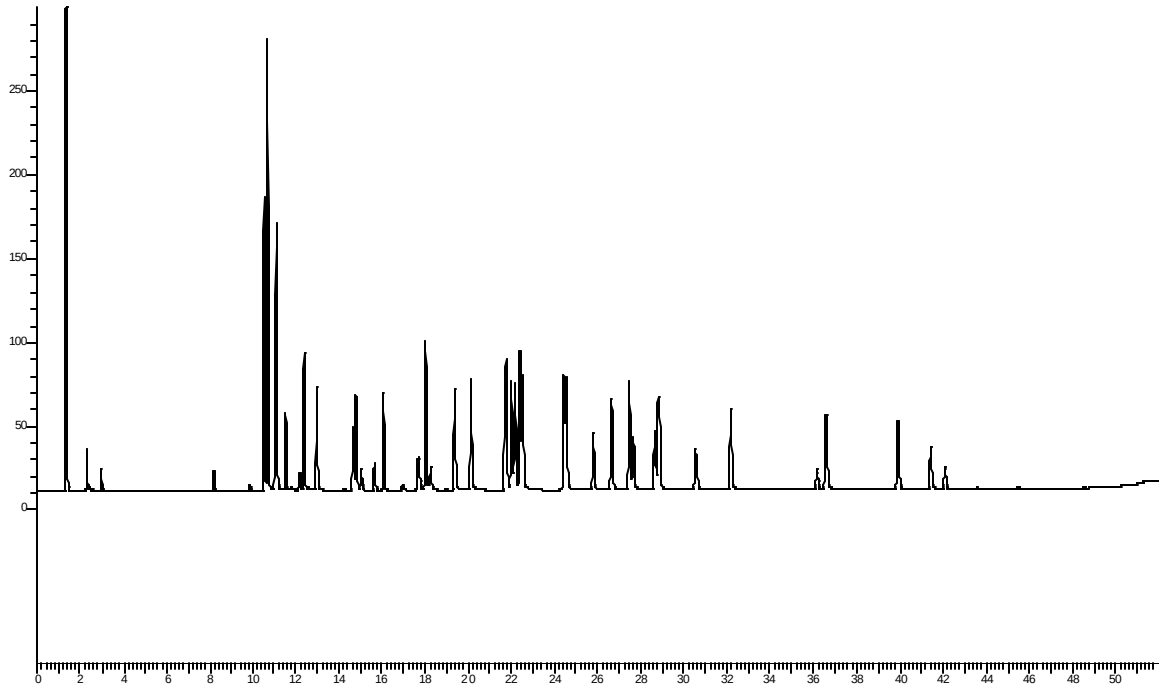


Representative SPMD sample - Site 6 Repilcate A (Buck Creek)

Note: Agilent 6890 series gas chromatograph (GC) equipped with a HP-5MS (30 m x 0.25 mm i.d. x 0.25 µm film thickness) capillary column (Agilent Technologies, Inc., Wilmington, DE) with the following temperature program: injection at 50 °C, held for 2 min, then 25 °C/min to 130 °C, held for 1 min, followed by 6 °C/min to 310 °C and held at 310 °C for 5 min.

Figure 2

GC-ECD Analysis of OC-Pesticide Standards

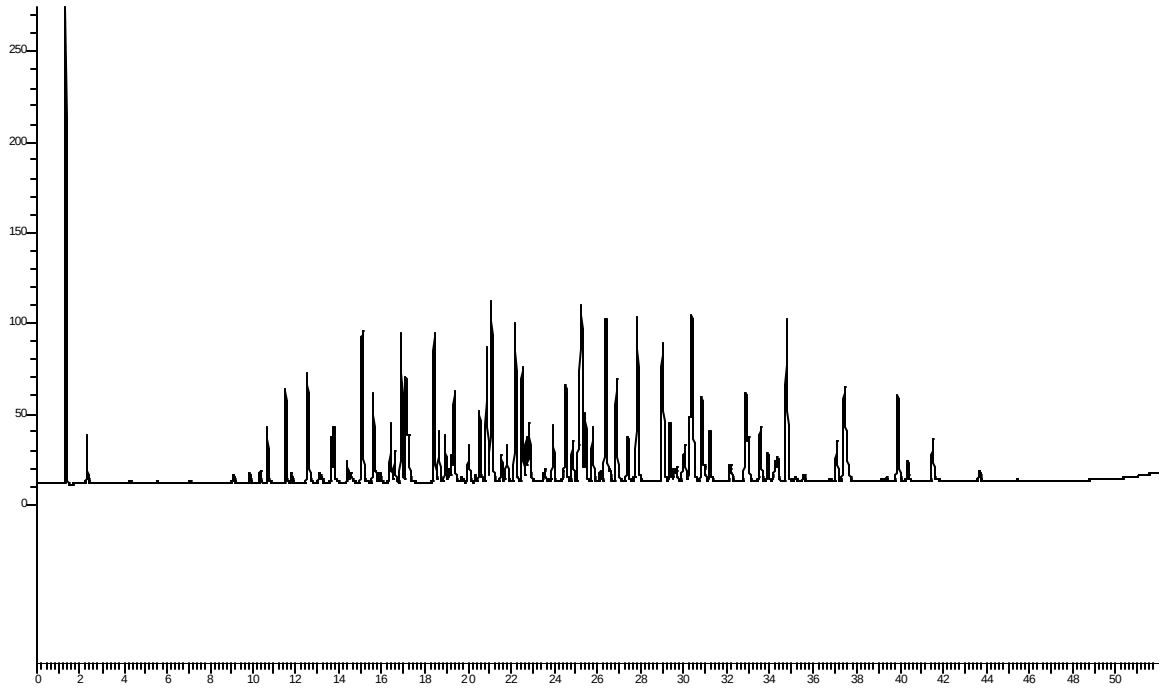


OC-Pesticide mixed standard, calibration Level # 4 (i.e. mid-range). See Table IX for components and retention times.

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 3

GC-ECD Analysis of PCB Standard

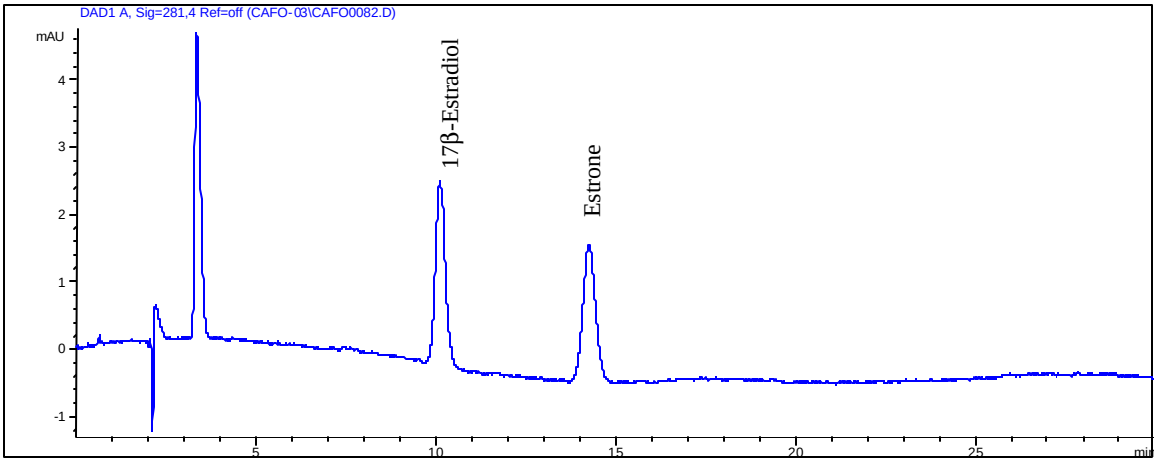


500 total ng/mL 1:1:1:1 mixture of Aroclor® (1242:1248:1254:1260) standard, calibration Level # 4 (i.e. mid-range). See Table IX for components and retention times.

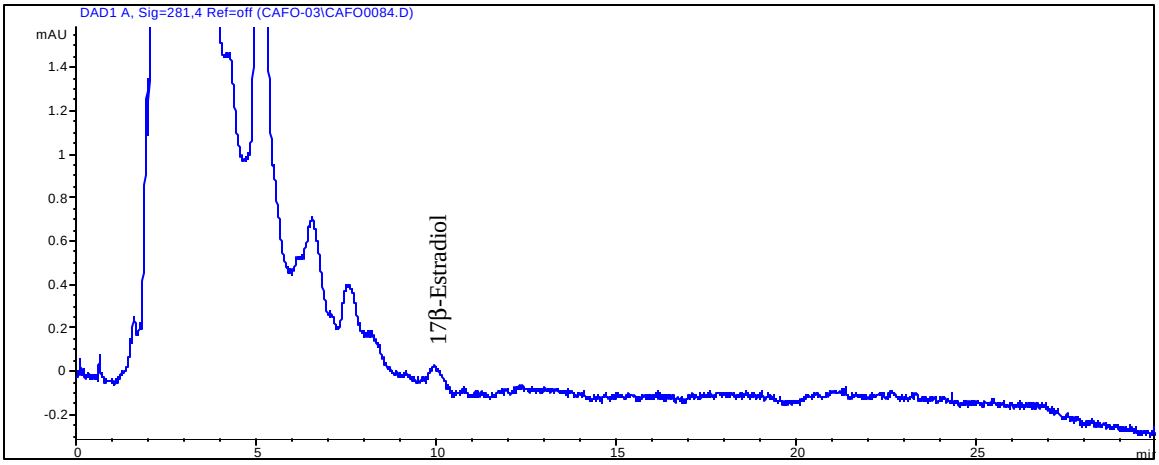
Note: Hewlett Packard 5890 series gas chromatograph (GC) equipped with a DB-35MS (30 m x 0.25 mm i.d. x 0.25 µm film thickness) capillary column (J&W Scientific, Folsom, CA) with the following temperature program: injection at 90°C; then 15°C/min to 165°C; followed by 2.5°C/min to 250°C; then at 10°C/min to 320°C. The electron capture detector (ECD) was maintained at 330°C (Hewlett Packard, Inc., Palo Alto, CA).

Figure 4

HPLC Analysis for Hormones



200 ng on column of a mixed Hormone standard (mid-level standard). See Table IX for component retention times.

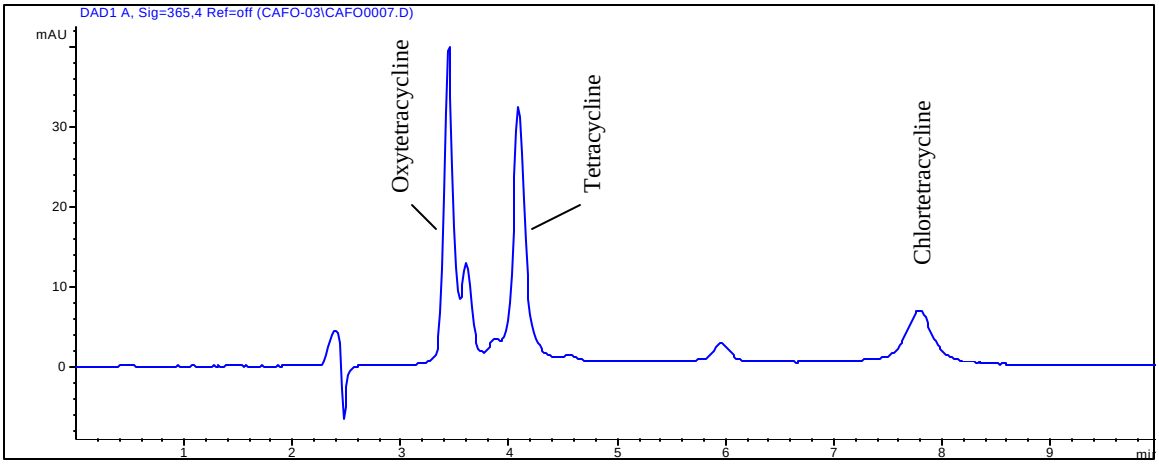


Representative POCIS sample – Site 5 Replicate A (Northeast River station #3)

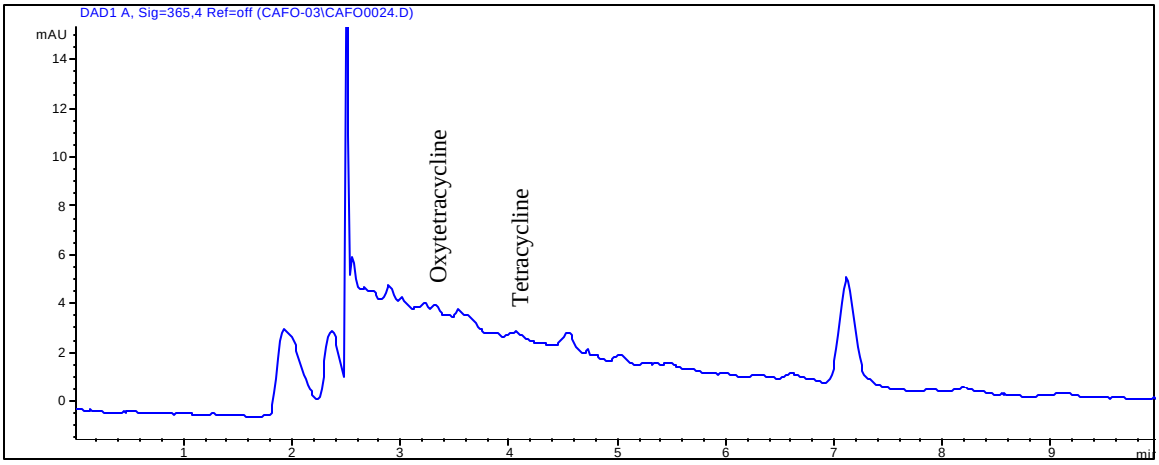
Note: Hewlett Packard 1090 Series II liquid chromatograph (HPLC) equipped with a C_8 (150 x 4.6 mm, 5 µm d_p) analytical column (Supelco, Bellefonte, PA) with a mobile phase of 65:35 water:acetonitrile and a 1 mL/min flow rate. The diode array detector was maintained at a wavelength of 281 nm for estrogen detection (Hewlett Packard, Inc., Palo Alto, CA).

Figure 5

HPLC Analysis for Antibiotics



500 ng on column of a mixed Antibiotic standard (high-level standard). See Table IX for component retention times.



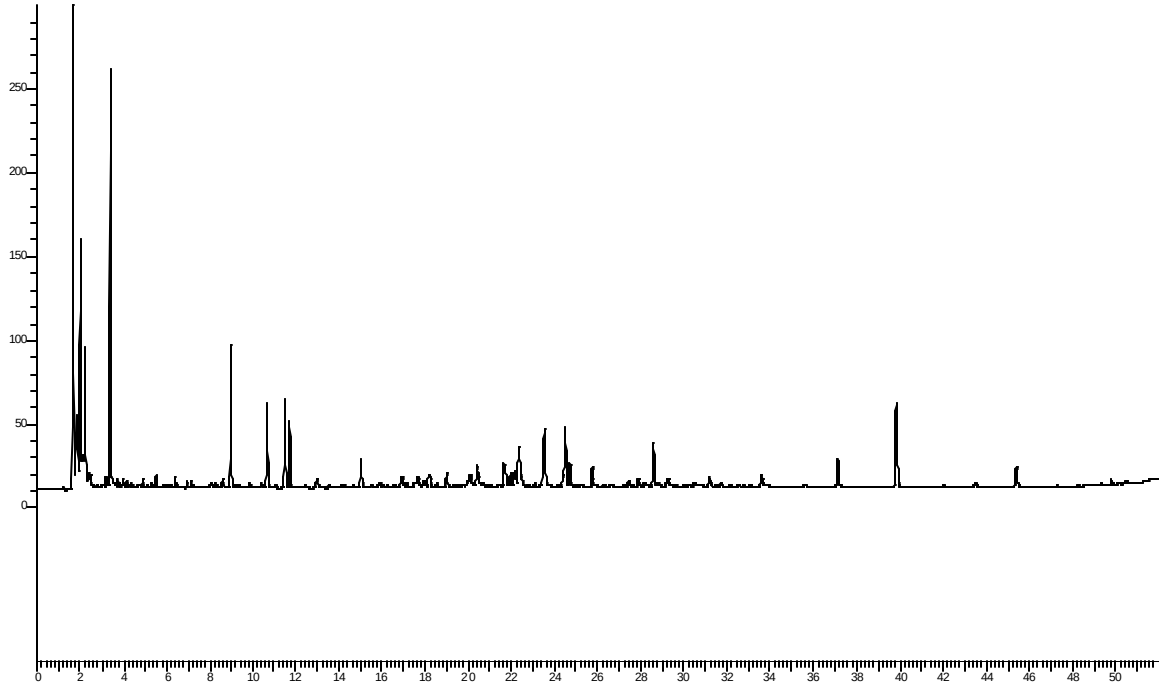
Representative POCIS sample – Site 6 Replicate B (Buck Creek)

Note: Hewlett Packard 1090 Series II liquid chromatograph (HPLC) equipped with a C_8 (150 x 4.6 mm, 5 µm d_p) analytical column (Supelco, Bellefonte, PA) with a mobile phase of 80:20 25 mM KH_2PO_4 (pH 3) buffer:acetonitrile and a 1 mL/min flow rate. The diode array detector was maintained at a wavelength of 365 nm for estrogen detection (Hewlett Packard, Inc., Palo Alto, CA).

Figure 6

Representative GC-ECD Profile of an

SPMD "OC Pesticide" Fraction (SG2)



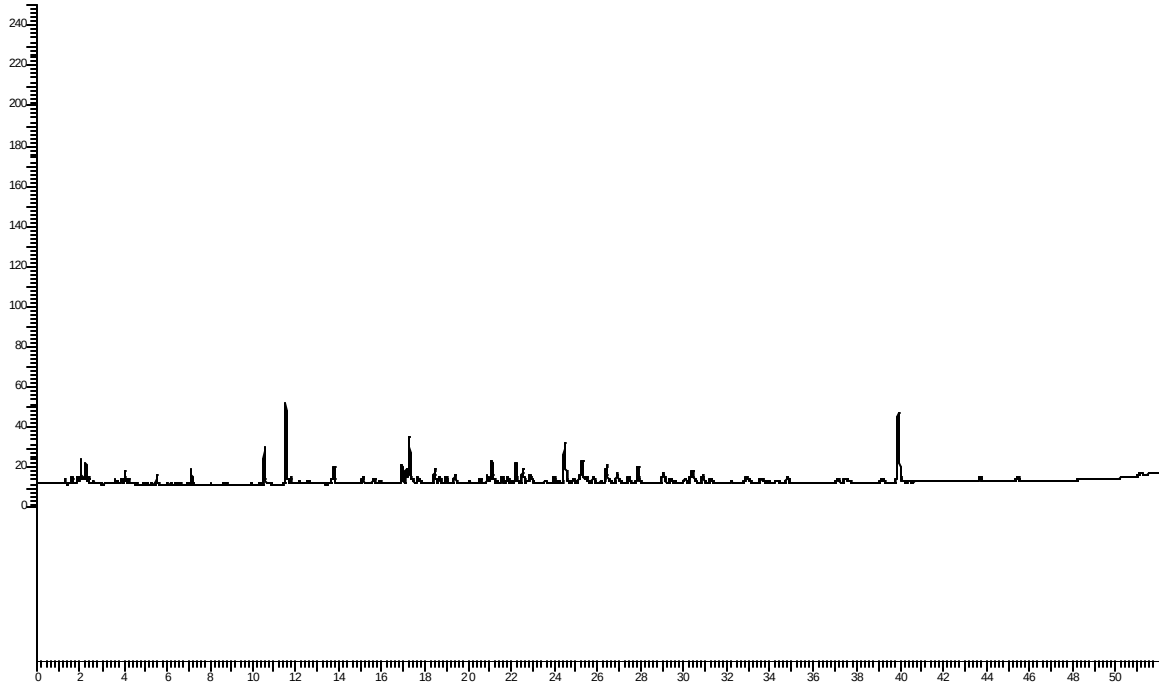
Site # 1 Elk River Station #2 Replicate "A"

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 7

Representative GC-ECD Profiles of an

SPMD "PCB" Fractions (SG1)



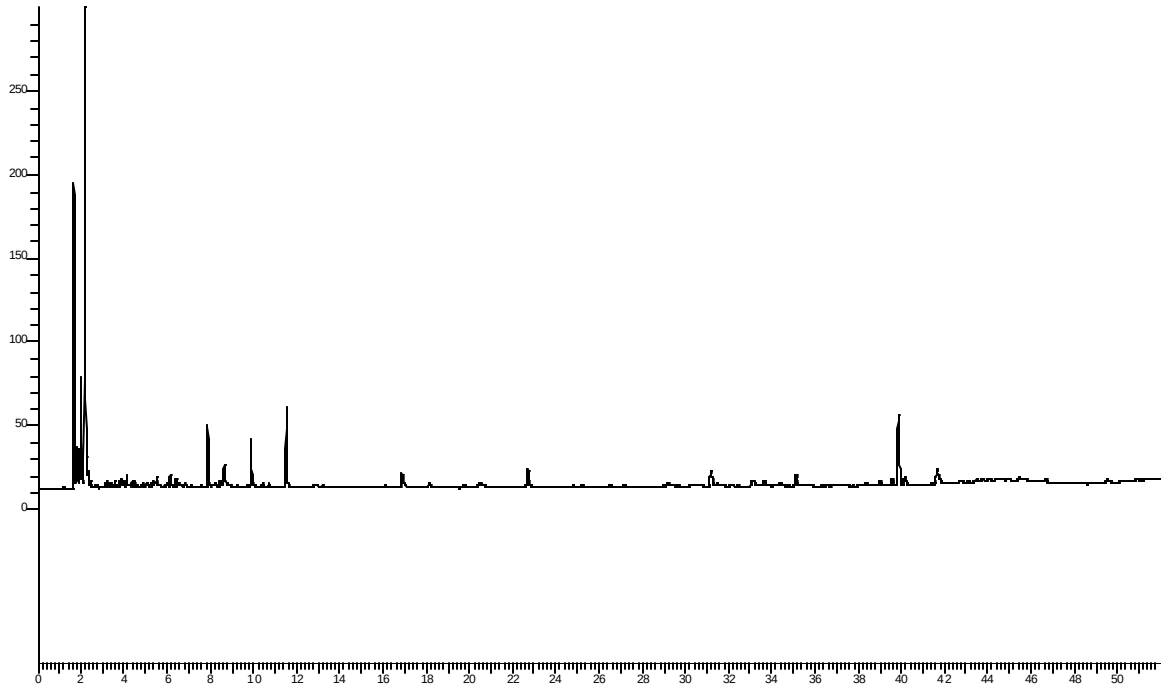
Site # 1 Elk River Station #2 Replicate "A"

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^{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).

Figure 8

Representative GC-ECD Profile of an SPMD

"Polar OC Pesticide" Fraction (FL2)



Site # 1 Elk River Station #2 Replicate "A"

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).