Quality Assurance Project Plan

Monitoring 303(d) Listed Pesticides, PCBs, and PAHs in the Lower Columbia River Drainage Using a Semipermeable Membrane Device

by
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303(d) Listings Addressed in this Study:

Lower Columbia (WA-CR-1010) – 4,4'-DDT, 4,4'-DDE, Dieldrin, PCBs, PAHs

Ecology EIM Number: AJOH0041

Approvals

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Approved by:	October 8, 2003
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Approved by:	August 27, 2003
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Approved by:	August 28, 2003
Stuart Magoon, Director, Manchester Environmental Laboratory	Date
Approved by:	October 8, 2003
Cliff Kirchmer, Ecology Quality Assurance Officer	Date

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A. Project Management

A1. Distribution List

U.S. Environmental Protection AgencyHelen Rueda - EPA Region 10, Oregon Operations OfficeLorraine Edmond - EPA Region 10, Seattle

U.S. Geological Survey Kathleen McCarthy - USGS, Portland

Oregon Department of Environmental Quality Gene Foster - Organic Chemistry Section Manager

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Cliff Kirchmer - Quality Assurance Officer

Stuart Magoon - Manchester Environmental Laboratory Director

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Kim McKee- Southwest Regional Office, TMDL Unit Supervisor

Environmental Sampling Technologies

Terri Spencer - Laboratory Manager

National Council for Air and Stream Improvement Paul Weigand

A2. Project/Task Organization

The individuals directly involved with this project and their specific responsibilities are listed below.

Helen Rueda - U.S. Environmental Protection Agency, Region 10 (503-326-3280): EPA grant office. Monitor the project and provide guidance as needed to assure successful completion. Review and approve Quality Assurance Project Plan (QA Project Plan) and project reports.

Gene Foster - Oregon Department of Environmental Quality (503-229-5983 ext. 273): Review and approve QA Project Plan and project reports; provide technical assistance and coordination with Oregon.

Cliff Kirchmer - Ecology Environmental Assessment Program, QA Officer (360-407-6455): Review and approve QA Project Plan and subsequent revisions. Assess project performance in terms of QA Project Plan requirements.

Stuart Magoon - Ecology Environmental Assessment Program, Manchester Environmental Laboratory Director (360-871-8801): Review and approve QA Project Plan. Coordinate and schedule laboratory analyses, data review, and validation.

Will Kendra - Ecology Environmental Assessment Program Watershed Ecology Section Manager (360-407-6698): Oversight responsibility for all work plan tasks and deliverables. Review QA Project Plan and project reports.

Dale Norton - Ecology Environmental Assessment Program, Toxics Studies Unit Supervisor (360-407-6765): Project Manager. Review and approve QA Project Plan and project reports; provide sampling assistance and budget management.

Art Johnson - Ecology Environmental Assessment Program, Toxics Studies Unit (360-407-6766): Project Lead. Prepare QA Project Plan and project reports; conduct field work; coordinate sample analysis with laboratory; and resolve problems related to the analyses. Final review of data before being transmitted to EPA/DEQ and entered into the Ecology Environmental Information Management (EIM) Query System.

Morgan Roose - Ecology Environmental Assessment Program, Toxics Studies Unit (360-407-6458): Assist with field work.

John Weakland - Ecology Environmental Assessment Program, Manchester Environmental Laboratory (360-871-8820): Organics Unit Supervisor.

Myrna Mandjikov - Ecology Environmental Assessment Program, Manchester Environmental Laboratory (360-871-8814): Pesticide/PCB Analyst.

Dickey Huntamer - Ecology Environmental Assessment Program, Manchester Environmental Laboratory (360-871-8809): PAH Analyst.

Terri Spencer - Environmental Sampling Technologies, Laboratory Manager (816-232-8860): SPMD preparation, dialysis, and GPC cleanup. Shipment of extracts to Ecology Manchester Environmental Laboratory.

Karol Erickson - Ecology Environmental Assessment Program, Watershed Studies Unit (360-407-6694): Ecology Grant Officer.

Carolyn Lee - Ecology Environmental Assessment Program, Toxics Studies Unit (360-407-6430): EIM Data Entry.

A3. Problem Definition/Background

The States of Washington and Oregon currently have 303(d) listings in the Lower Columbia River below Bonneville Dam for several chlorinated compounds exceeding human health criteria in fish tissue (Appendix A). The contaminants include polychlorinated biphenyls (PCBs) and the pesticides DDT, its breakdown product DDE and dieldrin. Oregon also has a segment listed for polynuclear aromatic hydrocarbons (PAHs), based on water column exceedences of human health criteria.

The interagency Columbia River Toxics Group (CRTG) has reviewed the available data and concluded that little is known about current inputs of these chemicals to the lower river. This information is needed to help EPA, Washington, and Oregon design a strategy to address toxics listings in the Lower Columbia.

Through the efforts of CRTG, EPA and the Washington State Department of Ecology (Ecology) have entered into an agreement providing funding to Ecology to conduct a surface water monitoring program for PCBs, DDT compounds, dieldrin, and PAHs in the main stem Lower Columbia River and selected tributaries. Because low water column concentrations are anticipated, a passive sampling technique employing a semipermeable membrane device (SPMD) will be used to concentrate and quantify the chemicals of interest.

The objectives of the Lower Columbia SPMD study are as follows;

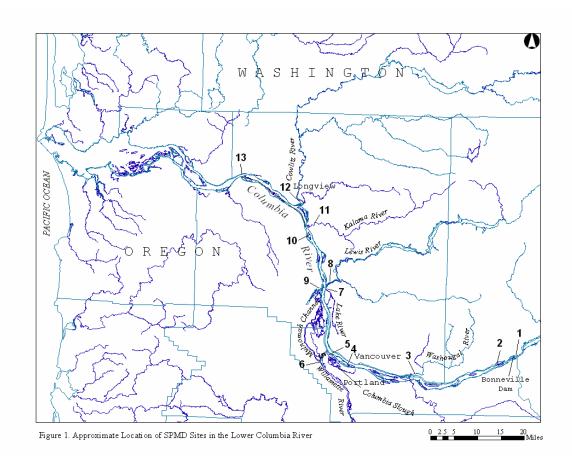
- 1. Measure ambient concentrations and estimate loadings of 303(d) listed organic compounds at five main stem and eight tributary sites in the Lower Columbia River between Bonneville Dam and the river mouth.
- 2. Evaluate seasonal differences in concentrations and loading estimates by sampling in late summer, winter, and spring.
- 3. Identify and rank sources of these contaminants to the river.

A4. Project/Task Description and Schedule

The purpose of this project is to conduct a surface water monitoring program for PCBs, DDT compounds, dieldrin, and PAHs in the Lower Columbia River drainage. Ecology, the Oregon Department of Environmental Quality (DEQ), and EPA have selected 13 sites for monitoring (Table 1, Figure 1).

Table 1. Proposed SPMD Sites in the Lower Columbia River.

Site No.	River Mile (approx.)	Location
1	147	Main stem above Bonneville
2	142	Main stem below Bonneville
3	121	Mouth of Washougal River
4	103	Main stem above Willamette River
5	102	Mouth of Columbia Slough
6	102	Mouth of Willamette River
7	88	Mouth of Lake River
8	87	Mouth of Lewis River
9	86	Mouth of Multnomah Channel
10	75	Main stem above Kalama River
11	73	Mouth of Kalama River
12	68	Mouth of Cowlitz River
13	54	Main stem below Longview



SPMDs will be deployed at each of these sites for a period of approximately one month during the late summer, winter, and spring of 2003-2004. The target compounds will be analyzed down to parts per quadrillion. The intent is to obtain data that represent the typical range of concentrations and loadings in the Lower Columbia and determine where the significant sources are located.

The monitoring program will be conducted by Ecology's Environmental Assessment Program (EA Program). The EA Program will provide the data to EPA and DEQ in a project report and electronically, and enter the data into Ecology's EIM Query System.

Field work for this project will begin in August 2003 and be completed in June 2004. The SPMDs will be prepared and extracted by Environmental Sampling Technologies (EST); chemical analyses will be done by the Ecology Manchester Environmental Laboratory (Manchester).

The project schedule is shown in Table 2.

Table 2. Proposed Schedule for the Lower Columbia River SPMD Study.

Task	Target Completion Date
Draft QA Project Plan Final QA Project Plan Sampling Laboratory Analysis Complete Draft Project Report Final Project Report, EIM Data Entry	July 2003 August 2003 Aug-Sept 03, Dec-Jan 04, May-June 04 August 2004 October 2004 December 2004

A5. Quality Objectives and Criteria for Measurement Data

Data quality indicators and associated measurement performance criteria for this project are identified in Table 3.

Table 3. Measurement Quality Objectives for Precision and Bias in the Sampling and Analysis of PCBs, Pesticides, and PAHs

Data	Measurement	QC Sample Used	QC Sample to Assess
Quality	Performance	to Assess Measurement	Error for Sampling (S)
Indicator	Criteria	Performance	Analytical (A) or both (S/A)
Precision	< 30% RPD	matrix spikes	A
	_ ≤ 30% RPD	spiked blanks	A
	\leq 30% RPD	lab duplicates	A
	≤ 30% RPD	field replicates	S/A
Accuracy	50-150% recovery	matrix spikes	A
	50-150% recovery	surrogate spikes	A
	50-150% recovery	spiked blanks	A
	20-200%	PAH isotopes	A
	< detection limit	method blanks	A
	\leq 10% of sample conc.	field blanks	S/A

Table 4 shows the detection limits Manchester has achieved on SPMD extracts. Although not on the 303(d) list for the lower Columbia, DDD is included in this project as a major breakdown product of DDT.

Table 4. Detection Limits for SPMD Extracts: Manchester Laboratory

Analysis	Analytical Method	Detection Limit (total ng/extract)
4,4'-DDT	GC/ECD EPA 8081	1
4,4'-DDE	GC/ECD EPA 8081	1
4,4'-DDD	GC/ECD EPA 8081	1
Dieldrin	GC/ECD EPA 8081	1
PCBs*	GC/ECD EPA 8082	40
PAH	GC/MS EPA 8270	100**
TAIL	GC/MS El A 6270	100

^{*} Aroclor-equivalents.

^{**}Expected detection limit based on extracts from other matrices.

Based on laboratory determined sampling rates for SPMDs and a 30-day exposure period of four membranes each, these detection limits translate into water column concentrations of approximately 0.1-0.2 ng/L for DDT compounds and dieldrin, 0.3 ng/L for PCBs, and 0.5 - 2 ng/L for PAHs (Table 5). These concentrations are low enough for comparison to EPA National Toxics Rule human health criteria for water.

Table 5. Estimated Water Column Detection Limits

			Detection	Limit	EPA NTR
Compound	Sampling Rate* (L/day)	Deployment (days)	SPMD Extract (ng)	Water (ng/L)	Human Health Criteria** (ng/L)
4,4'-DDT	3.2	30	1	0.010	0.59
4,4'-DDE	5.5	30	1	0.016	0.59
4,4'-DDD	3.1	30	1	0.011	0.83
Dieldrin	1.8	30	1	0.019	0.14
Total PCBs	4.8	30	40	0.28	0.17
PAHs	1.9-5.1	30	100	0.5-1.8	<u>≥</u> 2.8

^{*@10°}C.

The data for this project must accurately represent conditions existing during the time the SPMDs are deployed. Representativeness will be addressed by collecting the samples as described in this document. Field or laboratory conditions that may affect sample integrity will be documented in field logs or in laboratory case narratives.

Individual data sets must be comparable in order that results can be combined for decision making. Comparability will be addressed by consistently collecting, analyzing, and reporting the data as described in this document.

The project completeness goal for valid data is 95%.

A6. Special Training Requirements/Certification

No special training requirements or certifications are required for this project except for First Aid/CPR and boating safety. Information concerning the personnel qualifications for individuals performing this work is on file at Ecology Headquarters (HQ).

^{**10&}lt;sup>-6</sup> health risk for consumption of water and organisms.

A7. Documentation and Records

This information is covered by the Quality Assurance Manual for the Washington State Department of Ecology Manchester Laboratory, Volume 2.0.

B. Measurement/Data Acquisition

B1. Experimental Design

Historical Data - Water column concentrations for the chemicals of interest in the Lower Columbia drainage are poorly known, especially for the tributaries. The U.S. Geological Survey (USGS) has used SPMDs to measure concentrations of PCBs, chlorinated pesticides, and PAHs in the Columbia River between Northport (r.m. 735) and Bradwood (r.m. 39) (McCarthy and Gale, 1999). The study included eight sites below Bonneville Dam, two of which were tributaries. Table 6 shows their low-flow data.

Table 6. USGS SPMD Data on Organochlorines and PAHs in the Lower Columbia River During 1997 Low-Flow (estimated dissolved concentrations in ng/L; parts per trillion).

Location	River Mile	Total PCBs*	4,4'-DDT	4,4'-DDE	4,4'-DDD	Dieldrin	Total PAH**
Main Stem							
Warrendale	141	0.6	nd	0.7	1.0	0.1	34
Hayden Island	102	0.1	nd	0.1	0.2	0.05	6
Columbia City	82	1.0	nd	0.3	0.3	0.07	17
Longview	69	0.7	nd	0.4	0.2	0.04	8
Beaver Army Terminal	54	0.5	nd	0.2	0.2	0.04	14
Bradwood	39	0.3	nd	0.1	0.1	0.04	5
Tributaries							
Lake River	87	0.9	nd	0.2	0.2	0.1	11
Willamette River	101	2.0	nd	0.2	0.4	0.1	48

from McCarthy and Gale (1999).

nd = not detected.

^{*}um of otho-substituted congeners.

^{**}Sum of acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)pyrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzoanthracene, and benzo(g,h,i)perylene.

PAH occurred in the highest concentrations of 5–48 ng/L, followed by PCBs and DDT compounds at 0.1–2.0 ng/L. Dieldrin concentrations were generally less that 0.1 ng/L.

USGS took the conservative approach of not adjusting their results to account for site-specific differences in temperature, water velocity, or membrane fouling, all of which affect chemical uptake. Also, the technique of using Performance Reference Compounds to more accurately estimate SPMD sampling rates had not been developed at that time. USGS therefore cautioned that their data were "only approximations of the exposure-period average dissolved concentrations of OC and PAH compounds" (McCarthy and Gale, 1999).

The USGS data suggest that mainstem PCB concentrations are slightly elevated downstream of the Portland-Vancouver area (Columbia City site) while DDT compounds, dieldrin, and PAHs are highest at Warrendale, approximately six miles below Bonneville Dam. There was a trend toward decreasing concentrations moving downstream from Columbia City (PCBs) and from Warrendale (DDTs, dieldrin, and PAHs). The Willamette River appears to be a significant source of PCBs and PAHs.

USGS concluded that concentrations in the Portland-Vancouver area were primarily from local rather than upstream sources. They noted a significant reduction in mainstem concentrations, attributed to dilution, volatilization, and settling of particulate matter (McCarthy and Gale, 1999). Lower concentrations of these chemicals were generally observed during high flow conditions, but these data were only discussed in passing in the report.

In an earlier unpublished study, Battelle used passive samplers consisting of simple polyethylene sheets to monitor organochlorines at ten sites in the Columbia River between the Yakima River and Longview (Lefkovitz et al., 1996). The data for the lower Columbia River are summarized in Table 7.

Table 7. Battelle Poly Sheet Data on Organochlorines in the Lower Columbia River During Spring 1994 (estimated dissolved concentrations in ng/L; parts per trillion)

Location	Approximate River Mile	Total PCBs*	Total DDT**	Dieldrin
Main Stem				
Above John Day River	220	0.04	0.52	
Near Kalama	87	0.30	1.4	
Near Longview	66	0.29	1.2	
Tributaries				
Columbia Slough	102	20	17	
Willamette River	101	2.9	0.69	0.33

Unpublished data provided by E.A. Crecelius, Battelle Marine Sciences Laboratory.

Battelle's results suggest there are significant PCB and DDT sources between John Day Dam and Kalama. Columbia Slough, just upstream of the Willamette River, appeared to be contaminated with these chemicals. Concentrations measured with poly sheet samplers agreed reasonably well with the lipid-filled SPMDs used in the USGS study--within a factor of 3 for pesticides and a factor of 10 for PCBs (Lefkovitz et al., 1996). PAHs were not analyzed.

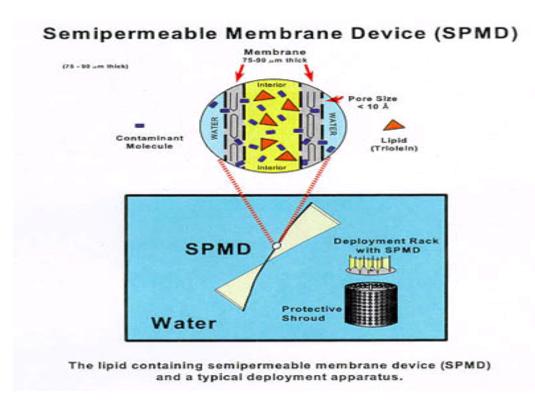
SPMDs – Because concentrations of 303(d) listed chemicals in the Lower Columbia River are below the detection limits of routine sampling and analytical methods, the present study will use SPMDs for their detection and quantification.

SPMDs were developed by the USGS Columbia Environmental Research Center and are now of standardized design, patented, and commercially available through Environmental Sampling Technologies (EST), St. Joseph, MO (http://www.spmds.com). Details of SPMD theory, construction, and application can be found at http://wwwaux.cerc.cr.usgs.gov/spmd/spmd_overview.htm. Ecology has used SPMDs to monitor organochlorines in the Spokane River, Walla Walla River, and Lake Chelan (EILS, 1995; Johnson et al. in prep; Coots and Era-Miller, 2002).

^{*}Sum of 30 congeners.

^{**}Sum of 2,4' and 4,4' isomers.

Each SPMD is composed of a thin-walled, layflat polyethylene tube (91 x 2.5 cm) filled with triolein, the major nonpolar lipid found in aquatic organisms (Figure 2). The polyethylene tubing mimics a biological membrane by allowing selective diffusion of organic compounds. Passive sampling of hydrophobic organic chemicals is driven by membrane- and lipid-water partitioning. When placed in water, dissolved organic compounds are concentrated over time.



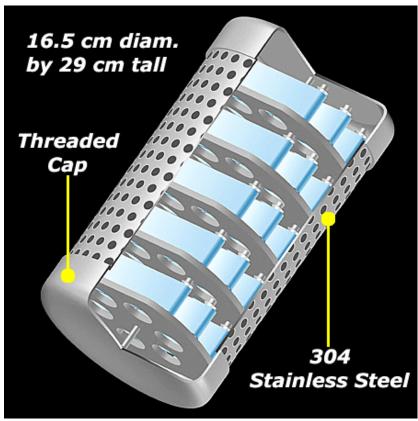


Figure 2. SPMD Membranes and Deployment Device

A SPMD membrane will effectively sample 1–10 liters of water per day, depending on the compound in question. The typical deployment period is 20-30 days. The membranes are then extracted and analyzed for the chemicals of interest. A combination of laboratory calibration data and PRCs spiked into deployed SPMDs are used in conjunction with field temperature to calculate average dissolved concentrations.

SPMDs provide a time-weighted average concentration for the chemicals of interest and only measure the dissolved and, therefore, readily bioavailable fraction. Studies have shown the results are comparable to other low-level sampling methods such as liquid-liquid extraction and solid-phase extraction (Ellis et al., 1995; Rantalainen et al., 1998). Results from all of these methods are subject to uncertainty, but the other methods have the added drawbacks of being time consuming, expensive, and only providing a single point measurement. Disadvantages of SPMDs include the potential for losing them in field studies and fact that determination of a total water concentration must rely on calculations based on theoretical partitioning between the dissolved and particulate form of a chemical.

Study Design - For the Lower Columbia River study, SPMDs will be deployed at the 13 locations listed in Table 1. The Washougal, Willamette, Lewis, Kalama, and Cowlitz rivers are the largest and most developed in the region. Columbia Slough, Lake River, and Multnomah Channel are included in recognition of known or suspected contamination with target compounds (McCarthy and Gale, 1999; Lefkovitz et al., 1996; Gene Foster, DEQ, personal communication; Bruce Sutherland, DEQ, personal communication). Main stem stations were located above major tributaries and above and below Bonneville Dam. Station placement will allow an assessment of the occurrence and relative importance of unsampled sources, using simple mass balance. Exact station locations will be selected based on reconnaissance of the study area.

SPMDs will be deployed during the late summer, winter, and spring for a period of approximately 30 days each, as indicated in Figure 3. The deployments are timed to provide representative data over the range of flow conditions that normally occur in the drainage. August-September is the low-flow period. The Willamette River and other tributaries have their highest flow rates in the winter due to rain, while high flow in the Columbia results primarily from snow-melt in the late spring. The SPMDs will therefore be deployed during August-September 2003, December-January 2003-04, and May-June 2004.

The SPMDs will be placed in well-mixed locations. To the extent possible, these locations will be representative of water quality at each site. It is recognized that some of the sampling sites may not be well-mixed laterally. There is not adequate funding for this project to assess the importance of cross-channel variability. Water column concentrations and loadings obtained through this study should be considered estimates.

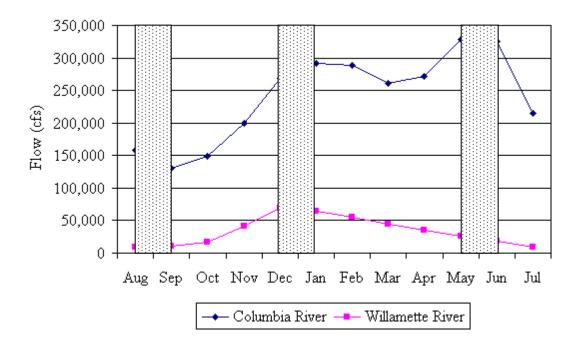


Figure 3. Sampling Periods Compared to Average River Flow

The SPMD extracts will be analyzed for seven PCB Aroclors¹, DDT and breakdown products DDE and DDD, dieldrin, and 22 PAH compounds. The complete list of chemicals to be analyzed is in Appendix B.

Temperature will be monitored continuously during deployment. At the beginning, middle, and end of each deployment period, ancillary data will be obtained on total suspended solids (TSS), total organic carbon (TOC), and dissolved organic carbon (DOC). Conductivity will be measured in the field. Flow data will be obtained through USGS and the EA Program Stream Hydrology Unit.

Dissolved concentrations of the target compounds will be calculated using an Excel spreadsheet developed by USGS (Appendix C). Total concentrations will be estimated using the following equation developed by Meadows et al. (1998): $C_{w\text{-tot}} = (1 + TOC \; K_{oc} \; / \; M_w) \; C_w \; , \text{where} \; K_{oc} \; \text{ is the organic carbon-water equilibrium partition coefficient,} \; M_w \; \text{is the mass of water,} \; \text{and} \; C_w \; \text{is the dissolved concentration.}$

B2. Sampling Methods Requirements

Deployment and retrieval procedures for SPMDs will follow USGS and EST guidance (Huckins et al., 2000); http://www.spmds.com.

Standard SPMDs (91 x 2.5 cm membrane containing 1 mL triolein) and the stainless steel canisters (16.5 x 29 cm) and carriers that hold the membranes during deployment will be obtained from EST. The membranes are preloaded onto the carriers by EST in a clean-room and shipped in solvent-rinsed metal cans under argon atmosphere. Four membranes will be used in each canister, with one canister per sampling site, not including field replicates. The SPMDs will be kept frozen until deployed.

On arrival at the sampling site, the cans will be pried open, carriers slid into the canisters, and the device anchored in the stream. The SPMDs will be located out of strong currents, situated in such a way as to minimize the potential for vandalism, and placed deep enough to allow for any anticipated fluctuations in water level. Because SPMDs are potent air samples, this procedure will be done as quickly as possible. Field personnel will wear nitrile gloves and not touch the membranes.

The SPMDs will be deployed for approximately 30 days, as recommended by USGS and EST. The retrieval procedure is essentially the opposite of deployment. The cans holding the SPMDs must be carefully sealed and the SPMDs must be maintained at or near freezing until they arrive at EST for extraction.

^{.1}

¹ In the United States, PCBs were primarily manufactured and sold under the trade name Aroclors. PCBs are typically analyzed as equivalent concentrations of commercial Aroclor mixtures (e.g., PCB-1254) or as individual compounds, referred to as PCB congeners. Because of the expense of a congener analysis, the present study will analyze PCBs as Aroclor-equivalents

An Onset StowAway Tidbit will be attached to each canister to monitor temperature. The latitude and longitude of each sampling site will be recorded by a global positioning receiver (GPS). Stream flow will be obtained from established gauges.

TSS, TOC, and DOC will be collected as simple grabs. DOC samples will be filtered in the field (0.45 um). The water samples will be placed on ice immediately after collection. A Beckman model RB-5 conductivity bridge, or equivalent meter, will be used to measure conductivity in the field. A meter or thermometer will be used to record the temperature when water samples are collected, to provide backup data in the event that a Tidbit is lost. Sampling methods for water quality parameters and methods for measuring field parameters will follow the Ecology guidance in Cusimano (1993) and Ward (2001).

Field blanks and replicate samples will be prepared and collected as described in section B5.

The SPMDs and a chain-of-custody record will be shipped from the field to EST by overnight Federal Express, in coolers with blue ice or ice in poly bottles. The cans holding the SPMDs will be labeled showing project name, sampling site, assigned Manchester sampling number, number of cans per sample, and collection date.

The water samples will be returned to Ecology HQ within one-to-two days of collection and held in a secure cooler for next day transport with chain-of-custody record to Manchester. A label will be placed on each water sample indicating project name, sampling site, assigned Manchester sample number, collection date, and analysis required.

Sample holding times will be observed (section B3) and chain-of-custody maintained throughout the above procedures.

To ensure successful completion of this project, backup SPMDs, canisters, tidbits, and anchoring equipment will be on hand for each sampling event, in the event of loss or damaged to the SPMDS at any point during the deployment. Extra sample bottles, spare parts, extra batteries, backup meters, and other needed sampling gear will also be carried along for each field trip.

B3. Sample Handling and Custody Requirements

Sample handling and custody requirements for SPMDs were addressed in section B2. No holding times have been established for SPMDs. The membranes are kept frozen prior to and after deployment. The extracts are stored at 4+/-2°C.

Sample containers, preservation, and holding times for water samples will be as described in Table 8. Sample containers will be obtained from Manchester, with preservative added.

Table 8. Field Procedures (water samples).

Parameter	Min. Sample Size	Container ^a	Preservation	Holding Time
TSS	1000 mL	1 L poly bottle	Cool to 4°C	
TOC	50 mL	125 mL poly bottle	HCl to pH<2, 4°C	
DOC	50 mL	125 mL poly bottle	HCl to pH<2, 4°C	

Chain-of-custody procedures, field documentation, and sample tracking will be in accordance with the Manchester Laboratory Users Manual, July 2002. Date and time of collection, location, sample size, Manchester sample number, location coordinates, and field observations will be recorded in ink on a field log.

B4. Analytical Methods Requirements

EST will extract the SPMDs (referred to as dialysis), perform GPC cleanup, and ship the ampoulated extracts to Manchester. The dialysis method used by EST is a patented procedure (Huckins et al., 2000). EST's dialysis and GPC methods are documented in SOPs E14, E15, E19, E21, E33, E44, and E48, which are on file at the EA Program.

Table 9 shows the types and numbers of samples to be analyzed, expected range of results, and sample preparation and analysis methods. Pesticides and PCBs will be analyzed by GC/ECD. PAH will be analyzed by GC/ID-SIM-MS (SOP 730083). Other methods may by used by Manchester after consulting with the project lead. Reporting limit requirements for this project are discussed in section A5. Manchester will report at the lowest level consistent with the methods used. The deuterated PAH and the PCB congeners used as PRCs will be quantified in the analyses (see Field QC Samples). All organics will be reported as total ng per extract.

Table 9. Laboratory Procedures

Analysis	Sample Matrix	Number of Field Samples*	Expected Rang of Results	geSample Prep Method	Analytical Method
PCBs DDTs, dieldrin PAHs TSS TOC DOC	SPMD extract SPMD extract SPMD extract whole water whole water whole water	16/48 16/48 16/48 39/117 39/117	50-500 ng 1-500 ng 500-5,000 ng 1 - 500 mg/L 1-10 mg/L 1-10 mg/L	dialysis/GPC** dialysis/GPC** dialysis/GPC** N/A N/A N/A	SW8082 SW8081 SW8270 ⁺ EPA 160.2 EPA 415.1 EPA 415.1

^{*}per sampling period/total samples (includes replicates and field blanks)
**EST SOPs E14, E15, E19, E21, E33, E44, E48

If problems are encountered in analyzing the samples, the project lead will be consulted at the earliest opportunity. Manchester's normal turn-around time of 30-45 days will meet the needs of this project. Excess sample extracts will be saved for a period of 60 days after reporting the data to the project lead.

B5. Quality Control Requirements

The field QC samples to be analyzed for this project are shown in Table 10.

^{*}SIM modification

Table 10. Field Quality Control Samples.

Parameter	PRC Spikes	Field Blanks	Replicate Samples
SPMD Sampling Rate	all samples*	NA	NA
Pesticides/PCBs	NA	1/deployment	2/deployment
PAHs	NA	1/deployment	2/deployment
TSS	NA	NA	none
TOC	NA	NA	none
DOC	NA	NA	none

^{*}Spike one membrane per sample prior to deployment.

NA = Not Applicable.

Prior to shipping to Ecology, EST will spike the SPMDs with PRCs. These are analytically non-interfering compounds with moderate to relatively high fugacity (escape tendency). The loss rate of PRCs is proportional to the uptake of target compounds. Loss rates during field exposure are used to adjust for the effects of temperature, water velocity, and biofouling on SPMD sampling rates determined in the laboratory. PRCs can be thought of as an in situ calibration mechanism. It has been shown that uptake rates of compounds with a wide range of $K_{ow}s^2$ can be predicted by loss rates of PRCs with a much narrower K_{ow} range (Huckins et al., 2002).

EST will spike PRCs into all SPMD membranes used for this project. The PRCs will include labeled PAH compounds, PCB #4, and PCB #29. The spiking level will be approximately 0.2 ug of each compound.

For the first deployment, 24 deuterated PAH compounds will be used as PRCs. The laboratory will analyze the samples using injection internal standards to estimate the recoveries of the isotopically labeled compounds added. The isotope recoveries of the deployed samples compared to the amounts added will give the losses of the PRCs during deployment and these losses can be used for PRC calculations. The differences in the deployed vs. undeployed membranes can be used to estimate the amounts of isotopically labeled compounds remaining before dialysis and GPC cleanup. These amounts are then used as isotopically labeled internal standards to estimate the amounts of target native PAH compounds concentrated by the SPMD membranes.

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 $^{^{2}}$ octanol-water partition coefficient; a measure of a chemical's tendency to bioaccumulate.

For the second and third deployments a different method is planned in which the PRCs are added as carbon 13 labeled compounds to the SPMD membranes before deployment and the isotopically labeled internal standards (isotope dilution) are added as deuterium labeled compounds just before extraction and cleanup. These can be distinguished on the mass spec. Because of the expense of carbon 13 labeled compounds, PAH PRCs will be limited to six or fewer compounds.

Because SPMDs absorbs vapors while being exposed to air, a field blank is needed to record chemical accumulation during deployment, retrieval, and transport. The field blank SPMD, consisting of four SPMD membranes, is opened to the air for the same amount of time it takes to open and place the SPMDs in the water. The blank is then resealed and refrozen. The blank is taken back into the field and opened and closed again to mimic the retrieval process. The blank is processed and analyzed the same as deployed SPMDs.

There will be one SPMD field blank per deployment. Field blanks will be analyzed at the two sites judged to have the greatest potential for air-borne contamination--Willamette and Cowlitz Rivers (cities of Portland and Longview) and one site judged to have a low potential--main stem below Longview (prevailing west wind).

Replicate samples will provide estimates of the total variability in the data (field + laboratory). Two replicate SPMD canisters will be deployed for each sampling period. The site for replicate sampling will be rotated to obtain variability estimates for as many locations as possible.

The laboratory QC samples to be analyzed for this project are shown in Table 11.

Table 11. Laboratory Quality Control Samples.

Laboratory	Analysis	Method	Surrogate	Matrix	Duplicate	Spiked
and Matrix		Blanks	Spikes	Spikes	Analyses	Blanks
EST SPMDs	Prep/Dialysis/GPC	5/batch	all samples*	2/batch	NA	NA
Manchester SPMD extracts	Pesticides/PCBs	2/batch	none	none	1/batch	2/batch
	PAHs	2/batch	none	none	1/batch	2/batch
Water "	TSS TOC DOC	1/batch 1/batch 1/batch	NA NA NA	NA NA NA	1/batch 1/batch 1/batch	1/batch 1/batch 1/batch

^{*}Pesticides/PCBs only (PAH analysis by isotope dilution).

NA = Not Applicable.

EST will prepare the following method blanks for each SPMD deployment: 1) A spiking blank-SPMD exposed while spiking the SPMDs, to represent laboratory background. This blank is held frozen at EST and later dialyzed with project samples. 2) A day-zero SPMD blank to serve as a reference point for PRC loss. 3) A dialysis blank-SPMD from the same lot as the project batch, to represent background during dialysis and cleanup. 4) A day-zero blank SPMD, manufactured just prior to dialysis, to serve as a control. 5) A reagent blank to assess contamination independent of the SPMDs. All of these blanks will be analyzed with the first quarter's sample set. The results will be used to determine which of these blanks should be analyzed with subsequent sample sets.

Prior to dialysis, EST will add surrogate compounds for the pesticide/PCB analysis to one SPMD membrane in each field sample and each blank. (PAH isotopes were spiked prior to deployment.) This will provide an estimate of accuracy for the entire analytical procedure. The surrogates will be dibromooctafluorobiphenyl and decachlorobiphenyl. The spiking level will be approximately 10 ng per membrane. Manchester will supply the surrogate spikes to EST.

For each dialysis batch, EST will do a matrix spike and matrix spike duplicate (MS/MSD) of field quality SPMDs (four membranes each) using target compounds for the study. The spiking levels will be approximately 10 ng/membrane for DDT

compounds (4,4'-DDT, -DDE, -DDD) and dieldrin; approximately 50 ng/membrane of Aroclor-1260; and approximately 0.4 ug/membrane of the PAH compounds. Manchester will supply these spikes.

Manchester will analyze their own method blanks with each batch of SPMD extracts. Two method blanks will be prepared for each batch.

No additional surrogate or matrix spikes are requested for Manchester's analyses.

For each batch of SPMD extracts, Manchester will analyze one sample in duplicate to provide estimates of analytical precision. The duplicate to be analyzed will be indicated on the sample tag and in the chain-of-custody form. In order to assess the relative importance of field vs. laboratory variability, the duplicate analysis will be done for sites where field replicates are being collected.

Manchester will analyze two laboratory control samples (spiked blanks) with each batch of SPMD extracts. Results from these samples will be used to verify that analytical precision is in control and that the level of bias due to calibration is acceptable.

Laboratory QC elements will meet or exceed requirements in the methods and SOPs cited in this QA Project Plan.

Manchester's routine QC samples for TSS, TOC, and DOC will meet the needs of this project.

B6. Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Field equipment being used during this project includes a Beckman model RB-5 conductivity bridge, a precision thermometer, and GPS. This equipment is maintained by the EA Program's instrument technician. The field lead will inspect and test each piece of equipment before taking it into the field. An extra conductivity bridge and thermometer will be taken on each field trip.

For the analytical instrumentation, testing, inspection, and maintenance will be performed in accordance with the above referenced analytical SOPs and manufacturer's recommendations.

B7. Instrument Calibration and Frequency

No calibration is required for the conductivity meter or thermometers. The Tidbits are calibrated against an NIST thermometer.

For the analytical instrumentation, calibration will be performed in accordance with the analytical SOP and manufacturer's recommendations.

B8. Inspection/Acceptance Requirements for Supplies and Consumables

No special requirements are needed.

B9. Data Acquisition Requirements

The only data being used from other sources is river flow. These data will be obtained from the USGS and Ecology, both of which have established QA/QC programs for their flow monitoring networks.

B10. Data Management

Data management will be in accordance with the Quality Assurance Manual for the Washington State Department of Ecology Manchester Environmental Laboratory, Volume 2.0.

C. Assessment/Oversight

C1. Assessments and Response Actions

The project lead will be responsible for identifying any significant conditions that would adversely affect the quality and usability of the data. The lead will have the responsibility for initiating and implementing response actions for problems identified. The lead will verify that the response actions were implemented effectively.

Assessments and response concerning the analytical aspect of the project are addressed in the Quality Assurance Manual for the Washington State Department of Ecology Manchester Laboratory, Volume 2.0. The information covers examples of conditions indicating out-of-control situations, who is responsible for initiating the corrective actions, and what steps may be taken.

C2. Reports to Management

A final project report will be prepared for EPA and DEQ and the data will be provided in electronic format. The report will include:

- Maps of the study area showing monitoring stations.
- Coordinates and detailed descriptions of each sampling site.
- Descriptions of field and laboratory method.
- Discussion of data quality and the significance of any problems encountered in the analyses.
- Summary tables of the chemical and ancillary data.
- Description of methods used to calculate water column concentrations from SPMD data
- Discussion of spatial and temporal patterns observed in the study area.
- Loading calculations.
- Source rankings.
- Recommendations for follow-up actions to address toxics listings in the Lower Columbia River

D. Data Validation and Usability

D1. Data Review, Validation, and Verification Requirements

The data will be reviewed by a qualified analyst at Manchester and by the laboratory's Organics Unit supervisor. The laboratory will verify the completeness, correctness, and conformance/compliance of the data set against method and procedural requirements laid out in this QA Project Plan. The laboratory will verify the analytical quality of the data set. The project lead will be responsible for overall validation and final approval of the data in accordance with project purpose and use of the data.

D2. Validation and Verification Methods

Manchester will verify the data in accordance with the Quality Assurance Manual for the Washington State Department of Ecology Manchester Laboratory, Volume 2.0 and EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, October 1999.

The project lead will perform the final review and approval of the data prior to transmitting it to EPA/DEQ or entering it into EIM as valid. The lead will review the case narratives and look at field blanks, field replicates, PRCs, surrogate recoveries, spiked blank recoveries, matrix spike recoveries, lab duplicates, and lab blanks to ensure they are acceptable. The lead will determine if the data are reasonable and consistent. The lead will ensure that any anomalies in the data are appropriately documented.

D3. Reconciliation with User Requirements

A data quality assessment will be conducted by the project lead to include:

- Reviewing the criteria for measurement data, sampling design, and data collection documentation for consistency.
- Reviewing the case narratives, calculating basic statistics, and generating graphs of the data to learn about the structure of the data and identify patterns, relationships, or potential anomalies.
- Selecting the most appropriate procedures for summarizing and analyzing the data, based on sampling design, data review, and intended use of the data.
- Drawing conclusions from the data and evaluating the performance of the sampling design.

If the data quality indicators do not meet project requirements outlined in this QA Project Plan, the data may be discarded. The project lead will evaluate the cause of the failure and make the decision to discard the data or re-sample if possible. If the failure is tied to the analysis, calibration, and maintenance, techniques will be reassessed as identified by the appropriate lab personnel. If the failure is associated with the sample collection, the errors will be corrected.

E. Budget and Staff Time

Estimates of laboratory/equipment costs and staff time for this project are summarized below. A detailed cost breakdown for sample analysis and equipment is provided in Appendix D.

SPMD Services (EST) \$18,180 Chemical Analyses (Manchester) \$28,350 Equipment \$3,470 Total = \$50,000

Total Days/FTEs = 108/0.43

F. References

Coots, R. and B. Era-Miller. 2003. Total Maximum Daily Load Study: DDT and PCBs in Lake Chelan. Washington State Department of Ecology, Olympia, Washington. Publication Number 03-03-105.

Cusimano, B. 1993. Field Sampling and Measurement Protocols for the Watershed Assessments Section. Washington State Department of Ecology, Olympia, Washington. Publication Number 93-e04.

EILS. 1995. Department of Ecology 1994-94 Investigation of PCBs in the Spokane River. Environmental Investigations and Laboratory Services Program, Washington State Department of Ecology, Olympia, Washington. Publication Number 95-310.

Ellis, G. S., Huckins, J. N., Rostad, C. E., Schmitt, C. J., Petty J. D., and P. MacCarthy. 1995. Evaluation of Lipid-Containing Semipermeable Membrane Devices (SPMDs) for Monitoring Organochlorine Contaminants in the Upper Mississippi River. Environmental Toxicology Chemistry 14:1875-1884.

Huckins, J. N. et al., 2000. A Guide to the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants. USGS Columbia Environmental Research Center, Columbia Missouri.

Huckins, J. N., J. D. Petty, J. A. Lebo, F. V. Almeida, K. Booij, D. A. Alvarez, W. L. Cranor, R. C. Clark, and B. B. Mogensen. 2002. Development of the Permeability/Performance Reference Compound Approach for In Situ Calibration of Semipermeable Membrane Devices. Environmental Science Technology 36(1):85-91.

Johnson, A., B. Era-Miller, S. Golding, and R. Coots. 2004-Draft. A Total Maximum Daily Load Evaluation for Chlorinated Pesticides and PCBs in the Walla Walla River. Washington State Department of Ecology, Olympia, Washington.

Lefkovitz, L., E. Crecelius, and N. McElroy. 1996. The Use of Polyethylene Alone to Predict Dissolved-Phase Organics in the Columbia River. Poster presented to Society Environmental Toxicology Chemistry, 17-21 November 1996, Washington, D.C.

McCarthy, K. A. and R. Gale. 1999. Ivestigation of the Distribution of Organochlorine and Polycyclic Aromatic Hydrocarbon Compounds in the Lower Columbia River Using Semipermeable Membrane Devices. U.S. Geological Survey, Water-Resources Investigation Report 99-4051.

Meadows, J. C., K. R. Echols, J. N. Huckins, F. A. Borsuk, R. F. Carline, and D. E. Tillitt. 1998. Estimation of Uptake Rates for PCB Congeners Accumulated by Semipermeable Membrane Devices and Brown Trout (*Salmo trutta*). Environmental Science Technology 32:1847-1852.

Rantalainen, A. L., M. G. Ikonomou, and I. H. Rogers. 1998. Lipid-Containing Semipermeable Membrane Devices (SPMDs) as Concentrators of Toxic Chemicals in the Lower Fraser River, British Columbia. Chemosphere 37:1119-1138.

Ward, B. 2001. Stream Sampling Protocols for the Environmental Monitoring and Trends Section. Washington State Department of Ecology, Olympia, Washington. Publication Number 01-03-036.

Appendix A.

303(d) Listings for the Lower Columbia River

Appendix A1. Washington 1998 303(d) Listings for the Lower Columbia River

WRIA	MEDIA	PARAM	LAT	LONG	BASIS
25	Tissue	4,4'-DDE	46.275	123.75	Laflamme and Gilroy, 1996., excursions beyond the National Toxics Rule criterion in sturgeon fillets in 1994 and 1995.
25	Tissue	Dieldrin	46.145	123.28	Tetra Tech, 1993, 3 excursions beyond the National Toxics Rule criterion in the edible tissue of a individual White Sturgeon at RM 49.
25	Tissue	Total PCBs	46.245	123.56	Laflamme and Gilroy, 1996., excursions beyond the National Toxics Rule criterion in sturgeon, L. sucker and carp fillets in 1994 and 1995.
25	Tissue	Total PCBs	46.145	123.28	Tetra Tech, 1993, 3 excursions beyond the National Toxics Rule criterion in the edible tissue of a individual White Sturgeon at RM 49.
25	Tissue	Total PCBs	46.275	123.75	Laflamme and Gilroy, 1996., excursions beyond the National Toxics Rule criterion in Carp, Sturgeon, L. Sucker, Chinook, Coho and Steelhead fillets in 1994 and 1995.
27	Tissue	Dieldrin	46.005	122.86	Tetra Tech, 1993, 3 excursions beyond the National Toxics Rule criterion in the edible tissue of a individual White Sturgeon at RM 75.
27	Tissue	Total PCBs	46.005	122.86	Tetra Tech, 1993, 3 excursions beyond the National Toxics Rule criterion in the edible tissue of a individual White Sturgeon at RM 75.

Appendix A2. Oregon 303(d) Listings for the Lower Columbia River

SUB-BASIN	NAME	PARAMETER	CRITERIA TEXT	SEASON	SUPPORTING DATA OR INFORMATION	LIST DATE
-CROSSES SUBBASINS	Columbia River 0 to 35.2	DDT Metabolite (DDE)	public health advisories	Year Around	Levels of DDE/DDT found in some fish (carp, peamouth, sucker) exceed health criteria, OR/WA Health Depts. have issued recommendations regarding fish consumption for particular groups (WSDH/OHD,96); reduced bald eagle reproduction in LCR noted (USFWS,96).	1998
-CROSSES SUBBASINS	Columbia River 0 to 35.2	PCB	public health advisories	Year Around	Levels of PCBs found in some fish (carp, peamouth, sucker) exceed health criteria, OR/WA Health Depts. have issued recommendations regarding fish consumption for particular groups (WSDH/OHD,96); reduced bald eagle reproduction in LCR noted (USFWS,96).	1998
-CROSSES SUBBASINS	Columbia River 142 to 188.6	PCB	Table 20	Year Around	USGS data collected at RM 141. 35 day average concentration of 1004 pg/L. Criterion = 79 pg/L. Dissolved concentration estimated from semipermeable-membrane device data. (USGS Report 99-4051). Oregon health Division crayfish advisory at Bonneville Dam, issued March 1, 2002.	2002
-CROSSES SUBBASINS	Columbia River 35.2 to 98	DDT Metabolite (DDE)	public health advisories	Year Around	Levels of DDE/DDT found in some fish (carp, peamouth, sucker) exceed health criteria, OR/WA Health Depts. have issued recommendations regarding fish consumption for particular groups (WSDH/OHD,96); reduced bald eagle reproduction in LCR noted (USFWS,96).	1998
-CROSSES SUBBASINS	Columbia River 35.2 to 98	PCB	public health advisories	Year Around	Levels of PCBs found in some fish (carp, peamouth, sucker) exceed health criteria, OR/WA Health Depts. have issued recommendations regarding fish consumption for particular groups (WSDH/OHD,96); reduced bald eagle reproduction in LCR noted (USFWS,96).	1998
-CROSSES SUBBASINS	Columbia River 98 to 142	DDT Metabolite (DDE)	public health advisories	Year Around	Levels of DDE/DDT found in some fish (carp, peamouth, sucker) exceed health criteria, OR/WA Health Depts. have issued recommendations regarding fish consumption for particular groups (WSDH/OHD,96); reduced bald eagle reproduction in LCR noted (USFWS,96).	1998
-CROSSES SUBBASINS	Columbia River 98 to 142	PCB	public health advisories	Year Around	Levels of PCBs found in some fish (carp, peamouth, sucker) exceed health criteria, OR/WA Health Depts. have issued recommendations regarding fish consumption for particular groups (WSDH/OHD,96); reduced bald eagle reproduction in LCR noted (USFWS,96).	1998
-CROSSES SUBBASINS	River	Polynuclear Aromatic Hydrocarbons	Table 20	Year Around	USGS site at RM 141: 35 day average sample = 33500 pg/L. Criterion = 2800 pg/L. Dissolved concentration estimated from semipermeablemembrane device data. (USGS Report 99-4051).	2002

Appendix B.

Chemicals to be Analyzed in the Lower Columbia River SPMD Study

Chlorinated Pesticides

4,4'-DDT

4,4'-DDE

4,4-DDD

Dieldrin

PCBs

PCB-1016

PCB-1221

PCB-1232

PCB-1242

PCB-1254

PCB-1260

PAH

Naphthalene

2-Methylnaphthalene

1-Methylnaphthalene

1,1'-Biphenyl

2-Chloronaphthalene

2,6-Dimethylnaphthalene

Acenaphthylene

Acenaphthene

Dibenzofuran

1,6,7-Trimethylnaphthalene

Fluorene

9H-Fluorene, 1-methyl-

Dibenzothiophene

Phenanthrene

Anthracene

Carbazole

2-Methylphenanthrene

1-Methylphenanthrene

4,6-Dimethyldibenzothiophene

Phenanthrene, 3,6-dimethyl-

Fluoranthene

Pyrene

2-Methylfluoranthene

Retene

Benzo(a)anthracene

Chrysene

Chrysene, 5-methyl-Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo[e]pyrene
Benzo(a)pyrene
Perylene
Indeno(1,2,3-cd)pyrene
Dibenzo(a,h)anthracene
Benzo(ghi)perylene

Appendix C. Estimated Water Concentration Calculator From SPMD Data (D. Alvarez, USGS)

To calculate the estimated water concentrations (C_w) from SPMD data, enter the appropriate information into the highlighted yellow cells.

Enter a temperature value (10, 18, or 26) in °C which most closely approximates the actual exposure water temperature.

(NOTE: a standard 81 cm SPMD has lipid volume of 0.001L, membrane volume of 0.0037L, and a total volume of 0.0047L.)

If a PRC was used, the k_{e-PRC} can be calculated by k_{e-PRC} = [In(C_{SPMDo}/C_{SPMD})]/t. If a PRC was not used, enter the same number for the k_{e-PRC} as for the k_{e-cal}-

$$k_{e-PRC} (d^{-1}) = 0.021$$

The k_{e-cal} value is the laboratory calibration value for the native PRC analog.

$$k_{e-cal}$$
 (d⁻¹)= 0.021 (NOTE: the k_{e-cal} for D₁₀-Phenanthrene is 0.021 d⁻¹)

Estimated water concentrations can not be calculated for all compounds.

For compounds in which laboratory R_s values do not exist, the term N/A will appear in place of a numerical value, indicating the inability to estimate the water concentration. The final Estimated Water Concentration values appear in the light blue highlighted cells.

	Project N	lame:	Water Sampling Project No. 1					
Compound	Log K _{ow}	K_{SPMD}	Laboratory R _s	PRC corrected R _s	Theoretical	Total Analyte	Water Conc.	Model Used
			(L/d)	(L/d)	t _{1/2}	(ng/SPMD)	(pg/L)	
p,p'-DDE	6.14 ^a	2.50E+05	6.9	6.9	118.1	10.0	69.0	linear
Dieldrin	4.60 ^a	2.38E+04	4.0	4.0	19.4	10.0	47.2	curvilinear
p,p'-DDD	5.75 ^a	1.54E+05	3.8	3.8	131.6	10.0	125.3	linear
p,p'-DDT	5.47 ^a	1.04E+05	5.6	5.6	60.2	10.0	85.0	linear
Total PCB g, h	6.40 ^{g, h}	3.33E+05	4.8	4.8	226.2	10.0	99.2	linear
Naphthalene	3.45 ^f	1.90E+03	0.9	0.9	6.9	10.0	988.7	curvilinear
Acenaphthylene	4.08 ^f	8.26E+03	1.4	1.4	19.2	10.0	137.1	curvilinear
Acenaphthene	4.22 ^f	1.11E+04	2.3	2.3	15.8	10.0	115.4	curvilinear
Fluorene	4.38 ^f	1.55E+04	1.7	1.7	29.7	10.0	280.1	linear
Phenanthrene	4.46 ^f	1.82E+04	3.4	3.4	17.4	10.0	66.5	curvilinear
Anthracene	4.54 ^f	2.12E+04	3.6	3.6	19.2	10.0	53.3	curvilinear
Fluoranthene	5.20 ^f	6.83E+04	4.6	4.6	48.4	10.0	103.5	linear
Pyrene	5.30 ^f	8.00E+04	5.2	5.2	50.1	10.0	91.6	linear
Benz[a]anthracene	5.91 ^f	1.89E+05	3.6	3.6	171.2	10.0	132.3	linear
Chrysene	5.61 ^f	1.27E+05	5.1	5.1	80.9	10.0	93.4	linear
Benzo[b]fluoranthene	5.78 ^f	1.60E+05	3.4	3.4	153.1	10.0	140.1	linear
Benzo[k]fluoranthene	6.20 ^f	2.68E+05	4.0	4.0	218.3	10.0	119.0	linear
Benzo[a]pyrene	6.35 ^f	3.16E+05	4.3	4.3	239.5	10.0	110.7	linear
Indeno[1,2,3-cd]pyrene	6.75 ^f	4.68E+05	4.2	4.2	363.1	10.0	113.4	linear
Dibenzo[a,h]anthracene	6.51 ^f	3.73E+05	3.3	3.3	368.2	10.0	144.3	linear
Benzo[g,h,l]perylene	6.90 ^f	5.33E+05	2.4	2.4	723.1	10.0	198.4	linear

The linear model of estimation was used in cases where a compound's log K_{ow}>6.

This calculator applies only to SPMDs which conform to the surface area-to-volume ratio of a standard SPMD.

If multiple log K_{nw} values were found in the literature, a mean value was selected using the t test at 95% Confidence for rejection of outliers.

a Mackay, D.; Shiu, W-Y; Ma, K-C Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Volume V, Lewis Publishers, Boca Raton, 1997.

^b Oliver, B.G.; Niimi, A.J. Environ. Sci. Technol., 1985, 19:9, 842-849.

^c Simpson, C.D.; Wilcock, R.J.; Smith, T.J.; Wilkins, A.L.; Langdon, A.G. Bull. Environ. Contam. Toxicol., 1995, 55:1, 149-153.

^d Veith, G.D.; DeFoe, D.L.; Bergstedt, B.V. J. Fish Res. Board Can., 1979, 36, 1040-1048.

^e Syracuse Research Corporation, On-Line Log Kow Estimator (KowWin), http://esc.syrres.com/interkow/logkow.htm.

Huckins, J.N.; Petty, J.D.; Orazio, C.E.; Lebo, J.A.; Clark, R.C.; Gibson, V.L.; Gala, W.R.; Echols, K.R. Environ. Sci. Technol., 1999, 33, 3918-3923.

⁹ Meadows, J.C.; Echols, K.R.; Huckins, J.N.; Borsuk, F.A.; Carline, R.F.; Tillit, D.E. Environ. Sci. Technol., 1998, 32, 1847-1852.

^h Rantalainen, A.L.; Cretney, W.; Ikonomou, M.G. Chemosphere, 2000, 40, 147-158.

Appendix D.

Cost Estimate for Analysis and Equipment

Appendix D. Cost Estimate for Analysis and Equipment

Description	Quantity	Unit Price	Subtotals						
SPMD Services (Environmental Sampling Technologies)									
SPMDs on Carriers (60/deploy)	180	40	6840*						
SPMD Trip Blanks (4/deploy)	12	40	456*						
SPMD Backups (8/deploy)	24	40	912*						
Spike Charges	108	3	324						
Dialysis + GPC (14/deploy)	42	252	10055*						
1 3/		-	\$18,180						
Chemical Analyses (Ecology Man	chester Environ	ımental Labor	atory)						
Pesticides/PCBs (21/deploy)**	63	120	7560						
PAHs (21/deploy.)**	63	200	12600						
TSS, TOC, DOC (39/deploy)	117	70	<u>8190</u>						
			\$28,350						
Equipment									
Temperature Tidbits	14	120	1680						
SPMD Canisters	4	325	1300						
Anchor Components			490						
•		-	\$3,470						
	\$50,000								

^{*5%} Government Discount Rate Applied to Price.

^{**}Includes One Laboratory Duplicate, Matrix Spikes, and Two EST Blanks (Per Deployment); Silica Gel Cleanup for PAH; Analytical Cost Based on 50% Discounted Price at Manchester, True Costs are 2X.