Analysis of SPMD Samples From The

October/November 2004 Deployment in Lake Anna, VA

for PCBs as Bioavailable Organic Contaminants

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July 27, 2005

EXECUTIVE SUMMARY

This report summarizes findings using lipid-containing semipermeable membrane devices (SPMDs) to assess the bioavailable levels of polychlorinated biphenyls (PCBs) in the waters of Lake Anna in Spotsylvania and Louisa Counties, Virginia. The work was conducted as part of a continuing collaborative effort between the U.S. Geological Survey's (USGS), Columbia Environmental Research Center (CERC), and the Virginia Department of Environmental Quality (VADEQ) to assess waterborne hydrophobic contaminants within the Commonwealth of Virginia, specifically to assess levels of PCBs in conjunction with the Lake Anna Section 206 Aquatic Ecosystem Restoration Project. CERC scientists fabricated SPMDs and VADEQ personnel deployed them for 35 days (from October 4, 2004 to November 8, 2004 or from October 5, 2004 to November 9, 2004) at ten sites in Lake Anna. SPMDs were successfully recovered from nine of the ten deployment sites within Lake Anna. VADEQ personnel subsequently returned the SPMDs to CERC where they were processed and analyzed for PCBs. Concentrations of total PCBs were present above the gas chromatographic (GC) method quantitation limit (MQL) at six of these nine study sites. Previously developed models were employed to estimate the water concentrations of PCBs within Lake Anna as given in Summary Table I of this Executive Summary. The results from the nine study sites, along with the analytical method detection limit (MDL) and MQL for total PCBs are reported herein. Limitations of the study design (e.g. number of SPMDs composited, duration of deployment, and MQL) prevented determinations of aqueous concentrations of total PCBs within Lake Anna at levels which are < 100 pg/Liter. Quality control measures employed in the processing and

analysis of the SPMDs deployed in Lake Anna support the conclusion that any PCBs present in the waters of Lake Anna at concentrations greater than 100 pg/Liter would have been quantified.

Summary Table I

Results from the Lake Anna 2004 SPMD Study

Site #	**Site Description**	**ng Total PCBs/SPMD Corrected for Background**	**Estimated water Concentration of Total PCBs (pg/Liter)**
#1	Lower North Anna	<MQL	N.D.
#2	Contrary Creek	180	1200
#3	Pamunkey Creek	1100	3400
#4	Terry's Run	59	180
#5	Upper North Anna	73	270
#6	Upper North Anna, near Goldmine Creek	SPMDs lost during deployment	
#7	Middle North Anna	<MQL	N.D.
#8	Rock Creek (Hot Side near Outfall into Cold	170	570
#9	North Anna River 100 yards below Lake Anna Dam.	57	120
#10	Terry's Run at Route 651	<MDL	N.D.

Note: "N.D." indicates that the water concentrations of PCBs were **N**ot **D**etermined because the ng/SPMD determinations at these sites were below the analytical limits of quantitation.

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INTRODUCTION

Lake Anna, in Spotsylvania and Louisa Counties, Virginia, (Figure 1) was created by the impoundment of the North Anna River in 1971 to serve as a source of coolant water for Virginia Power's nuclear plant. In April of 2004, (in conjunction with the Lake Anna Section 206 Aquatic Ecosystem Restoration Project, administered by the US Army Corps of Engineers [USACE]), staff from the Norfolk District USACE, the Virginia Department of Environmental Quality (VADEQ), and scientists from Mary Washington College in Fredericksburg, Virginia, met and discussed the problems in Lake Anna and developed methodology to identify and prioritize areas of concern within the lake and its tributaries for further investigation and possible remediation. It was determined that one of two primary problems present in the Lake Anna system was polychlorinated biphenyl (PCB) contamination. Whereas the cause of this PCB contamination was speculative, and not enough information was known to locate specific areas of concern or contamination, a plan was made to delineate areas within the lake that have elevated concentrations of PCBs and to identify and prioritize any areas of concern.

Unfortunately, there is a paucity of water concentration data for toxicologically significant waterborne contaminants such as PCBs. The levels of these very hydrophobic compounds in waters are usually below the detection limits of commonly employed low volume (i.e., $\leq$ 5 L) sampling and analytical methods. Even when high volume solid phase extraction systems are used for the analysis of environmental waters, concerns of 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 still exist. Also, episodic changes in environmental contaminant concentrations may not be detected, because sampling with

conventional methods provide data only for a single point or small window in time. To address these environmental sampling issues, scientists at the U.S. Geological Survey's (USGS) Columbia Environmental Research Center (CERC) have developed a semipermeable membrane device (SPMD) for *in situ* passive integrative sampling of biologically available aquatic contaminants, including PCBs, dissolved in a water column (1-5).

The SPMDs consisted of layflat, low-density polyethylene (LDPE) tubing containing a thin film of high-molecular weight (~800 Da), high-purity triolein. 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 suggests that only dissolved chemicals will be sampled by SPMDs, which has been confirmed by Ellis et al. (6). For compounds with log octanol-water partition coefficients (K_{ow}s) $\leq$ 6.0, the dissolved phase is the major source of residues accumulated in aquatic organism tissues (7). Also, residue transfer through the polymeric cavities in the LDPE membrane of SPMDs appears to mimic the transport of contaminants through biomembranes (8), which leads to bioconcentration of recalcitrant hydrophobic contaminants.

In theory, lipid containing SPMDs are well suited for all neutral organic compounds with log octanol-water partition coefficients (K_{ow}s) $\geq$ 3.0 (including the PCBs targeted for this project), and generally all persistent organic pollutants (POPs). Sampling of hydrophobic organic compounds with log K_{ow}s >5.0 will generally remain integrative (i.e., no significant losses of residues accumulated in the device, even when ambient concentrations fall) throughout a

standard 30 day (d) exposure period. A 1-mL triolein "standard SPMD" will passively extract hydrophobic contaminant residues from about 1 to 10 L of water per day (5). Therefore, hydrophobic contaminants may be extracted from more than 100 L of water by a single 1-mL triolein SPMD during a 30 d exposure period. When sampling is integrative and uptake is linear, residue concentrations in SPMDs represent time weighted average (TWA) concentrations of exposure water. However, sampling is often not integrative throughout a 30 d exposure period when the log K_{ow}s of compounds of interest are between 3.0 and 5.0. When performance reference compounds (PRCs; see description below) are used in SPMDs (9), ambient water concentrations can be determined even when SPMD concentrations approach equilibrium (i.e., residue uptake is curvilinear). However, the reduced amount of chemical accumulated by an SPMD during the curvilinear phase of uptake is no longer representative of integrative sampling. Differences in exposure conditions such as turbulence/flow rate, biofouling and temperature affect SPMD sampling rates. Depending on the design of the deployment apparatus used to protect SPMDs, the effects of environmental conditions on a chemical's sampling rate can be as great as an order of magnitude. Thus, site-specific *in situ* SPMD sampling rates are needed to determine ambient concentrations of chemicals from their respective levels in SPMDs. The use of PRCs as described by Huckins et al. (9) permits the estimation of *in situ* sampling rates. PRCs are compounds added to SPMD lipid prior to deployment, which have moderate to relatively high release rates over the course of a sampling period and do not interfere with the analysis of the chemicals targeted in a study. Generally, a mixture of PRCs with a range of K_{ow}s is used for environmental SPMD exposures (see "PRC Identification and Use" section for further information). Huckins et al. (9) have shown that the *in situ* rate of loss of PRCs can be used to adjust laboratory calibration data of the chemicals of concern to site-specific field conditions (5,

9). Furthermore, two different studies have shown that estimates of ambient water concentrations derived from SPMD concentrations are generally within two fold of the average concentrations of the same chemicals measured throughout the exposure period using a liquid-liquid extraction reference method (5, 6, 10).

The objectives of the work conducted by USGS CERC scientists, associated with this project, were to assess the levels of total PCBs in Lake Anna using the SPMD technology and to subsequently provide previously unattainable water column concentrations of PCBs to evaluate any impairment of water quality. In support of the objective to delineate areas within Lake Anna that have elevated concentrations of PCBs, USGS CERC scientists provided SPMDs for VADEQ to deploy at ten locations in the reservoir. After the SPMDs had been submerged at each site for 35 days, during which time they sequestered PCBs, VADEQ personnel retrieved the devices and shipped them to the USGS CERC laboratory for processing and analysis (Figure 2). The data and findings reported herein indicate that these objectives have been attained.

EXPERIMENTAL

Materials and Reagents

All laboratory chemicals were of the highest available purity (reagent grade) and organic solvents were Optima grade from Fisher Scientific Co., Pittsburgh, PA. Florisil ® (60-100 mesh) was obtained from Fisher Scientific Company, Pittsburgh, PA. The Florisil was heated at 475 ^{o}C for 8 hours, blended with 5 % (w/w) of deionized water, equilibrated at 130 ^{o}C for 48 hours, and stored at room temperature in a with P_2O_5 as a desiccant. Silica gel (SG-60, 70-230 mesh) was

obtained from Thomas Scientific, Swedesboro, NJ. The silica gel (SG) was washed with 40:60 (V:V) methyl t-butyl ether (MTBE): hexane followed by 100% hexane, then, after solvent removal, activated at 130 ^{o}C for 72 hours before use. The SG was with P_2O_5 as a desiccant. Low density polyethylene (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 Nu-Check Prep Inc., Elysian, MN. Although the purity of triolein was certified as ≥ 99% (Lot T-235-05-L), it was further purified by the method of Lebo et al. (11) prior to use in the preparation of SPMDs.

SPMD Preparation

All of the SPMDs used in this project consisted of 90-cm long by 2.5-cm wide layflat LDPE tubing (cleaned up as described by Huckins et al. [5]) containing 1.0 mL of purified triolein. The SA/V (membrane surface area to total SPMD volume) ratio of SPMDs used in this study was ≈ 90 cm^2/mL and triolein represented ≈ 20% of the mass of the SPMDs. The average weight of an individual SPMD was 4.5 g with a range of 4.4 to 4.6 g. This variation in SPMD mass was due to slight differences in the thickness of the LDPE membrane. These specifications conform to a "standard SPMD" as defined by Huckins et al. (5).

The four SPMDs and the SPMD Field Blanks, for each deployment site, were spiked with five perdeuterated compounds 1) Acenaphthylene-d_{10}, 2) Acenaphthene-d_{10}, 3) Fluorene-d_{10}, 4) Phenanthrene-d_{10}, and 5) Pyrene-d_{10}, which are performance reference compounds (PRCs). A discussion of PRCs follows. The SPMDs 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 VADEQ for deployment.

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 (5). The functional basis of the PRC approach has been previously described in detail by Huckins et al. (9). In this study Phenanthrene-d_{10} was selected for the PRC calculations as it was found to dissipate, at all sites, during deployment at greater than 20 % and less than 80 %. The rate constants for Phenanthrene-d_{10} dissipation from SPMDs at each sample site were determined and compared to PRC dissipation rate constants measured during laboratory calibration studies. The values so determined were similar for the nine sites and a mean value was used in the calculation of an exposure adjustment factor (EAF). Using the EAF ratios, calibration data for the PCBs (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, which is affected by the design of the deployment apparatus (i.e., baffling of media flow-turbulence), and 3) membrane biofouling. Based on our PRC research (9), the use of EAFs should permit the estimation of analyte water concentrations within ± 75 % of the actual time weighted average values.

Identification of Sampling Sites

Tables I and II give descriptions of site identifications and deployment conditions. Additional information on site locations is presented in Figure 1.

Sample Definition

In this study, an SPMD sample is defined as a composite of three-standard 1-mL triolein SPMDs. Thus, each site was represented by a three SPMD composite sample with one deployed SPMD kept in reserve.

Sample Transport, Storage, Deployment and Retrieval

After preparation and spiking of SPMDs with PRCs, the SPMDs were transferred to solvent-rinsed gas tight metal cans. The cans were immediately flushed with argon and sealed for storage. All cans with SPMDs were stored in a freezer at < 15 °C until shipping to VADEQ. SPMDs were shipped overnight in coolers. At each sample site (Table I, Figure 1), VADEQ personnel mounted four SPMDs into a specially prepared protective cage. Exposure periods and temperatures varied across sampling sites and deployments as shown in Table II. VADEQ personnel recorded site locations, average water temperatures, and the dates and times of deployment and retrieval. After exposures, SPMDs were recovered and sealed in the same cans as used for shipping to the field. All SPMDs, sealed in their cans, were then placed into coolers with ice and shipped overnight to CERC.

SPMD 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 as described in CERC SOP: P.453

entitled, “Documentation of Sample Receipt and Storage by Chemical Fate and Dynamics Branch.”

Sample Processing and Residue Enrichment : Sample processing was similar to published procedures (5) as described in CERC SOP: P002 entitled, “Procedure for Cleanup and Fractionation of SPMD Dialysates and Extracts of Other Environmental Samples for Chlorinated Pesticides, PAHs, PCBs and Other Targeted Contaminants,” with abbreviated details noted in the following sections (Figure 2).

SPMD Membrane Cleaning: The exterior membrane surfaces of all SPMDs were cleaned prior to dialysis. Sealed cans with SPMDs were opened and the SPMDs were removed and momentarily immersed (< 30 sec.) in 100 mL of hexane. Then the SPMDs were washed thoroughly to remove all remaining surface adhering material. Any SPMD tether loops outside the lipid containment seals were cut away and discarded. The SPMDs were then immersed in a glass tank containing 1-N HCl for approximately 30 seconds. Subsequently, they were rinsed with tap water to remove the acid. All surface water was removed from individual SPMDs by successive rinses of acetone followed by isopropanol.

SPMD Dialysis (i.e., Recovery of Analytes): Each SPMD was submersed in 175 mL of hexane in glass jars and was dialyzed individually at 18 ^{o}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 ^{o}C. The second dialysate was transferred into the flask containing the first dialysate. The dialysates from three SPMDs

from each deployment site were combined into a composite. These were reduced to 3 to 5 mL by rotary evaporation, filtered, and quantitatively transferred into test tubes. The solvent volume was then reduced to about 1.0 mL, using high purity nitrogen.

SEC Cleanup: The size exclusion chromatography (SEC) cleanup of study samples followed CERC SOP p.588 entitled, "The Use of Size Exclusion Chromatography (SEC) in the Cleanup of Dialysates from SPMDs and Other Extracts." A Perkin-Elmer Series 410 HPLC (Perkin-Elmer, Inc., Norwalk, CT) was employed as the solvent delivery system. This HPLC unit was equipped with a Thermo Finnigan AS3000 variable-volume injection auto sampler (Thermo Finnigan, Inc. San Jose, CA). 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. A DFW-20 series fixed wavelength UV absorption detector (D-Star Instruments, Inc. Manasses, VA) operating at 254 nm, a Hewlett-Packard Co, HP 3396 Series II Integrator (Hewlett Packard, Inc., Palo Alto, CA), and an ISCO Foxy® 200 (ISCO, Inc., Lincoln, NE) fraction collector completed the SEC system. The isocratic mobile phase was 98:2 (V:V) dichloromethane:methanol (DCM:MeOH) with a flow rate of 4.0 mL per minute.

In keeping with CERC SOP p.588, the SEC system was calibrated on a daily basis using compounds of environmental interest and potentially interfering materials. These compounds, in sequence of elution, were 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). 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. The fractions collected were amended with approximately 2 mL of isooctane, reduced to a volume of about 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 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. 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 (in SG-1) and PRCs (in SG-2).

Gas Chromatographic Analysis of PRCs: Analyses of SG-2 Fractions for PRCs was conducted on 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. Analysis of the SG-2 fractions was performed using a DB-5 (30 m x 0.25 mm i.d x 0.25 μm film thickness.) capillary column (J&W Scientific, Folsom, CA) with the following temperature program: injection at 60^{o}C with a 2 minute hold at 60^{o}C, then 10^{o}C/min to 110^{o}C and held for 5 minutes at 110^{o}C, followed by 3^{o}C/min to 200^{o}C and held for 10 minutes at 200^{o}C, then 4^{o}C/min to 310^{o}C and held at 310^{o}C for 3 minutes. Detection was performed using a Hewlett Packard flame ionization detector (FID) operating at 330^{o}C. Quantitation was accomplished using an

eight point calibration curve spanning a 50-fold range of concentration from 0.2 to10 µg/mL for each of the five perdeuterated PRCs. 4-Terphenyl- d_{14} was used as the instrumental internal standard (IIS). Figures 3 and 4 show representative chromatograms of field blank SPMDs, and deployed SPMDs analyzed for PRCs.

Gas Chromatographic Analysis of PCB Congeners: Gas chromatographic analyses of SG-1 fractions for PCB congeners were conducted using a Hewlett Packard 5890 series II gas chromatograph (GC) equipped with two Hewlett Packard 7673A autosamplers (Hewlett Packard, Inc., Palo Alto, CA) to allow for dual column injection. In all analyses, 1.0 µL of sample extract was injected using the "cool-on-column" technique with hydrogen as the carrier gas (25 psig). Analyses were performed using both a DB-5 (60 m x 0.25 mm i.d. x 0.25 µm film thickness) capillary column (J&W Scientific, Folsom, CA) and a DB-17 (60 m x 0.25 mm i.d. x 0.25 µm film thickness) capillary column (J&W Scientific, Folsom, CA) with the following temperature program: injection at 60 ^{o}C; then ramped at 15 ^{o}C/min to 150 ^{o}C; followed by 1 ^{o}C/min ramp to 260 ^{o}C; and finally ramped at 10 ^{o}C/min to 300 ^{o}C with a final hold of 15 minutes at 300 ^{o}C. The electron capture detectors (ECDs, Hewlett Packard, Inc., Palo Alto, CA) were maintained at 330 ^{0}C with nitrogen at 55-60 mL/minute as make-up gas. Individual PCB congeners were identified on one or both GC capillary columns based upon known retention times for each congener in the calibration standards. The best resolved peak was picked from the column giving the best resolution, with some congeners being analyzed on both columns for confirmatory analysis. A 1:1:1:1 mixture of Aroclor® 1242, 1248, 1254, and 1260 was used to produce the PCB congener calibration standards. These standards were quantified based on pure primary PCB standards (Accustandard, New Haven, CT) and were used as secondary standards

(12) at five calibration levels to quantify up to 140 congeners and combined congener peaks in the study samples by an internal standard method. The levels of the PCB standards spanned a 160-fold concentration range from 50 to 8,000 total ng/mL. PCB congener I-30 was employed as the instrumental internal standard, and congeners I-30 and I-207 were used as retention time references. Determinations for total PCBs sequestered in deployed SPMDs were measured as the sums of the individual analytical responses from 140 individual PCB congeners as detected during GC-ECD analysis. Figures 5, 6, and 7 show representative chromatograms of SG-1 fractions for standards, field blank SPMDs, and deployed SPMDs analyzed for PCBs.

Quality Control: Field blank SPMDs accompanied the SPMDs deployed in Lake Anna. Field-blank SPMDs were used to determine if SPMDs were contaminated or losses of PRCs occurred during transport, deployment and retrieval. The field-blank SPMDs were treated the same as the deployed devices (more specifically, field blanks were exposed to study site air during the intervals of time required to mount, deploy and retrieve SPMDs from the various exposure sites), except that they were not exposed to study-site water. During the exposure intervals, field-blank SPMDs were sealed back in the same shipping cans and stored frozen by VADEQ personnel. The primary purpose of PRC spiked field-blanks is to provide a sample representative of the amount (N_o) of individual PRCs present in SPMDs at time zero (see Equation 10 in section on "Estimation of Water Concentrations from SPMD Levels"). Field blanks were processed and analyzed exactly like exposed SPMDs. The field blank samples exhibited no coincident GC peaks at levels significantly higher than those associated with the laboratory control SPMDs (i.e. matrix blank) and were indicative of successful deployments and retrievals (Table III).

The method detection limit (MDL) and method quantitation limit (MQL) for analysis of SPMD samples were determined for total PCBs by measuring the values of coincident GC-ECD peaks for all PCB congeners in blank samples processed with this study (Table III). The MDL was defined as the mean plus three standard deviations of values so determined (13). The MQL was defined as the mean plus 10 standard deviations of values so determined (13).

Although all of the aforementioned blanks are checks on different aspects of QC, we limit the use of "QC checks" to the following types of spikes: 1) daily (each operation day) injection of a known quantity of ^{14}C-surrogate (e.g., ^{14}C-phenanthrene) to evaluate of the performance of and the recovery through the SEC system; 2) spikes (e.g., ^{14}C-phenanthrene) of SPMD blanks to monitor dialytic recovery of each set of exposed SPMDs and to measure recovery through the dialysis, SEC, etc. steps, and 3) a matrix spike. This final QC check monitored the recovery of PCBs through the entire dialysis, fractionation and enrichment procedures by spiking a blank SPMD (i.e. a matrix spike) with a known quantity of PCBs (nominal amount of total PCBs was 5000 ng) and measuring recovery following dialysis, SEC, Florisil, and Silica Gel chromatographic cleanup. Thus, a QC check sample can represent individual cleanup and fractionation steps, as well as the entire procedure. These QC samples are designed to demonstrate acceptable outcomes of sample analyses (14).

RESULTS AND DISCUSSIONS

QC of Analytical Procedures: During cleaning of exposed SPMDs, no holes were found in the membranes, thereby demonstrating that the deployment cages used by VADEQ personnel

prevented punctures of the SPMDs during the 35 day exposures. Also, amounts sufficient to quantify at least one PRC (typically pyrene or phenanthrene) remained in SPMD samples, at the end of exposures at all sites. Visual inspection of SPMDs during processing indicated that membrane biofouling varied only slightly by site. No attempt was made to quantify these slight differences, because biofouling impedance of residue uptake is largely reflected by the magnitude of PRC sampling rates at each site.

SPMD Field blanks exhibited no coincident GC peaks at levels significantly higher than those associated with SPMD fabrication blanks and process blanks (i.e., controls). This finding demonstrated that no inadvertent SPMD contamination occurred during storage, shipping, deployment and retrieval. Thus, residues above those quantified in field-blank SPMDs did indeed originate from the water of study sites. During the processing and cleanup of samples, QC check samples for dialytic recovery, SEC performance, etc., and spiked SPMD blank samples for overall method recoveries gave results which were consistent with control limits (15) established at CERC for these processes (Figure 2). Recovery of ^{14}C-phenanthrene through the SEC system was 94 and 97 % (two runs). Recovery of ^{14}C-phenanthrene from the ^{14}C-phenanthrene spiked SPMD through dialysis and SEC was 92 %. Recovery of total PCBs through the entire processing sequence (Table III) was 82 %. These values are consistent with values typically obtained at CERC (15).

Observations and Findings: The reported values of PCB levels (Table IV) are from SG-1 fraction analyses only. The monochloro and dichloro PCB congeners elute from silica gel, in part or in whole, in the SG-2 fraction. The SG-2 fraction was not included in the analyses for total

PCBs because historic CERC data shows that carry-over of these congeners into SG-2 (using the materials and methods described in this report) represents less than 5 % of total PCBs. This level of potential processing loss was not considered to be significant in the determinations of total PCB levels where reported results were not corrected for recovery and were reported to only two significant figures. A more rigorous analysis, including determination of PCBs in the SG-2 fraction, was beyond the scope of this project.

During the gas chromatographic analysis of study samples for total PCB levels, as a sum of individually measured PCB congeners, two GC columns were used to obtain sufficient resolution for quantitation of the individual PCB congeners. Quantitation for each congener was done using the column giving the better resolution where the second column then became the conformational analysis (Table V). The results of the gas chromatographic analyses of the deployed SPMDs are given in Tables IV. The results of the gas chromatographic analyses of the deployment SPMDs are given for all PRCs in Table VI.

Total PCB analyses results are corrected for background, but are not corrected for recovery and therefore represent minimum levels of PCBs within the aquatic environments of Lake Anna. The backgrounds, MDLs, and MQLs (Table III) are given in units of ng/3-SPMD composite (because this is representative of the sample size and matrix as injected), SPMD analysis results (Tables IV) are given in units of ng/SPMD. Raw results (after subtracting out background) were divided by three to give these values. These units were used because they are applicable to deriving water concentrations from modeling equations.

Estimation of Water Concentrations from SPMD Amounts: In order to estimate water concentrations from SPMD amounts with a reasonable degree of certainty, several conditions must be met. First, the amounts of targeted contaminants and one or more PRCs must be accurately measured in exposed SPMDs. Second, appropriate calibration data for both target compounds and PRCs must be available. Third, site specific *in situ* sampling rates must be derived for target compounds using exposure adjustment factors (EAFs; see Equation 11). The EAF is a site specific ratio that is approximately equivalent to the *in situ* sampling rate of a selected PRC divided by the sampling rate of the same PRC from calibration data (6). A large amount of SPMD-calibration data is available along with the equations needed for estimating water concentrations from SPMD data (16). Measured amounts of PRCs and analytes in SPMD samples, and previously reported equations and calibration data (2, 5, 6), were used to extrapolate the concentrations of dissolved-phase (i.e., concentration of residues that are readily available) contaminants in water from study sites. Because the exchange of hydrophobic chemicals into SPMDs from water has been shown to be isotropic (2, 5, 6), the following first-order equation can be used to describe the overall accumulation of residues by SPMDs.

$$N = V_s K_{sw} C_w (1-\exp[-R_s t/V_s K_{sw}]) \quad (1)$$

and

$$C_w = N/(V_s K_{sw}[1-\exp(-R_s t/V_s K_{sw})]) \quad (2)$$

where N is the amount of the chemical sampled by an SPMD (typically ng), V_s is the volume of an SPMD (L), K_{sw} is the equilibrium SPMD-water partition coefficient (unitless), C_w is the

concentration of the chemical in ambient water, R_s is the SPMD sampling rate (L/d) and t is the exposure time (d). Equations 1 and 2 are more familiar when the exponent is given as $k_e t$, where k_e is the loss or dissipation rate constant (t^{-1}). Thus, k_e is

$$k_e = R_s/K_{sw}V_s \quad (3)$$

Equations 1 and 2 can be used for all three uptake phases of SPMDs, which include linear, curvilinear and equilibrium. During the linear uptake phase the exponent $R_s t/K_{sw}V_s$ is << 1 and the uptake rate constant is R_s/V_s. In this case, Equation 2 reduces to

$$C_w = N/R_s t \quad (4)$$

When Equation 4 applies, sampling is integrative or the amount of residues accumulated are additive and water concentrations represent TWAs. Typically, SPMD sampling is in the linear phase of uptake for compounds with log K_{ow} values ≥ 5.0 and exposures periods of up to one month.

In the case where the exponent $R_s t/K_{sw}V_s$ is >> 1, equilibrium is attained and Equation 2 reduces to

$$C_w = N/K_{sw}V_s \quad (5)$$

When Equation 5 applies to SPMD data, targeted chemicals have reached their maximum concentrations in SPMDs for a particular exposure concentration. Typically, SPMD sampling is in the equilibrium phase of uptake for compounds with log K_{ow}s ≤ 4.0 and exposure periods of one month or more.

When SPMDs are in the curvilinear region of uptake, Equation 2 must be used as is to estimate C_w. In terms of first-order half-lives ($t_{1/2}$s), the curvilinear phase of chemical uptake is operationally defined as the region time that exists between one $t_{1/2}$ and four $t_{1/2}$s. Note that for first-order kinetics, one $t_{1/2}$ is equivalent to

$$t_{1/2} = 0.693\ K_{sw}V_s/(R_s\ EAF) \qquad (6)$$

and four $t_{1/2}$s are equivalent to

$$4t_{1/2} = 2.772\ K_{sw}V_s/(R_s\ EAF) \qquad (7).$$

In this study, C_w was determined by Equation 4 when exposure time was ≤ one $t_{1/2}$ of an analyte, Equation 5 when exposure time was ≥ four $t_{1/2}$s of an analyte, and Equation 2 when exposure time was between one and four $t_{1/2}$s of an analyte. Estimation of a chemical's *in situ* $t_{1/2}$ in an SPMD and its ambient C_w at each sample site requires the derivation of the EAF (see Equation 11 below), as described by Huckins et al. (6). A key feature of the EAF is that it is relatively constant for all chemicals that have the same rate-limiting barrier to uptake. Measurement of the amount of a suitable PRC at the beginning and end of the exposure period is the first step in this process. The following equations are used to estimate the EAF for each exposure site.

$$N = N_o \exp(-k_{eP}t) \quad (8)$$

and by substituting the group $R_{sP}/K_{sw}V_s$ (Equation 3) for k_e

$$N = N_o \exp(-R_{sP}t/K_{sw}V_s) \quad (9)$$

Solving for R_{sP}

$$R_{sP} = K_{sw}V_s - (\ln [N/N_o])/t \quad (10)$$

and

$$EAF \approx R_{sP}/R_{sC} \quad (11)$$

Where N_o is the amount of a PRC in an SPMD just before deployment, N is the amount of PRC remaining in the SPMD following the exposure, R_{sP} is the calculated SPMD sampling rate for a PRC under a specific set of field or site conditions and R_{sC} is the measured sampling rate (i.e., from SPMD calibration studies) of the native equivalent of the deuterated PRC. Then the *in situ* or site specific sampling rate (R_{si}) of an analyte is the EAF times its laboratory calibration R_{sC}. An earlier study (6) has found that water concentration estimates based on EAFs were within two-fold of independently measured values.

Before SPMD uptake rates can be estimated from PRC loss rates, K_{sw} must be known or calculated for contaminants of interest. The finding that K_{sw} is independent of temperature

between 2 °C and 30 °C (16) greatly simplifies the determination of analyte K_{sw} values. In this study, two separate regression equations were required for the calculation K_{sw}s (5, 6)

$$\log K_{Lw} = -0.1257 (\log K_{ow})^2 + 1.9405 (\log K_{ow}) - 1.46 \quad (12)$$

and

$$\log K_{mw} = -0.0956 (\log K_{ow})^2 + 1.7643 (\log K_{ow}) - 1.98 \quad (13)$$

and

$$K_{sw} = (K_{Lw}V_L + K_{mw}V_m)/V_s \quad (14)$$

where K_{Lw} is the equilibrium lipid (triolein)-water partition coefficient, K_{mw} is the equilibrium membrane (LDPE)-water partition coefficient, V_L is the volume of lipid in the SPMD, and V_m is the volume of membrane. The standard deviations (S.D.s) for the fits of Equations 12 and 13 to literature data were 0.18 and 0.23, respectively. Equations 2, 4-8, and 10-14 have been incorporated into an Excel based calculator (5) for the estimation of water concentrations and the calculator was used for water concentration estimates in this work (see results in Table VII).

At this writing, a regression model has been developed (17) that combines data from Equations 12-14.

$$\log K_{sw} = -0.1618(\log K_{ow})^2 + 2.321 \log K_{ow} + a_o \quad (15)$$

where a_o is –2.61 for nonpolar compounds and –3.20 for moderately polar pesticides. The S.D. of the fit is 0.25 and the correlation coefficient $r^2 = 0.94$. Equation 15 will greatly simplify computation of K_{sw}s in future studies.

PRC Data: Exposure conditions varied in this study (Table II). To reduce the probability of scenarios where the amount of PRC residues remaining in SPMDs after exposures is too little or too great to measure significant differences between time zero and final concentrations, we chose five deuterated PAHs for this study with a 10-fold range in their K_{ow}s (i.e., log K_{ow} of acenaphthylene-d_{10} ≈ 4.0 and log K_{ow} of pyrene-d_{10} ≈ 5.0). Because the rates of release of hydrophobic organic compounds from SPMDs are inversely proportional to compound K_{ow} (2, 5, 6, 10), it seemed probable that the concentration of at least one of the five PRCs used would be representative of a 20 to 80 % change in the time zero concentration (i.e., the criteria proposed by Huckins et al [5] for the acceptability of PRC data). The upper limit of an acceptable change from time zero concentration was set at 80 % because of the concern that concentrations would fall below the MQL for the PRC. Generally, concentrations of acenaphthylene-d_{10}, acenaphthene-d_{10}, and fluorene-d_{10} in exposed SPMDs were below their MQLs at all sites. Although these PRCs could not be used for the determination of EAFs, their almost complete dissipation suggest that target compounds with equivalent K_{ow}s would have approached or attained equilibrium during these exposures. Concentrations of phenanthrene-d_{10} in SPMDs were well above the MQLs at all sites and represented a 40-83 % change from time zero. Therefore, phenanthrene-d_{10} was used to calculate EAFs at all exposure sites. In Table VI, the results of phenanthrene-d_{10} analyses are given in terms of the rate constant k_{eP}, which is equivalent to $R_{sP}/K_{sw}V_s$. Values of k_{eP}s can be readily converted into *in situ* R_{sP}s by the following equation

$$R_{sP} = k_{eP}K_{sw}V_s \qquad (16)$$

Values of phenanthrene-d_{10} k_{eP}s ranged from 0.015 to 0.051 (≈ 3.4-fold difference). The calibration data (k_{ec}s or R_{sc}s) used for PRCs were generated under conditions as follows: a flow velocity of 0.004 cm/sec and at temperatures of 10, 18 and 26 °C (5).

Water concentrations were thusly calculated (Table VII) for the study sites in Lake Anna.

Comments on SPMD Concentration Data: The results of the analyses of SPMDs exposed to Lake Anna, Virginia water are given in Table IV. These data have been corrected for the backgrounds of appropriate field blank samples and subsequently used to calculate total PCB water concentrations (Table VII). The high recovery (Table VI) of pyrene-d_{10} (a PRC) indicates that photolysis of PRC did not occur during deployment and that the EAFs used in calculating water concentrations are accurate. In addition to the inherent limitations of estimation of water concentrations by application of SPMD technology (i.e. the two-fold margin of error), the utility of this technology is further limited by three other factors, 1) Sample size, i.e. number of SPMDs used, 2) Length of deployment, and 3) sensitivity of the analytical method used to determine the levels of contaminants sequestered. Insertion of the total PCB MQL value (Table IV), with adjustment of units to ng/SPMD, into the Excel calculator for water concentration estimations gives minimum values at which water concentrations can be estimated under the specific conditions as they existed during the deployment phase of this study. Because the value of k_{eP}s is specific for each site, an average value was applied to the MQL for the 35-day deployments associated with this study using a three SPMD composite. This exercise demonstrates that any PCBs in Lake Anna, present at levels above 100 ng/Liter, would have provided sufficient PCBs

to be measured at quantifiable levels to allow for estimation of waterborne concentrations using SPMD technology.

Aqueous concentrations of PCBs in Lake Anna were only observed at two sites at greater than 1.0 ng/Liter (Table VII). The elucidation of the potential biological effects from exposure to these levels of PCBs will require further research. The water concentrations of the PCBs found in these samples may be of concern.

ACKNOWLEDGEMENTS

We gratefully acknowledge the funding of the US Army Corps of Engineers and the Virginia Department of Environmental Quality. We specifically acknowledge the support of Roger Stewart and other Virginia Department of Environmental Quality personnel involved in the deployment, retrieval, shipment, and delivery of these samples to CERC for processing and analysis.

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Table I

2004 Lake Anna SPMD Deployment Locations

Site #	Description	Latitude	Longitude	River Mile
#1	Lower North Anna	38° 00’ 48.2”	077° 42’ 54.5”	8-NAR034.92 *
#2	Contrary Creek	38° 03’ 50.6”	077° 51’ 18.0”	8-CON003.86
#3	Pamunkey Creek	38° 07’ 37.3”	077° 51’ 03.0”	8-PMC002.14
#4	Terry’s Run	38° 08’ 23.3”	077° 53’ 06.4”	8-TRY000.59
#5	Upper North Anna	38° 06’ 17.5”	077° 51’ 48.1”	8-NAR052.59
#6	Upper North Anna, near Goldmine Creek	38° 06’ 50.0”	077° 55’ 50.8”	8-NAR057.58
#7	Middle North Anna	38° 05’ 27.4”	077° 48’ 51.4”	8-NAR047.57 *
#8	Rock Creek (Hot Side near Outfall into Cold side)	37° 59’ 44.1”	077° 44’ 57.9”	8-RCK002.48
#9	North Anna River 100 yards below Lake Anna Dam.	38° 00’ 46.0”	077° 42’ 35.8”	8-NAR034.41
#10	Terry’s Run at Route 651	38° 10’ 08.1”	077° 54’ 57.0”	8-TRY003.46 *

* Existing station. Stations were not at the exact location, but were within a tenth of a mile.

Note: See Figure 1 for map of study sites deployment locations.

Table II

2004 Lake Anna SPMD Deployment Conditions

Site #		Date / Time	Depth	Temp. (ºC)	pH	Specific Conductivity (us/cm)
#1	Deployed	10/4/04 13:40	49 ft.	25.4	7.2	38.0
	Retrieved	11/8/04 14:10	50 ft.	19.5		
#2	Deployed	10/4/04 12:20	5 ft.	23.7	4.13	121
	Retrieved	11/8/04 13:30	3 ft.	13.1	6.15	
#3	Deployed	10/4/04 10:50	27 ft.	22.9	7.47	57.7
	Retrieved	11/8/04 11:50	27 ft.	16.14		
#4	Deployed	10/4/04 10:05	5 ft.	22.3	7.91	59.3
	Retrieved	10/4/04 11:30	6 ft.	14.98		
#5	Deployed	10/4/04 11:20	21 ft.	23.1	7.41	57.3
	Retrieved	11/8/04 12:10	22 ft.	16.0		
#6	Deployed	10/4/04 12:20	12 ft.	22.6	8.48	62
	Retrieved	11/8/04 12:30	Not retrieved – was not at site.			
#7	Deployed	10/4/04 13:25	21 ft.	24.1	7.35	57.0
	Retrieved	11/8/04 13:10	22 ft.	16.7		
#8	Deployed	10/5/04 10:55	29 ft.	25.5	7.36	56.1
	Retrieved	11/9/04 10:45	30 ft.	21.2		
#9	Deployed	10/5/04 12:25	4 ft.	24.1	7.65	56.0
	Retrieved	11/9/04 12:00	2 ft.	18.6		
#10	Deployed	10/5/04 14:15	4 ft.	18.2	7.12	82.6
	Retrieved	11/9/04 12:55	4 ft.	10.6		

Table III

2004 Lake Anna SPMD Study, Quality Control Results

(Total PCBs by GC-ECD Analysis)

QC Sample Description	ng/3-SPMD Composite
Field Blank # 1	51
Field Blank # 2	65
Field Blank # 3	54
SPMD Fabrication Blank	87
SPMD Processing Blank	45
Average (i.e. Background) =	61
Stdev =	17
MDL =	110
MQL =	230
PCB Spike Verify	5200
SPMD PCB Spike	4270
Recovery =	**82 %**

Table IV

2004 Lake Anna SPMD Study Results

(Total PCB by GC-ECD Analysis)

Site Identification	**ng/SPMD Corrected for Background**
Site # 1	<MQL
Site # 2	180
Site # 3	1100
Site # 4	59
Site # 5	73
Site # 7	<MQL
Site # 8	170
Site # 9	57
Site # 10	<MDL
MDL =	17 ng Total PCB above Background
MQL =	56 ng Total PCB above Background

Table V

GC-ECD Congener Specific Analysis for PCBs

Column Selection by Congener

Congener Identification	Analytical Column	Congener Identification	Analytical Column	Congener Identification	Analytical Column	Congener Identification	Analytical Column
001	DB-17	048	DB-17	109	DB-5	170	DB-5&17
003	DB-17	049	DB-5	110	DB-5	171	DB-17
004	DB-17	051	DB-17	112	DB-5	172	DB-5
005	DB-17	052	DB-5	113	DB-5	173	DB-5
006	DB-17	053	DB-5	114	DB-17	174	DB-17
007	DB-17	054	DB-17	115	DB-17	175	DB-5
008	DB-17	055	DB-17	117	DB-5	176	DB-17
009	DB-17	056,060	DB-5	118	DB-5	177	DB-5
010	DB-17	057	DB-5	119	DB-17	178	DB-5
011	DB-17	058	DB-5	122	DB-17	179	DB-5
015	DB-17	063	DB-17	123	DB-5	180	DB-5
016	DB-5&17	064	DB-17	128	DB-5	183	DB-17
017	DB-5&17	066	DB-17	129	DB-5	185	DB-17
018	DB-5	067	DB-17	130	DB-17	187	DB-5
019	DB-5	069	DB-17	131	DB-17	189	DB-5
020	DB-17	070	DB-5	132	DB-17	190	DB-5&17
022	DB-5	071	DB-5	133	DB-5	191	DB-5
024	DB-5&17	072	DB-5	134	DB-5	193	DB-5
025	DB-5	074	DB-5	136	DB-5	194	DB-5
026	DB-17	075	DB-5	137	DB-5	195	DB-17
027	DB-17	082	DB-5	138	DB-17	196	DB-5
028	DB-5&17	083	DB-17	139	DB-17	197	DB-5
031	DB-17	084	DB-5	141	DB-5	198	DB-5
032	DB-17	085	DB-5	144	DB-17	199	DB-5
033	DB-17	086	DB-5	146	DB-5	200	DB-5
034	DB-5	087	DB-17	147	DB-5	201	DB-5
035	DB-5	090	DB-17	149	DB-5	202	DB-17
037,059	DB-5	091	DB-5	151	DB-5	203	DB-17
040	DB-17	092	DB-5	153	DB-5&17	205	DB-5
041	DB-17	095	DB-5&17	156	DB-5&17	206	DB-17
042	DB-17	096	DB-5	157	DB-5	208	DB-17
043	DB-5	097	DB-5	158	DB-5	209	DB-5&17
044	DB-5	099	DB-17	163	DB-17		
045	DB-5	101	DB-17	164	DB-17		
046	DB-5	102	DB-5	166	DB-5		
047	DB-5&17	105	DB-17	167	DB-5		

NOTE: Dual column analysis required for complete resolution and quantification of individual congeners.

Table VI

2004 Lake Anna Study

Results of GC-FID Analysis of SG2 Fractions and Determinations of k_{e-P}

(µg/SPMD)

	Acenaphthylene-d_{10}	Acenaphthene- d_{10}	Fluorene- d_{10}	Phenanthrene- d_{10}	Pyrene- d_{10}
Fab Blank	1.47	1.63	1.74	2.02	2.55
FB #1	1.54	1.71	1.84	2.17	2.55
FB #2	1.60	1.78	1.92	2.21	2.67
FB #3	1.56	1.73	1.85	2.17	2.63
Mean =	1.54	1.71	1.84	2.14	2.60
STDEV =	0.05	0.06	0.07	0.08	0.06
% RSD =	3.5	3.6	4.0	3.9	2.3
Site # 1	0.02	0.04	0.15	0.47	1.86
Site # 2	0.03	0.18	0.35	0.98	1.98
Site # 3	0.00	0.01	0.16	0.43	1.82
Site # 4	0.00	0.01	0.10	0.42	2.04
Site # 5	0.00	0.04	0.16	0.54	1.98
Site # 7	0.00	0.02	0.10	0.42	2.01
Site # 8	0.00	0.00	0.14	0.49	1.83
Site # 9	0.00	0.00	0.00	0.36	1.80
Site # 10	0.06	0.17	0.46	1.28	2.41

k_{e-P} Values from PRC Phenanthrene- d_{10} data

Site Identification	**k_{e-P} (d^{-1})**	**k_{e-cal} (d^{-1})**
Site # 1	0.043	0.021
Site # 2	0.022	0.021
Site # 3	0.046	0.021
Site # 4	0.047	0.021
Site # 5	0.039	0.021
Site # 7	0.047	0.021
Site # 8	0.042	0.021
Site # 9	0.051	0.021
Site # 10	0.015	0.021

Note: $k_{e-P} = [\ln(C_{SPMDo}/C_{SPMD})]/t$ where t = 35 d,
and k_{e-cal} for Phenanthrene d_{10} is 0.021 d^{-1}

Table VII

2004 Lake Anna Study

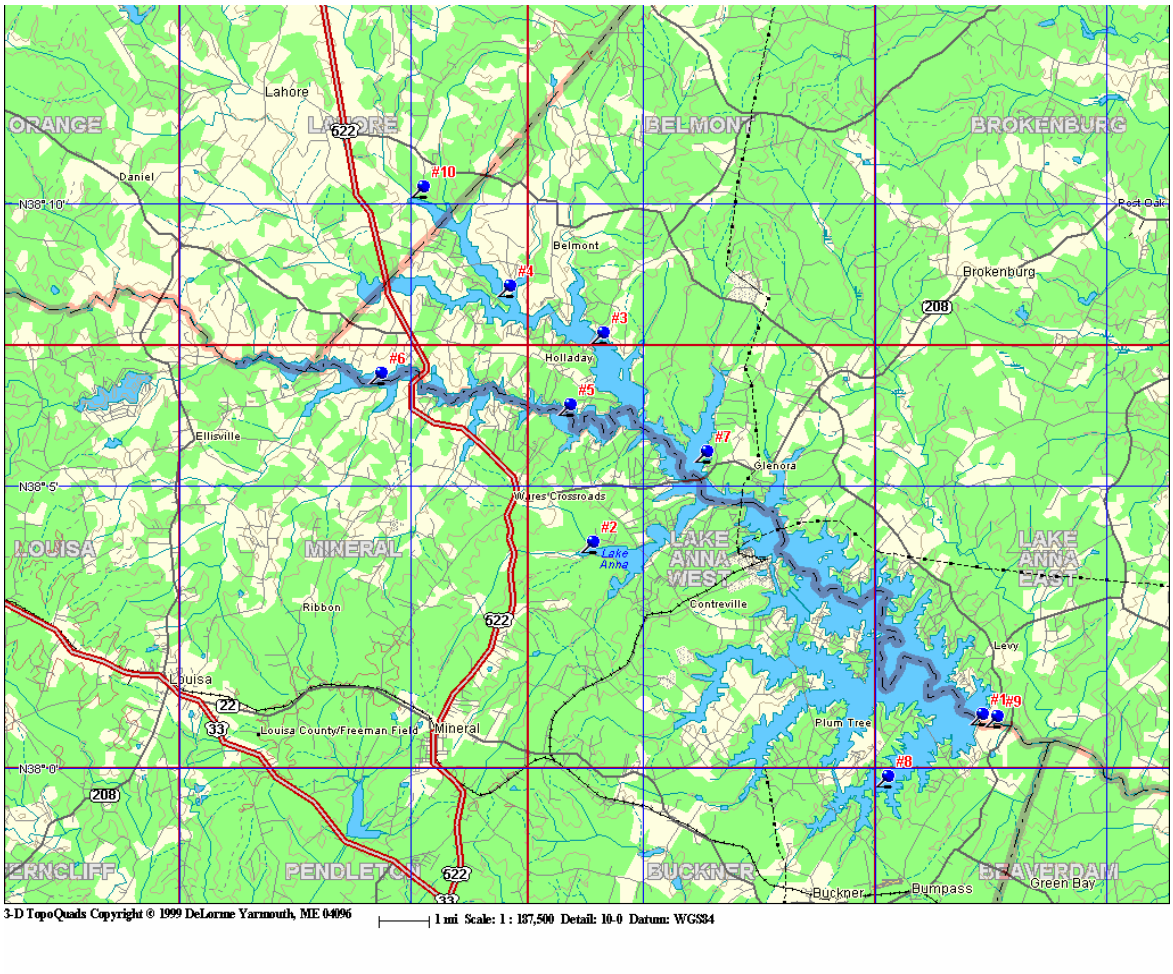
Total PCB Water Concentrations Derived from SPMD Data

Site Identification	**pg/Liter**
Site # 1	N.D.
Site # 2	1200
Site # 3	3400
Site # 4	180
Site # 5	270
Site # 7	N.D.
Site # 8	570
Site # 9	120
Site # 10	N.D.

Note: "N.D." indicates that the water concentrations of PCBs were **N**ot **D**etermined because the ng/SPMD determinations at these sites were below the analytical limits of quantification.

Figure 1

2004 Lake Anna SPMD Deployment Locations



Study Site Identification	Field Location Description
#1	Lower North Anna
#2	Contrary Creek
#3	Pamunkey Creek
#4	Terry's Run
#5	Upper North Anna
#6	Upper North Anna, near Goldmine Creek (SPMDs Lost during deployment)
#7	Middle North Anna
#8	Rock Creek (Hot Side near Outfall into Cold side)
#9	North Anna River – 100 yards below Lake Anna Dam.
#10	Terry's Run at Route 651

Figure 2

SPMD Processing Scheme for PCB Analysis

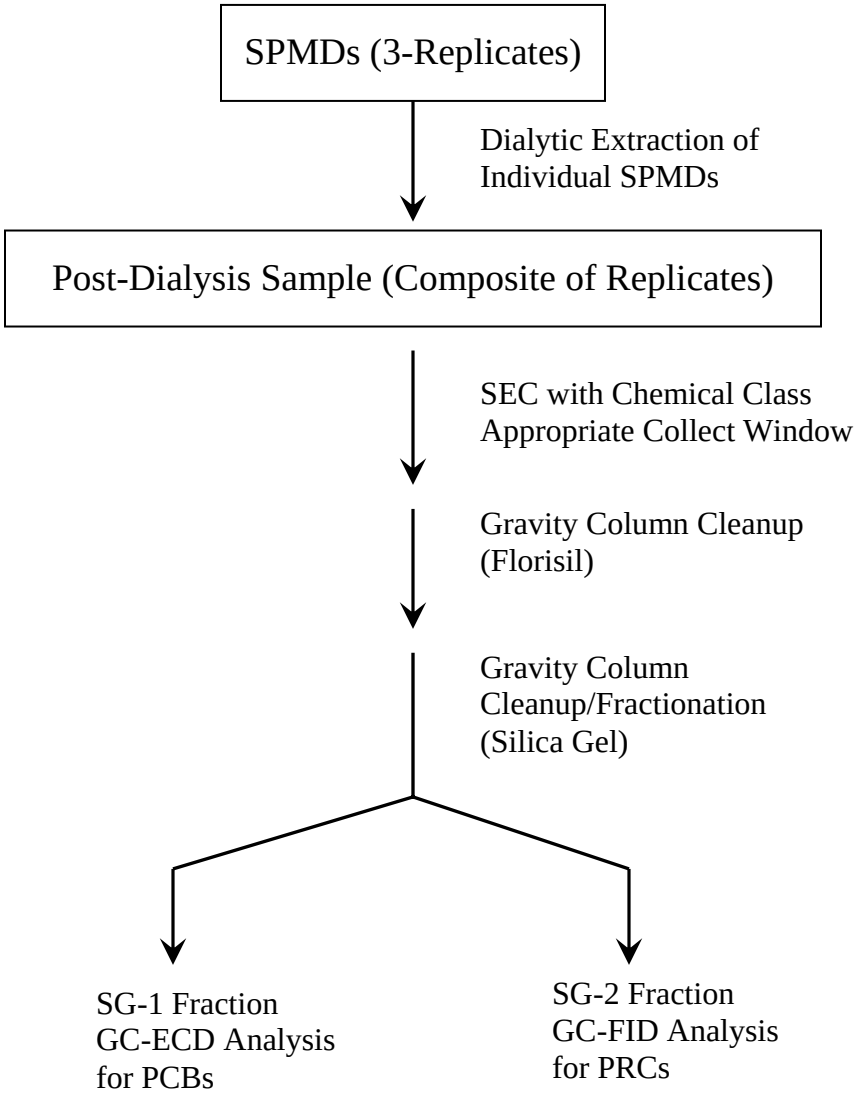
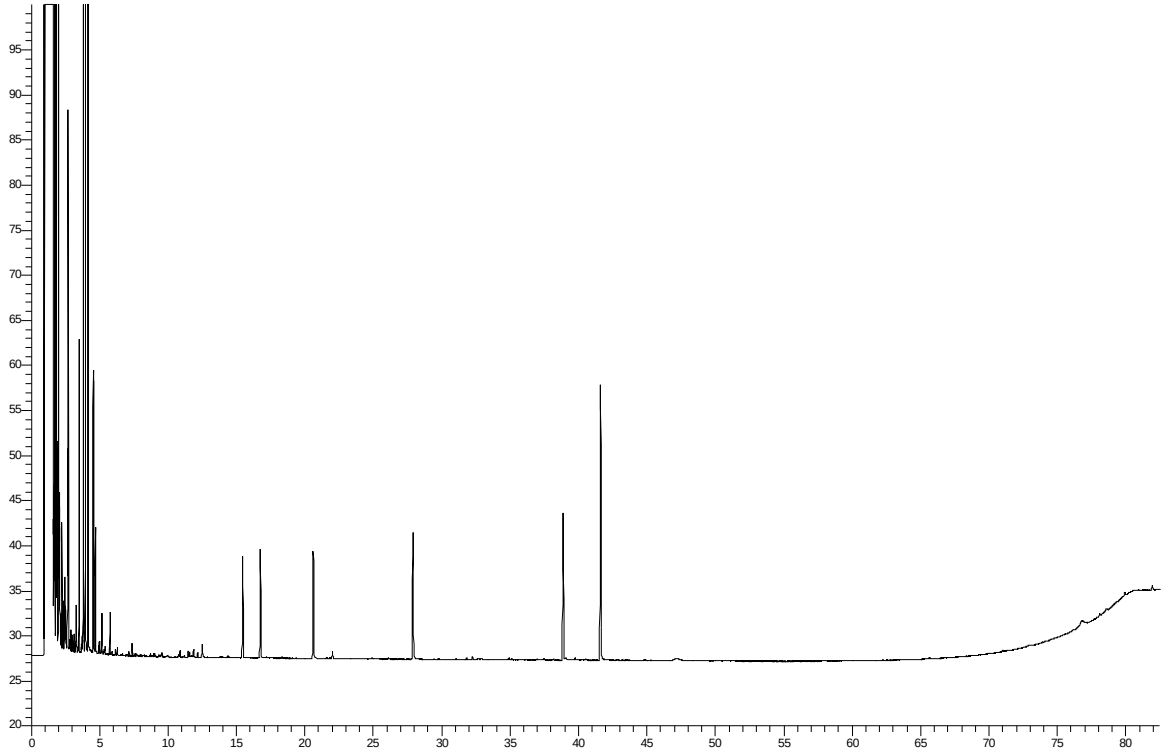


Figure 3

Representative GC-FID Analysis of SG-2 Fraction of Field Blanks SPMDs for PRC Determinations



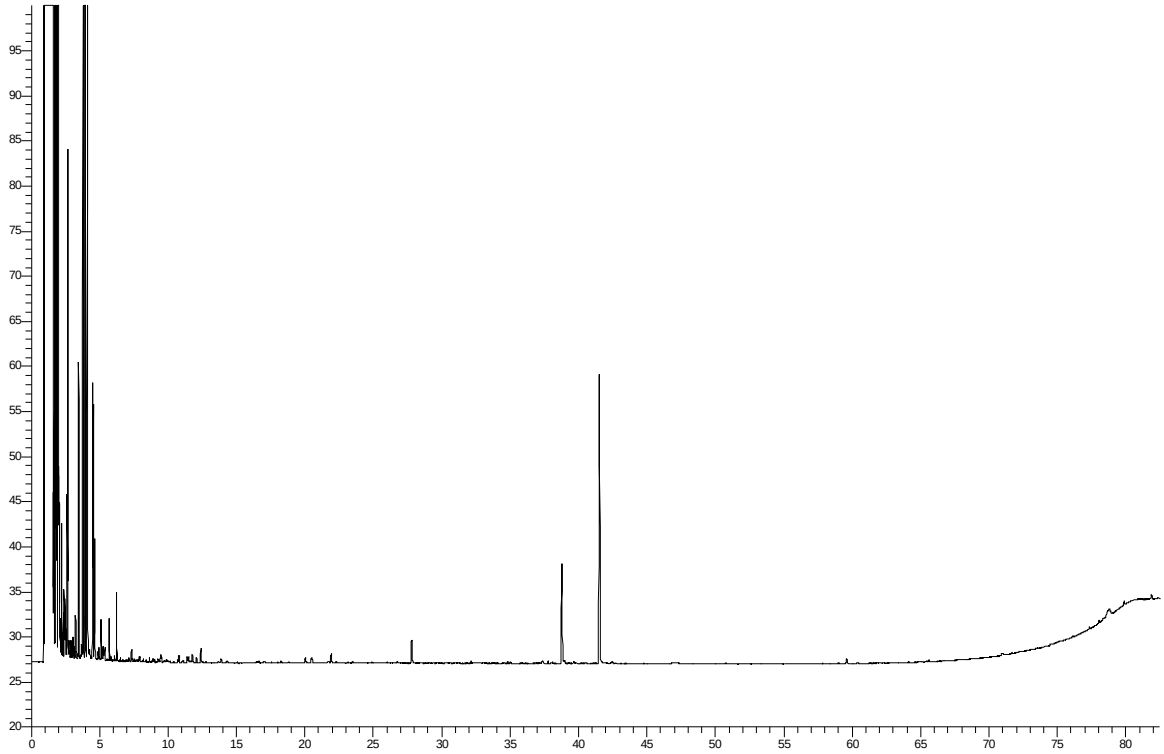
SPMD Field Blank # 3

NOTE: This chromatogram is representative of the determinations of C_{SPMD} values (@ time zero) from analyses of SPMD blanks (Table VI)

Retention Time	**Peak Identification**
15.8	Acenaphthylene-d_{10}
17.1	Acenaphthene- d_{10}
21.0	Fluorene- d_{10}
28.3	Phenanthrene- d_{10}
39.3	Pyrene- d_{10}
42.0	4-Terphenyl- d_{14} (IIS)

Figure 4

Representative GC-FID Analysis of SG-2 Fraction of Deployment SPMDs for PRC Determinations

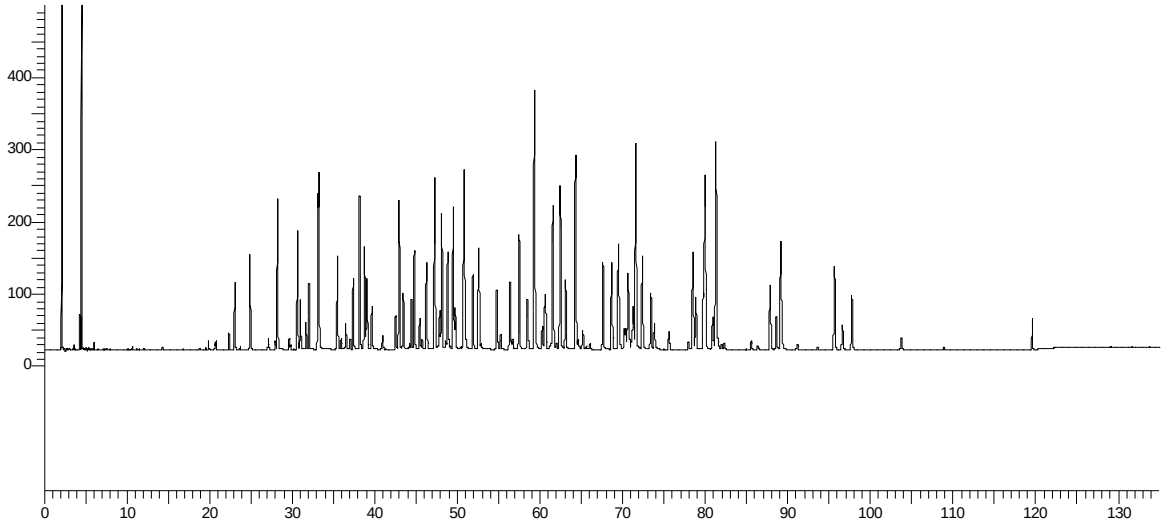


Deployed SPMD from Site # 3

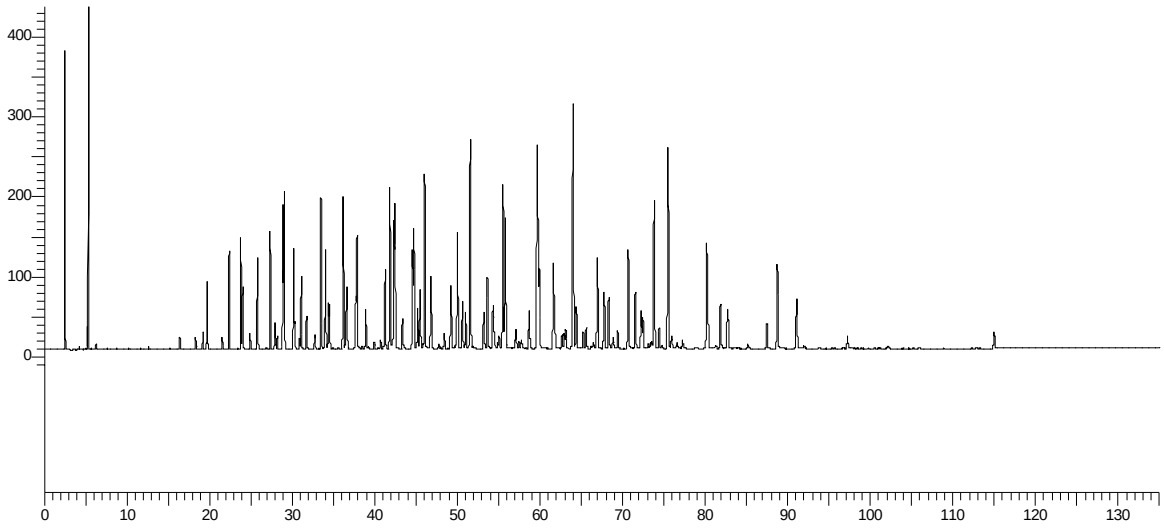
NOTE: This chromatogram is representative of the determinations of C_{SPMD} values from analyses of Deployed SPMDs (Table VI)

Figure 5

GC-ECD Analyses of PCB Standard



4000 ng/mL Total PCB Standard on DB-17

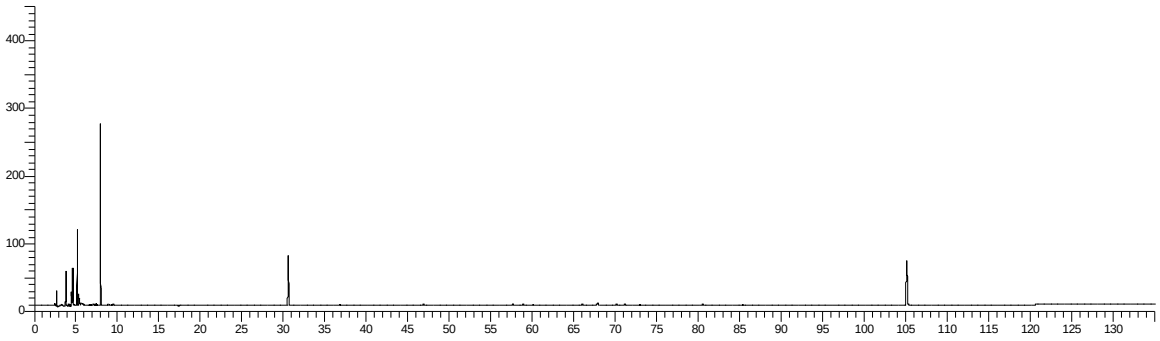


4000 ng/mL Total PCB Standard on DB-5

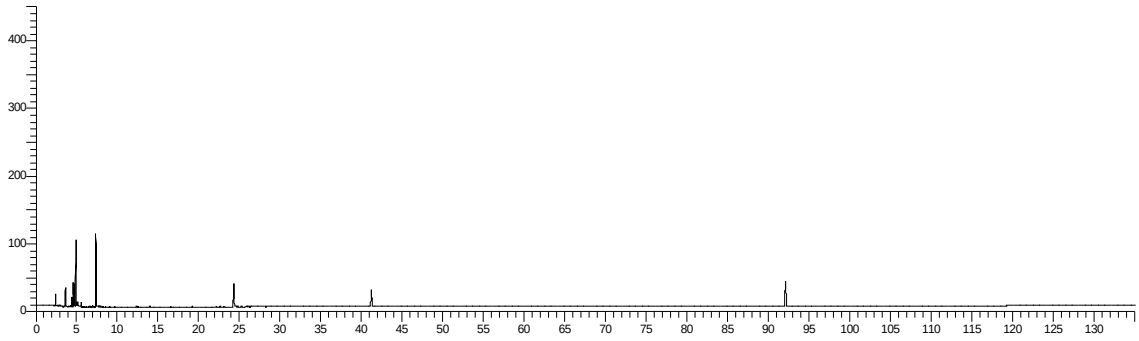
NOTE: Dual column analysis required for complete resolution and quantification of individual congeners. Peaks at ~ 30.5 (DB-17) and ~ 24.5 (DB-5) minutes are from I-30. Peaks at ~ 105 (DB-17) and ~ 92 (DB-5) minutes are from I-207.

Figure 6

Representative GC-ECD Analysis of SG-1 Fraction of Field Blank SPMDs for PCBs



SPMD Field Blank # 3 on DB-17

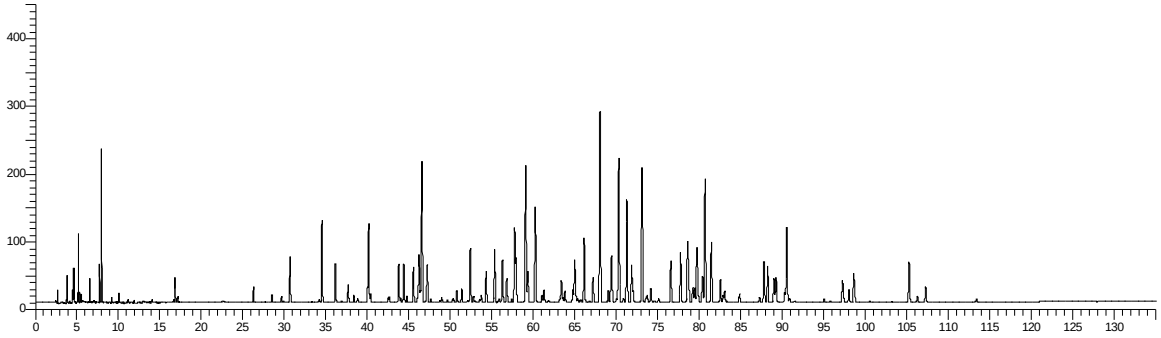


SPMD Field Blank # 3 on DB-5

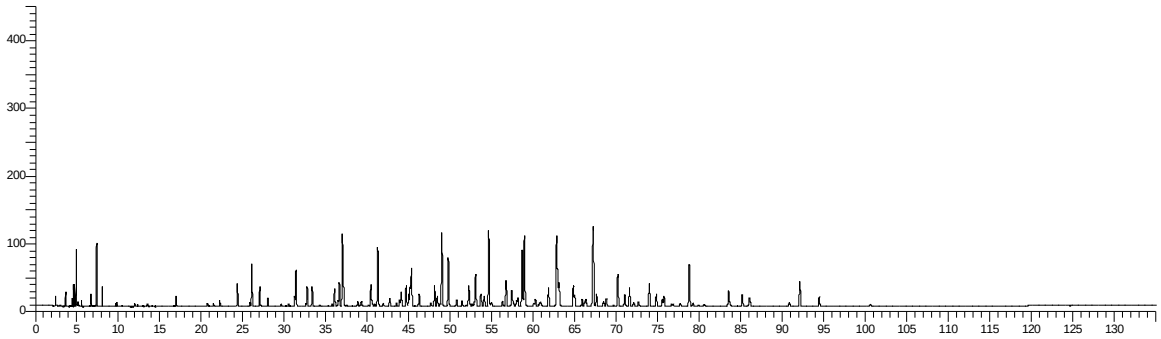
NOTE: Dual column analysis required for complete resolution and quantification of individual congeners. Peaks at ~ 30.5 (DB-17) and ~ 24.5 (DB-5) minutes are from I-30. Peaks at ~ 105 (DB-17) and ~ 92 (DB-5) minutes are from I-207.

Figure 7

Representative GC-ECD Analysis of SG-1 Fraction of Deployment SPMDs for PCBs



Deployed SPMD from Site # 3 on DB-17



Deployed SPMD from Site # 3 on DB-5

NOTE: Dual column analysis required for complete resolution and quantification of individual congeners. Peaks at ~ 30.5 (DB-17) and ~ 24.5 (DB-5) minutes are from I-30. Peaks at ~ 105 (DB-17) and ~ 92 (DB-5) minutes are from I-207.