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Memorandum

From: Dave Dilks

Date: February 26, 2020

Project: SRRTTF9

To: Spokane River Regional Toxics Task Force

CC:

SUBJECT: WORKING DRAFT: Preliminary Design of a Long-Term Monitoring/Tracking Program

Summary

LimnoTech reviewed fifteen different sampling methodologies across a range of environmental media to assess their suitability for use in a long-term monitoring program to determine if PCB concentrations are decreasing over time. The review considered several aspects of suitability, including: representativeness, ability to discern trends, ability to accurately measure low concentrations, sustainability, and cost. Based upon this review, recommendations for the long-term monitoring program are provided in a tiered fashion as shown below:

Highest Consideration	
• Year-old wild rainbow trout	• *in situ* solid phase extraction
Secondary Consideration	
• Passive sampling: SPMD	• Solid-phase passive devices: water column
• Particulates (sediment trap)	• Osprey eggs
Opportunistic Inclusion	
• Small volume grab samples	• Multi-age fish tissue
• Point source discharges	
Not Recommended	
• Large volume water column composites	• Particulates (centrifugation)
• Biofilm	• Sediment grab samples
• Enzyme-linked immunosorbent assay	• Solid-phase passive devices: sediment

Year-old wild rainbow trout and *in situ* solid phase extraction best satisfy the assessment criteria, and are recommended for primary consideration. Four other media/methodologies merit additional consideration. Passive water column sampling provides significant benefits, but the technology may be evolving from SPMDs to solid-phase passive devices. Particulates (sediment trap) and osprey eggs also have desirable attributes, but concerns about their trend-detection capabilities prevent them from receiving the highest recommendation.

Three media/methodologies (small volume grab samples, multi-age fish tissue, and point source discharges) contain significant limitations, but can be useful in supporting trend assessment to the extent that they are included in other monitoring programs being conducted independent of the Task Force. Six media/methodologies, while worthwhile for other monitoring objectives, are not recommended for purposes of this long term monitoring program. These include large volume water column composites, particulates (centrifugation), biofilm, and all sediment-based monitoring.

Background

The Washington State Department of Ecology has included language in the NPDES permits for the Spokane River dischargers in Washington that requires the permittees to create and participate in the Spokane River Regional Toxics Task Force (SRRTTF) and to make measurable progress toward meeting applicable water quality criteria for PCBs. Several categories of metrics are used to demonstrate measurable progress, with one category corresponding to Outcomes, i.e. "Progress toward achievement of the applicable water quality criteria for PCBs in the Spokane River which could be demonstrated by achievement of the applicable water quality standards, health standards, and/or measured reductions of toxics to or in the Spokane River" (Ecology, 2014). Demonstration that this progress is occurring will require the establishment of a long-term monitoring program.

The objective of this memorandum is to provide recommendations for appropriate media and methodologies to be included in a sustainable long-term monitoring program to determine if PCB concentrations are decreasing in response to source reduction actions. The memorandum is divided into the following sections:

1. Objectives
2. Candidate media/methodologies
3. Evaluation methodology
4. Assessment
5. Recommendations

Objectives

Providing a clear specification of objectives is an essential step in design of a monitoring program. The first requirement of the scope of work for this task is to "Define the goals and objectives for a long-term sustainable monitoring program along with the associated methodologies for such a program so that the effectiveness of PCB reduction activities in the watershed can be tracked by monitoring one or more media taking into account current measurement methodologies and their limitations relative to their ability to discern the potential magnitude of future reductions in PCB levels." Monitoring objectives can be specified at different levels, stating with broad management objectives and progressing to levels of greater scientific detail.

High Level Management Objectives

The primary management-level objectives for this monitoring are embedded in the task description and in the definition of measurable progress both provided above:

- The selected methodologies must be capable of assessing progress toward achievement of the applicable water quality criteria for PCBs in the Spokane River, in terms of reductions of toxics to or in the Spokane River.
- The selected methodologies must be sustainable long-term.

Management/Scientific Objectives

The next level of monitoring objectives is designed to bridge the gap between high level management objectives and the technical detail needed to select the specific media/methodologies to be contained in the monitoring plan. These "management/scientific" objectives can be stated as:

- Measurements from the selected media/methodologies should accurately represent current PCB loads and concentrations.
- The selected media/methodologies should be capable of efficiently discerning when trends over time occur.

- The selected media/methodologies should be capable of accurately representing concentrations as they decrease in response to future load reductions.
- The selected media/methodologies should remain relevant/acceptable over the lifetime of the monitoring program.
- The selected media/methodologies should have costs consistent with the resources available to the Task Force.

Candidate media/methodologies will be evaluated on their ability to satisfy specific attributes that corresponds to the above objectives, as discussed below.

Representativeness

The ability of a selected measurement technique to accurately represent current PCB loads and concentrations has three components: 1) Temporal representativeness, 2) Spatial representativeness, and 3) Physical representativeness. In terms of temporal representativeness, measurements should reflect current, rather than historical loading conditions. Temporal representativeness can be evaluated in terms of what is called the period of integration of the method, i.e. the length of time over which a sample reflects ambient concentrations. A water quality grab sample has a very short period of integration, as it represents near instantaneous loading conditions. Passive samplers have a period of integration equal to the amount of time that they are deployed in the river. PCB concentrations in tissue from older fish is an example of a potentially poor temporal indicator, to the extent that the fishes' body burden has a long period of integration and potentially reflects historical PCB loads and concentrations.

Spatial representativeness refers to the extent to which measurements reflect condition representing overall PCB load to the system. The use of bottom sediments from a localized hot spot is an example of a potentially poor indicator of overall spatial conditions, to the extent that concentrations at the hot spot primarily reflect a small-scale localized load and response.

Physical representativeness refers to the extent to which measurements reflect total PCB concentrations in the river itself. Direct measurement of total PCB concentrations has excellent physical representativeness. The use of surrogates (e.g. dissolved phase PCBs, PCB concentrations in terrestrial predators) has potentially poor physical representativeness if the correlation between surrogate measure and total PCB concentration is not well established.

Capable of Efficiently Discerning Trends

The selected media/methodologies should be capable of efficiently distinguishing whatever temporal trends that occur. This characteristic is primarily reflected by the variability (or, more accurately, lack of variability) in individual sample results, as larger variability requires more samples and/or time to discern a trend. Collection of a single water column grab sample per year is an example of poor trend discernment, as the high variability in concentration among samples would require an extremely long period of time to distinguish all but very dramatic concentration trends.

Applicability at Low Concentrations

The selected media/methodologies should be capable of accurately representing PCB concentrations as they decrease in response to future load reductions. Water column grab samples are an example of a potentially poor indicator, if future concentrations drop to levels approaching limits of detection and/or lowest achievable blank concentrations.

Sustainability

There should be high confidence that the selected media/methodologies will remain relevant and acceptable over the lifetime of the monitoring program. This will be reflected both by the presence of an accepted application protocol, as well as the length of time that the methodology has been consistently applied. Selection of a methodology that is still undergoing refinement may result in future commitment to an abandoned technology.

Cost Effectiveness

The cost of the monitoring program must be consistent with the resources available to the Task Force. This will be reflected in terms of field cost, laboratory cost per sample, and number of samples required to establish a trend.

Candidate Media/Methodologies

A review of past Ecology studies and the scientific literature, in conjunction with recommendations made by Task Force members, have resulted in a total of fifteen candidate media/methodologies to be evaluated (Table 1). Eight of the methodologies correspond to the water column, three methodologies correspond to bottom sediments, two methodologies correspond to fish tissue, and two methodologies (point source discharges and osprey) fall into the media category of other. The remainder of this section describes each of the candidate media/methodologies.

Table 1. Media and Methodologies to Be Evaluated.

	Medium			
Methodology	Water Column	Sediments	Fish Tissue	Other
	Small volume grab samples	Grab samples	Multiple sizes and/or multiple species	Osprey eggs
	Large volume composites	Enzyme-linked immunosorbent assay (ELISA)	Targeted species and year class	Point source discharges
	In situ solid phase extraction	Solid-phase passive devices		
	Passive sampling: SPMD			
	Solid-phase passive devices			
	Particulates (sediment trap)			
	Particulates (centrifugation)			
	Biofilm			

Water Column

Eight methods have been identified to represent total PCB concentrations in the water column:

- Small volume grab samples
- Large volume composites
- In situ solid phase extraction
- Passive sampling: SPMD
- Solid-phase passive devices
- Particulates (sediment trap)
- Particulates (centrifugation)
- Biofilm

Small Volume Grab Samples

Small volume grab sampling consists of direct immersion of a small (~2 liter) glass bottle into the water column. Sample bottles are returned to the laboratory for direct measurement of total (i.e. dissolved plus particle-bound) PCB concentration. Small volume grab sampling has served as the basis of all of the Task Force's monitoring efforts.

Large Volume Composites

Large-volume water sampling collects a greater quantity (e.g. 20 liters) of water than small volume grab samples to provide a sufficient amount of PCBs such that they can be more accurately quantified. The PCBs in large volume samples are pre-concentrated prior to analysis. Ecology (Hobbs et al, 2019a) used two different methods for pre-concentration: 1) an XAD-2 resin followed by solvent extraction of the XAD, and 2) a solvent liquid-liquid extraction.

in situ Solid-Phase Extraction

in situ solid-phase extraction is conducted through the use of active samplers called continuous low-level aqueous monitoring devices (CLAMs). The CLAM is a submersible device that extracts water on-site through a solid phase extraction (SPE) disk. The SPE disk is returned to the laboratory for analysis of total PCB concentrations.

Passive Sampling: SPMD

Passive sampling consists of deployment of a sampling device for an extended period that allows concentrations in the device to approach equilibrium with the surrounding environment. Semipermeable membrane devices (SPMDs) are one passive sampling approach used to concentrate dissolved PCBs from the water column. An SPMD consists of a low-density polyethylene tube filled with a highly purified lipid (e.g. triolein). The tube is thin-walled and generally considered nonporous except for small cavities created freely dissolved PCBs are able to pass through the pores and are sequestered and concentrated in both the lipid and the polyethylene itself. Dissolved PCB congener concentrations are calculated using models that estimate the uptake rate of chemicals into passive samplers.

Solid-Phase Passive Devices

A range of solid-phase passive devices made from various plastic materials such as polyoxymethylene (POM) and low-density polyethylene (LDPE) have been evaluated and show promise in terms of measuring low-level concentrations of freely dissolved PCBs in water. Various configurations of the passive samplers are possible in terms of their size and shape, but currently, two major configurations are generally used: (1) sheets and thin films, and (2) coatings. LDPE and POM are most often used as thin sheet- or film-forms in various thickness, shapes, and dimensions (U.S. EPA/SERDP/ESTCP, 2017).

Particulates (Sediment Trap)

Sediment traps consist of vertical collection cylinders suspended in the middle of the water column, which collect solid particulate matter as it settles. Sediment traps have been deployed by Ecology to assess PCB concentration in particulate matter at Upriver Dam and Ninemile Dam in 2012-2013 (Era-Miller, 2014), and at the eastern Spokane Tribal boundary during 2015 – 2016 (Era-Miller and McCall, 2017).

Particulates (Centrifugation)

Centrifugation has been used as a sampling method for low-level pollutants with an affinity for particulates, such as PCBs. Passing a water sample through a centrifuge concentrates the particles and the particle-bound PCBs, providing a greater quantity of PCB mass and improving detection capabilities. Analysis of the supernatant from the centrifuge allows the dissolved/colloidal phases of PCBs to be quantified.

Biofilm

Biofilm, a collection of living and dead periphyton, microbial biomass, and organic detritus attached to bottom substrates is known to absorb and sequester organic contaminants from the water column (Hobbs et al, 2019b). Biofilm PCBs were analyzed at multiple locations in the Spokane River by Ecology in 2018 and 2019.

Bottom Sediments

Bedded sediments provide a surrogate indication of water column PCB concentrations, as PCBs in the water column sorb onto particulate material and settle to the bottom of the river. Three methodologies have been identified to measure PCB concentrations in bottom sediments: sediment grab samples, enzyme-linked immunosorbent assay (ELISA), and solid-phase passive devices.

Sediment Grab Samples

Sediment grab samples, as the name implies, consist of directly collecting a sample of the bottom sediments, and transporting it to the laboratory for measurement of total PCB concentration.

Enzyme-Linked Immunosorbent Assay (ELISA)

The enzyme-linked immunosorbent assay (ELISA) estimates sediment PCB concentrations based upon the specific binding of PCB to antibodies. It is a rapid and less expensive measurement technique than traditional methods. The method is semi-quantitative not quantitative. Because of the ease of use and rapidity, the method is often used for field screening of PCBs (National Research Council, 2001).

Solid-Phase Passive Devices

The sampling technologies described above for solid-phase passive sampling of the water column can be applied to estimate sediment pore water PCB concentrations, by deploying the device in bottom sediments (U.S. EPA/SERDP/ESTCP, 2017).

Fish Tissue

Fish tissue PCBs concentrations have been a commonly-used indicator of contamination, both for trend assessment as well as for setting fish consumption advisories. Fish tissue monitoring can target different species or age classes, depending on the objective of the monitoring. For purposes of this assessment, two types of fish sampling are being evaluated: 1) a single age class of a given species, and 2) multiple age classes of a given species.

Other

Two other media/methodologies are being considered that fall outside the categories of water column, sediment, and fish. They are direct measurement of PCBs in osprey eggs and point source discharges.

Osprey Eggs

The primary diet of some predator species, such as osprey, is fish. Osprey eggs have high lipid content, facilitating the bioaccumulation of lipophilic contaminants like PCBs. USGS has conducted extensive research on organic contaminants in osprey eggs. Results of this research have demonstrated that osprey eggs have many positive qualities regarding measuring hydrophobic contaminant trends in surface water, including (Henny et al., 2010; Mathieu and McCall, 2016).

- They are known to bioaccumulate lipophilic contaminants
- Their diet consists of 99^{+}% fish
- Osprey generally forage with 1-2 miles of their nest site
- Osprey are available in high numbers
- The removal of "sample egg" from the usual 3-egg clutch has shown limited effect on productivity of sampled nests
- Opsrey are tolerant of short-term nest disturbance (i.e. taking an egg from a nest)

Point Source Discharges

The Comprehensive Plan (LimnoTech, 2016) identified wastewater discharges as the second largest mass delivery mechanism of PCBs to the Spokane River, second only to the outlet of Lake Coeur d'Alene. As such, changes in loads in PCB loads from these treatment plants should correlate strongly to changes in in-river PCB concentration.

Evaluation Methodology

This section provides an approach that allows the candidate media/methodologies to be compared against each other. It begins with a discussion of evaluation methodologies used in other monitoring design studies, and builds upon them to provide a methodology tailored to the Task Force's needs.

Prior Evaluations

Previous Ecology studies (Hobbs et al, 2019a; Era-Miller et al, 2017) developed approaches for evaluating candidate monitoring methodologies for water column PCBs. While these evaluations did not necessarily have the same objectives of this study (e.g. they consider only a subset of the media/methodologies to be evaluated here), they provide an excellent starting point for developing a Task Force-specific evaluation methodology.

Era-Miller (2014)

Era-Miller (2014) collected data from the Spokane River at the Spokane Tribal boundary during three hydrologic regimes (spring high flow, summer low flow and winter moderate flow) to establish recommendations for a long-term toxics monitoring at this site. Three collection and extraction techniques were used on whole water samples: CLAM (Continuous Low-level Aqueous Monitoring device), large volume composites analyzed with XAD-2, and small volume samples analyzed with liquid-liquid extraction. PCB were also analyzed on suspended sediments collected with sediment traps deployed for four months at a time.

Era-Miller (2014) developed a rating system to evaluate the various methods based on a yes or no answer to the four following questions:

1. Was there a clear environmental signal above the analytical background noise (this was based on laboratory method blank and transfer blank contamination)?
2. Was the variability of field replicates and split samples of acceptable quality?
3. Is the field collection method easily reproducible on a larger scale?
4. Were detection limits low enough to evaluate State water quality standards?

Each collection method/analytical method combination was rated as either good, poor, or okay based on the majority of yes or no answers (excludes the answer of not applicable):

- All Yes = Good,
- Majority Yes = OK,
- Half or fewer Yes = Poor

Surface water grabs and composite samples were determined to not be a good monitoring tool for PCBs in the Spokane River, because the congener sample data in general did not give a clear environmental signal above the analytical background noise. The CLAM collection method was determined to be a good surrogate for grab sampling, as PCB congeners gave a clear environmental signal and had good precision of field triplicates. One potential issue recognized with the CLAM was accurately determining the total volume of water filtered through the device during deployment. Sediment trap sampling was rated "good" as results gave a clear environmental signal above the analytical background noise and laboratory duplicates and split samples showed low variability (high precision).

Hobbs et al (2019a)

The objective of this study was to characterize the precision and accuracy of three different high-volume collection methods for use with low-level analytical methods:

- *In situ* solid phase extraction using continuous low-level aquatic monitoring devices (CLAMs).
- Centrifugation and separation of solids and water for analysis.
- Large volume (20L) composite grab samples with filtration and extraction using XAD-2 resin at the analytical laboratory.

The evaluation criteria used to assess the overall reliability of the sampling approaches included method sensitivity, bias, and precision. The specific evaluation criteria used are shown in Table 2, and the rating scheme for evaluating the sampling approaches shown in Table 3.

Table 2. Evaluation approach for the field sampling methods (from Hobbs et al, 2019a)

	Evaluation approach	**Evaluation criteria**
Sensitivity	Evaluated using the ratio of total PCB in the sample to total PCB in the corresponding lab blank.	Represents the level of blank interference and is analogous to blank censoring thresholds. Methods evaluated against USEPA thresholds for blank censoring (USEPA, 2016).
Bias	Evaluated based on the maximum number of detections among sampling approaches.	Method with the highest number of detections receives the highest rating.
Precision	Evaluated based on the sample relative standard deviation or relative percent difference.	Study QAPP method quality objectives (Hobbs and McCall, 2016).

Table 3. Rating scheme for evaluation of sampling approaches (from Hobbs et al, 2019)

Rating	Sensitivity (sample-to-blank ratio)	Bias (number of detections)	Precision (sample RSD or RPD)	Overall rating
Good	S:B >5	Method with the maximum # of detections	<20%	A maximum of one indicator is rated fair, and no indicators are rated poor.
Fair	3<S:B<5	>50% the maximum # of detections	20-50%	One of the indicators is rated poor, or two or more indicators are rated fair.
Poor	S:B<3	<50% the maximum # of detections	>50%	Two or more of the indicators are rated poor

Their overall assessment is provided in Table 4. They found that pre-concentration approaches such as SPE media provide larger sample volumes in the field and therefore allow the detection of low concentrations. Conversely, they are more time consuming and more costly. Small volume grab samples are a less costly approach, but are subject to very low environmental concentrations being insufficient to be above the “noise” of the sampling approach. They ultimately recommended that studies which are focused on source identification or source tracking of toxics should rely on discrete grab samples, SPE disks, or passive samplers.

Table 4. Overall assessment of low-level sampling approaches (from Hobbs et al, 2019)

Method	Description	Volume Sampled (L)	Sensitivity	Bias	Precision	Overall Assessment	Sample Time	Sampling Cost	Comments
centrifuge sediment	continuous flow-through centrifuge system with a controlled flow rate of 3L/min	500 – 5,000	good	good	good	good	dependent on TSS of the water; 4 – 48 hours	high	labor-intensive; prolonged sample time can inhibit synoptic survey on a river
20L composite – XAD extraction	10 – 12 part composite sample over 24 – 48 hours into stainless steel canister; extracted in the lab using XAD-2 media	20	fair	poor	fair	fair	composite can be taken at desired frequency	low	stainless steel canisters are cumbersome in the field and lab; high shipping costs
20L composite – LL extraction	10 – 12 part composite sample over 24 – 48 hours into stainless steel canister; extracted in the lab in 2L aliquots using liquid-liquid extraction	20	poor	fair	fair	fair	composite can be taken at desired frequency	low	stainless steel canisters are cumbersome in the field and lab; high shipping costs
in situ SPE	continuous *in situ* pumping of water (5 – 75ml/minute) through an SPE media disk (C-18 media)	20 – 60	fair	good – fair*	good	good	12 – 48 hours	moderate	sampling device does not function well in turbid waters
2L composite grab	a two-part composite sample over 24 hours	~2	fair	fair	good	fair	1 – 24 hours	low	simple sampling protocols
Passive Approaches									
semipermeable membrane devices	polyethylene strips containing triolein oil deployed for 1-month in stainless steel canisters	NA	good	good	good	good	deployed for one month; three sampling trips required	moderate	not a direct measurement of water concentrations; requires a lot of data reduction and analysis

* The number of detections is lower than the maximum reported; however, the congener distribution is very similar; therefore, the rating is closer to ‘good’.

SRRTTF Assessment Methodology

This section provides a methodology for evaluating the candidate media/methodologies for use in supporting a long-term monitoring plan for the Task Force. Each media/methodology will be evaluated on their ability to satisfy the attributes described previously:

- Temporally representative
- Spatially representative
- Physically representative
- Trend discerning

- Applicable at low concentrations
- Sustainable
- Cost-effective

Similar to the ranking systems developed by Era-Miller (2014) and Hobbs et al (2019a), the ability of each media/methodology to satisfy an attribute will be judged as good, fair, or poor. In addition, a score of unknown will be given where insufficient information is available to rate a media/methodology for a particular attribute.

Temporally Representative

This criterion reflects the extent to which measurements reflect current, rather than historical loading conditions. Media/methodologies that reflect conditions from a year of less are deemed good. Media/methodologies that reflect conditions from one to five years are deemed fair. Media/ methodologies that reflect conditions from more than five years past are deemed poor.

Spatially Representative

This criterion reflects the extent to which measurements reflect conditions representative of overall PCB load to the system. Media/methodologies that reflect broad spatial conditions are deemed good; media/methodologies that have a strong potential to reflect more localized spatial conditions are rated fair; media/methodologies that are known to reflect extremely localized conditions that are non-representative of the systems as a whole are deemed poor.

Physically Representative

This criterion reflects the extent to which measurements reflect PCB concentrations in the river itself. Media/methodologies that directly reflect total PCB concentrations are deemed good; media/methodologies that are indirect but strongly correlated to river PCB concentrations are deemed fair; media/methodologies that are indirect and moderately or weakly correlated to river PCB concentrations are deemed poor.

Trend Discerning (Variability)

This criterion reflects the extent to which measurements are capable of efficiently distinguishing whatever temporal trends that occur. This will be evaluated via in the observed variability in individual sample results from historical sampling efforts. The evaluation recognizes two sources of variability, variability in replicate samples and temporal variability. Variability across replicates samples will be assessed building off of the evaluation criteria from Hobbs et al (2019a) discussed previously. The consideration of temporal variability is shown in Table 5.

Table 5. Ranking System for Assessing Variability

Rating	Replicate Variability (sample RSD or RPD)	Temporal Variability (sample RSD)	Overall rating
Good	<20%	<40%	Neither indicator is rated poor, and at least one indicator is rated good.
Fair	20-50%	40-60%	Both indicators are rated fair, or one indicator is rated good and the other is rated poor
Poor	>50%	>60%	One or both of the indicators are rated poor, and no indicator is rated good

Applicability at Low Concentrations

This criterion reflects the ability of accurately represent concentrations as they decrease in response to future load reductions. The assessment will be based on the evaluation criterion developed by Hobbs et al (2019a) for sensitivity, which they define as the ability of the method to detect a substance above the analytical background or noise of the system. Sensitivity is assessed in terms of the sample-to-blank ratio (S/B), i.e. the ratio of concentrations observed in the environment to the concentration observed in analytical blanks. Following the rating system form Hobbs et al (2019), media/methodologies that have a sample-to-blank ratio greater than five are deemed good; media/ methodologies that have a sample-to-blank ratio between three and five are deemed fair; media/methodologies that have a sample-to-blank ratio less than three are deemed poor.

Sustainability

This criterion reflects the confidence that the selected media/methodologies will remain relevant and acceptable over the lifetime of the monitoring program. Media/methodologies that have had been consistently applied over the last ten years and/or have officially adopted standard operating procedures for at least five years are deemed good; media/ methodologies that have been consistently applied for five years to ten years are deemed fair; media/methodologies for which no standard operating procedures have been established are deemed poor.

Costs

This criterion reflects the expected annual cost of the monitoring program, considering both field and laboratory expense. The scope of this effort does not allow for a detailed assessment of costs for each media/ methodology, so a three-tiered qualitative approach is taken similar to that of Hobbs et al (2019a). To provide some quantitative context, media/methodologies that are expected to cost less than $35,000 per monitoring event are deemed good (i.e. low); media/ methodologies that cost between $35,000 and $75,000 are deemed fair (i.e. moderate); and media/methodologies that cost more than $75,000 are deemed poor (i.e. high).

Evaluation

This section examines the data available for each candidate media/methodology in comparison with the ranking criteria described above.

Small Volume Grab Samples

Temporal Representativeness

Small volume grab samples represent instantaneous conditions at the time of sample collection, so an individual sample provides no temporal integration. Grab sampling can provide some degree of temporal integration via the process of compositing. With compositing, individual grab samples taken at different times are combined prior to laboratory analysis. The resulting concentration measurement therefore reflects the average concentration across the individual sample comprising the composite. Because the period of integration is less than one year regardless of whether samples are composited or not, small volume grab samples are rated as good in terms of temporal representativeness.

Spatial Representativeness

Grab samples, typically taken mid-channel in the Spokane River, are generally considered to accurately represent spatially-average concentrations the system. This is based upon the assumption that large lateral concentration gradients do not exist. This is likely a reasonable assumption for all locations except directly downstream of a near-bank load. For this reason, small volume grab samples are rated as good in terms of spatial representativeness.

Physical Representativeness

Grab samples directly reflect total PCB concentrations in the river, and therefore are rated as good for physical representativeness.

Trend Discerning (Variability)

The relative percent difference of replicate samples collected by the Task Force averaged 28% downstream of Plante's Ferry, and 81% upstream. Analysis of grab sample data collected by the Task Force across all monitoring events from 2014-2018 provide the station-specific coefficients of variation shown in Table 1.

Table 6.Coefficients of Variation of PCB Concentrations Calculated at Various Stations from Task Force 2014-2018 Monitoring

Nine Mile Dam (SR1)	USGS Gage (SR3)	Greene St. (SR4)	Plante's Ferry (SR7)	Barker Rd. (SR9)	Lake Coeur d'Alene SR15
0.46	0.60	0.60	0.59	1.26	1.06

A distinct spatial relationship exists, with relative percent differences and coefficients of variation being much lower at Plante's Ferry and all downstream stations. River concentration increase substantially between Barker Rd. and Plante's Ferry, and these results indicate that variability is much higher at lower river concentrations. Following the evaluation criteria provided in Table 5, small volume grab samples are rated poor for locations upstream of Plante's Ferry, and rated as fair for stations from Plante's Ferry downstream.

Low-Level Capability

Average signal to blank ratios by station for Task Force monitoring data are less than three for stations upstream of Plante's Ferry and between three and five for stations from Plante's Ferry downstream. Small volume grab samples are therefore rated as poor for locations upstream of Plante's Ferry, and rated as fair for stations from Plante's Ferry downstream.

Sustainability

Small grab samples have been used to measure PCB concentrations in the Spokane River since 2012, and there is no reason to believe that this method will become obsolete in the foreseeable future. For this reason, small volume grab samples are rated as good in terms of sustainability.

Cost

Field labor costs for small volume grab samples are low compared to other methods, as there is minimal preparation time beyond obtaining sample bottles, samples can be collected across multiple locations per day. Analytical costs are on the order of $1000/sample. For this reason, small volume grab samples are rated as good in terms of cost.

Large Volume Composites

Temporal Representativeness

Large volume composite samples represent near instantaneous conditions at the time of sample collection, with some small degree of temporal integration via the process of compositing and an individual sample provides no temporal integration. Because the period of integration is less than one year, large volume composites are rated as good in terms of temporal representativeness.

Spatial Representativeness

Large volume composite samples, typically taken mid-channel in the Spokane River, are generally considered to accurately represent overall concentration the system, given the assumption that large lateral or vertical gradients do not exist. This is likely a reasonable assumption for all locations except directly downstream of a near-bank load. For this reason, large volume composite samples are rated as good in terms of spatial representativeness.

Physical Representativeness

Large volume samples have good physical representativeness, as measurements directly reflect total PCB concentrations in the river.

Trend Discerning (Variability)

The coefficient of variation of large volume samples collected on two different occasions in the Spokane River were both 0.09 (Hobbs et al, 2019). Insufficient data exist to describe temporal variability. Given that large volume samples represent instantaneous conditions at the time of sampling, it is reasonable to assume that temporal variability is similar to that observed for small volume grab samples. Following the evaluation criteria provided in Table 5, large volume composites are rated poor for locations upstream of Plante's Ferry, and rated fair for stations from Plante's Ferry downstream.

Low-Level Capability

Ecology (Hobbs et al, 2019a) observed a signal to blank ratio for large volume sampling of the Spokane River of 8.8 during fall of 2016 (when river concentrations averaged 191 pg/l) and 2.5 during the summer of 2017 (when river concentrations averaged 22 pg/l). This corresponds to one rating of good and one rating of poor; combining these results in a rating of fair.

Sustainability

Ecology (Joy, 2006) published standard operating procedures for large volume composite sampling in 2006, resulting in a rating of good for sustainability.

Cost

Field labor costs for large volume composite samples are only slightly higher than for small volume grabs. Analytical costs are on the order of $1000/sample. For this reason, small volume grab samples are rated as good in terms of cost.

in situ Solid Phase Extraction

Temporal Representativeness

The period of integration for *in situ* solid phase extraction samplers is on the order of a few days, being reported as for up to 36 hours (Era-Miller and McCall, 2017) and 12 – 48 hours (Hobbs et al, 2019a). Because the period of integration is less than one year, *in situ* solid phase extraction samplers are rated as good in terms of temporal representativeness.

Spatial Representativeness

in situ solid phase extraction samplers deployed mid-channel are generally considered to accurately represent overall concentration the system, given the assumption that large lateral or vertical gradients do not exist. This is likely a reasonable assumption for all locations except directly downstream of a near-bank load. For this reason, *in situ* solid phase extraction samples are rated as good in terms of spatial representativeness.

Physical Representativeness

in situ solid phase extraction have good physical representativeness, as measurements directly reflect total PCB concentrations in the river. Care must be taken, however, to accurately quantify the volume of water being pumped through the media. Hobbs et al (2019) reported that flow rates through the CLAM pumps and the SPE disks declined exponentially over time at all the sites, such that monitoring of the rate of pumping throughout the deployment is important.

Trend Discerning (Variability)

Hobbs et al (2019a) reported a relative standard deviation among triplicate *in situ* solid phase extraction samples of 10%. Insufficient data exist to describe temporal variability. Because *in situ* solid phase extraction has a period of integration on the order of a few days, it is reasonable to assuming that temporal variability is no worse than fair, resulting in an overall rating of good for trend discerning.

Low-Level Capability

Hobbs et al (2019a) reported signal to blank ratios greater than 13, resulting in a rating of good.

Sustainability

Ecology (Wong, 2019) published standard operating procedures for in situ solid phase extraction sampling in 2019, resulting in a rating of good for sustainability. IT is noted, however, that Hobbs et al (2019a) recommended that a follow-up laboratory study should be conducted to test the accuracy of the SPE-CLAM device.

Cost

in situ solid phase extraction requires some lead time with the lab to clean media and spike with labelled compounds. Roughly a day of prep time is required for testing pumps and set-up. Typical time required for pumping is 12 to 48 hours. Some specialized materials (stainless steel SPE filter housing, CLAM pumps) are also required. Overall, the cost of in situ solid phase extraction is rated as moderate/fair.

Passive Sampling: SPMD

Temporal Representativeness

SPMDs are typically deployed on the order of 28 days (Hobbs and Friese, 2016). Because the period of integration is less than one year, SPMDs are rated as good in terms of temporal representativeness.

Spatial Representativeness

SPMDs deployed mid-channel are generally considered to accurately represent overall concentration the system, given the assumption that large lateral or vertical gradients do not exist. This is likely a reasonable assumption for all locations except directly downstream of a near-bank load. For this reason, SPMDs are rated as good in terms of spatial representativeness.

Physical Representativeness

SPMDs measure only dissolved-phase PCB concentrations. SPMD results can be converted into an estimate of total PCB concentration through concurrent measurement sorbent compounds (e.g. particulate organic carbon) and application of partition coefficients to estimate the fraction of total PCBs in dissolved form. Also, the specific uptake or rate of sampling of toxics can only be estimated with these devices; therefore, measured concentrations are considered an estimate (Hobbs et al, 2019). Performance reference compounds (PRCs) can be used to estimate the extent of equilibrium of the target contaminant(s) and provide a method to then adjust measured accumulated target contaminant levels to equilibrium concentrations. Because SPMD measurements provide only an indirect estimate of total PCB concentrations, they are rated as fair in terms of physical representativeness.

Trend Discerning (Variability)

For Spokane River SPMD replicate measurements conducted in 2010 and 2011, Sandvik and Seiders (2012) reported that 91% of results had RPDs of <=25%. Duplicate samples from SPMD results reported by Serdar (2001) had relative percent differences that ranged from 9 to 55%, and averaged 28%. In a recent study from the Wenatchee River in eastern Washington, Hobbs and Friese (2016b) found a relative percent difference between replicate SPMD samples from the Wenatchee River in eastern Washington to be 10%. Because SPMDs have a period of integration on the order of weeks, it is reasonable to assuming that temporal variability is no worse than fair, resulting in an overall rating of good.

Low-Level Capability

In a recent study from the Wenatchee River in eastern Washington, Hobbs and Friese (2016b) used semi-permeable membrane devices to estimate the PCB concentrations in the river water. During sampling events in 2015 and 2016, the semipermeable membrane devices had good sensitivity with an S/B ratio of ~25 at locations of suspected PCB sources and ~2.5 at upriver background locations. For this reason, SPMDs are rated good for low-level capability.

Sustainability

SPMDs have been is used the Spokane River since 1994 (Ecology, 1995), and were the primary basis for estimated water column PCB concentrations in the 2003-2007 source assessment (Serdar et al, 2011). Standard operating procedures for the use of SPMDs have also been published (e.g. Environment and Climate Change Canada, 2018), although not by Ecology. Given this long history of use, SPMDs are rated good for sustainability.

Cost

Pre-monitoring costs for SPMDs include preparation of the reference compound solution, and manufacture/rental of the carriers for the SPMDs. SPMDs should be checked during the month-long period of deployment. In addition to analytical costs for PCBs, collection and analysis of supplemental water samples for TSS and TOC/DOC to characterize PCB partitioning onto solids is also required. Overall, the cost of SPMDs is rated as moderate/fair.

Solid Phase Passive Devices

Temporal Representativeness

Passive samplers can be designed to be deployed for hours to days or months, depending upon the nature of the sampler (Menzie et al, 2016; U.S. EPA/SERDP/ESTCP, 2017). Because deployment times are less than one year, passive samplers are rated as good for temporal representativeness.

Spatial Representativeness

Passive samplers deployed mid-channel are generally considered to accurately represent overall concentration the system, given the assumption that large lateral or vertical gradients do not exist. This is likely a reasonable assumption for all locations except directly downstream of a near-bank load. For this reason, passive samplers are rated good for spatial representativeness.

Physical Representativeness

Passive samplers measure only dissolved-phase PCB concentrations. Passive sampling results can be converted into an estimate of total PCB concentration through concurrent measurement sorbent compounds (e.g. particulate organic carbon) and application of partition coefficients to estimate the fraction of total PCBs in dissolved form. Furthermore, if the passive samplers are deployed for too short of a duration for equilibrium to occur, performance reference compounds must be used to estimate the extent of equilibrium of the target contaminant and provide a method to then adjust measured accumulated target contaminant levels to equilibrium concentrations (U.S. EPA/SERDP/ESTCP, 2017). For this reason, passive samplers are rated fair for physical representativeness.

Trend Discerning (Variability)

No data exist defining the variability, either replicate or seasonal, for the use of solid phase passive devices to measure PCBs in Spokane.

Low-Level Capability

U.S. EPA/SERDP/ESTCP (2017) reports practical quantitation limits for PCB congers using POM of less than 0.4 pg/l for six out of seven congeners reports. PCB3 was the only congener with a larger practical quantitation limit of 17 pg/l. No Spokane data are available by which to judge the signal to blank ratio. Because passive samplers serve to concentrate environmental PCB levels, it is expected that they would rate as high in terms of low level capability.

Sustainability

There has been no deployment of solid-phase passive samplers to the Spokane River. A user's manual (U.S. EPA/SERDP/ESTCP, 2017) exists for laboratory, field, and analytical procedures for solid-phase passive sampling. While the document focuses on their use in contaminated sediments, there is sufficient discussion of the use of these methods in surface waters. The document notes, however, that "the science and practice of passive sampling is an evolving process". For this reason, passive samplers are rated poor for sustainability.

Cost

Solid phase passive devices require time for both deployment and subsequent retrieval, along with checking during the period of deployment. In addition to analytical costs for PCBs, collection and analysis of supplemental water samples for TSS and TOC/DOC to characterize PCB partitioning onto solids is also required. Overall, the cost of solid phase passive devices is rated as moderate/fair.

Particulates (Sediment Traps)

Temporal Representativeness

Sediment traps are typically deployed on the order of a few months, with prior Spokane River deployment durations of 68 to 132 days in 2012-2013, and approximately 4.5 months in 2015-2016. Because deployment times are less than one year, sediment traps are rated good for temporal representativeness.

Spatial Representativeness

Sediment traps deployed mid-channel are generally considered to accurately represent overall concentration the system, given the assumption that large lateral or vertical gradients do not exist. This is likely a reasonable assumption for all locations except directly downstream of a near-bank load. For this reason, passive samplers are rated good for spatial representativeness. It is noted that sediment traps are better suited for deployment in deeper, more quiescent water bodies, making them more suitable for use in the backwater areas of dams rather than the free-flowing portions of the Spokane River.

Physical Representativeness

Sediment traps estimate only the solids-bound portion of PCBs, and do not represent total PCB concentrations. To the extent that it can be assumed that the fraction of total PCBs in solids-bound form remains relatively constant, changes in solids-bound PCBs concentrations over time should accurately reflect changes in total PCBs concentrations. Because this assumption is somewhat uncertain, sediment traps are rated fair for physical representativeness.

Trend Discerning (Variability)

Sediment traps deployed in 2012-2013 showed little variation in PCB content, with a relative standard deviation of less than 1 percent. Greater variation was seen among measured sediment deposition rates at the three traps deployed per site, with a relative standard deviation ranging from 35 to 55%. The relative percent difference of PCB concentration in replicate sediment traps deployed in 2015-2016 ranged from 28 to 40%. Significant temporal variation was seen between flux rates for different deployment periods, with a relative standard deviation of 68%. Following the evaluation criteria provided in Table 5, sediment traps are rated fair for trend discerning.

Low-Level Capability

The signal to blank ratio for all sediment trap results from 2012-2013 were greater than 100, indicating excellent low-level capabilities.

Sustainability

The use of sediment traps to collect particulate matter has been taking place for decades, and the measurement of particle-sorbed PCBs for more than a decade. For this reason, sediment traps are rated good for sustainability.

Cost

Pre-monitoring costs for sediment traps include cleaning the glass cylinders and setting up the traps. A boat is needed along with specialized equipment. Traps need to be deployed and then retrieved after deployment. Analytical cost is $1,000 per sample. Considering all required activities, the cost of sediment traps is rated moderate/fair.

Particulates (Centrifugation)

Temporal Representativeness

This method integrates concentrations of the period of centrifugation, which is on the order of hours to days depending upon suspended solids concentrations. Era-Miller and McCall (2017) reported a sampling duration of 24 hours; Hobbs et al (2019a) sampled over an 8- to 46-hour period. Because sampling durations are less than one year, centrifugation is rated as good for temporal representativeness.

Spatial Representativeness

Centrifugation of water collected mid-channel is generally considered to accurately represent overall concentration the system, given the assumption that large lateral or vertical gradients do not exist. This is likely a reasonable assumption for all locations except directly downstream of a near-bank load. For this reason, centrifugation is rated good for spatial representativeness.

Physical Representativeness

Centrifugation was originally applied to estimate only the solids-bound portion of PCBs, which does not by itself represent total PCB concentrations. To the extent that it can be assumed that the fraction of total PCBs in solids-bound form remains relatively constant over time, changes in solids-bound PCBs concentrations over time should accurately reflect changes in total PCBs concentrations. Because this assumption is somewhat uncertain, centrifugation is rated fair for physical representativeness. Centrifugation can be combined with analysis of PCBs in dissolved form using some other method (e.g. large volume water sampling), in which case it rates as good for physical representativeness.

Trend Discerning (Variability)

The relative percent difference of centrifugation samples collected from the Spokane River from in 2016 and 2017 ranged from 5 to 8%. For this reason, centrifugation is rated as good for trend discerning.

Low-Level Capability

The signal to blank ratios from centrifugation of Spokane River samples ranged from 2.9 to 9.7 for the dissolved component, and from 51.7 to 79.8 for centrifuge sediments ((Hobbs et al, 2019). Centrifugation therefore is rated good for low level capabilities in terms of the sediment component, and fair for overall PCBs.

Sustainability

The use of centrifugation to estimate PCB concentrations on suspended particulate matter dates back to 1993 (Ecology, 1995) and the technology is still being used today. For this reason, centrifugation is rated as good for sustainability.

Cost

Centrifugation has high labor (about a week per sample) and equipment ($20,000) costs. In addition, training is very specialized for the necessary equipment. The analytical cost is $1,000 per sample for just the particulate component, with another $1000 per sample if the dissolved component is also analyzed. For this reason, centrifugation is rated as poor/high in terms of cost.

Biofilm

Temporal Representativeness

Biofilm integrates concentrations over two to three months (Hobbs et al, 2019b). It is noted however, that biofilm is more prevalent during warmer water periods, making it less suitable for assessing winter concentrations. Because durations are less than one year, biofilm is rated good for temporal representativeness.

Spatial Representativeness

Biofilm samples collected mid-channel (should suitable substrate exist) is generally considered to accurately represent overall concentration the system. As with other point measurements, this requires the assumption that large lateral or vertical gradients in concentration do not exist. This is likely a reasonable assumption for all locations except directly downstream of a near-bank load. For this reason, biofilm is rated as good for spatial representativeness.

Physical Representativeness

PCB in biofilm are an indirect measure of total PCBs, as they primarily reflect dissolved-phase water column PCB concentrations. Biofilm results can be converted into an estimate of total water column PCB concentration through the application of partition coefficients to estimate the fraction of total PCBs in dissolved form. There are limited data defining the relationship between water column PCB concentrations and resulting biofilm concentrations. Hobbs et al (2019b) provide some initial empirical data in this regard, but recognize that theirs is the first explicit field examination and comparison of the concentrations of halogenated organics in water and biofilms. For this reason, biofilm is rated as fair for physical representativeness.

Trend Discerning (Variability)

The relative percent difference of one paired set of biofilm samples from the Spokane River in 2018 was 24%. Hobbs and Friese (2016) reported a relative percent difference of one paired set of biofilm samples from the Wenatchee River of 6%. This replicability of results taken from samples at the same site and same time is very good, but the variability at a given site over time or at multiple sites from the same river is more problematic. RPDs for 2014 and 2015 samples at the same site in the Wenatchee ranged from 43 to 94%, with an average of 69% Observed biofilm PCB concentrations from the Spokane River in 2018 spanned several orders of magnitude (95 to 630,000 pg/g), while water column concentrations spanned less than a single order of magnitude. Given the above information, biofilm is rated fair for trend discerning.

Low-Level Capability

Hobbs et al (2019b) report a mean total PCB concentration across 5 method blanks of 12 pg/g. Observed biofilm PCB concentrations in the Spokane River in 2018 ranged 95 to 630,000 pg/g, resulting in a signal to blank ratio consistently above 7. This results in a rating for low level capability of good.

Sustainability

The use of biofilms to estimate PCB concentrations was first tested by Ecology in 2014. No formal standard operating procedures exist for their use. For this reason, they are rated fair in terms of sustainability.

Cost

Biofilm sampling generally requires a low level of effort, requiring the scraping rocks into bowls and compositing. Multiple sites can be sampled within a day. The analytical cost is $1,000 per sample. This results in biofilm being rated as good for cost.

Sediment Grab Samples

Temporal Representativeness

Sediments as a medium have an uncertain period of integration, because the period of contaminant exposure varies depending upon location-specific resuspension and deposition characteristics. Because exposure times could be more than one year, sediment grab samples are rated fair for temporal representativeness.

Spatial Representativeness

Locations with bottom sediments are rare in the Spokane River, such that selection of a location that is known to be representative of broad spatial conditions is unlikely. Due to the risk that a given sediment deposit reflects localized conditions that are non-representative of the systems as a whole, sediment grab samples are rated fair for spatial representativeness.

Physical Representativeness

Sediment PCB concentrations are driven by the solids-bound portion of PCBs, and do not directly reflect total water column PCB concentrations. To the extent that it can be assumed that the fraction of total PCBs in solids-bound form remains relatively constant, changes in solids-bound PCB concentrations over time should accurately reflect changes in total PCBs concentrations. Because this assumption is somewhat uncertain, grab samples are rated fair for physical representativeness.

Trend Discerning (Variability)

Although data are lacking to explicitly define either replicate or temporal variability of sediment grab samples for the Spokane River, Ecology data from 2013 and 2018 show that sediment PCB concentrations to varied by more than a factor of five between nearby sediment locations. While this variability is slightly less when considering PCB concentrations on an organic carbon-normalized basis, it is still large enough for sediment grabs to be rated no better than fair for trend discerning.

Low-Level Capability

Particle-bound PCB measurement from sediment traps were found to have an excellent signal to blank ratios, and the characteristic is expected to be equally applicable for sediment grab samples. For this reason, sediment grab samples are rated as good in terms of low-level capability.

Sustainability

Sediment grab sampling of PCBs dates back to at least 1993. This corresponds to a score of good for sustainability.

Cost

Sediment grab samples can be collected in less than a day and rate as good in terms of cost.

Solid Phase Passive Devices

Temporal Representativeness

Sediments as a medium have an uncertain period of integration, because the period of contaminant exposure varies depending upon location-specific resuspension and deposition characteristics. Because exposure times could be more than one year, solid phase passive devices are rated fair for temporal representativeness.

Spatial Representativeness

Locations with bottom sediments are rare in the Spokane River, such that selection of a location that is known to representative of broad spatial conditions is unlikely. Due to the risk that a given sediment deposit reflects localized conditions that are not representative of the systems as a whole, solid phase passive devices are rated fair for spatial representativeness.

Physical Representativeness

Sediment pore water PCB concentrations are driven by the solids-bound portion of PCBs, and do not directly represent total PCB water column concentrations. To the extent that it can be assumed that the fraction of total PCBs in solids-bound form remains relatively constant, changes in solids-bound PCB concentrations over time should accurately reflect changes in total PCBs concentrations. Because this assumption is somewhat uncertain, solid phase passive devices are rated fair for physical representativeness.

Trend Discerning (Variability)

No data exist defining the variability, either replicate or seasonal, for the use of solid phase passive devices to measure PCBs in Spokane. Given the large variability observed in sediment grab samples, it is expected that solid phase passive devices would be rated no better than fair.

Low-Level Capability

No Spokane data are available by which to judge the signal to blank ratio for solid phase passive devices. Because solid phase passive devices serve to concentrate environmental PCB levels, it is expected that they would rate as high in terms of low level capability.

Sustainability

There has been no deployment of solid-phase passive samplers to the Spokane River. A user's manual (U.S. EPA/SERDP/ESTCP, 2017) exists for laboratory, field, and analytical procedures for solid-phase passive sampling. The document notes, however, that "the science and practice of passive sampling is an evolving process". For this reason, passive samplers are rated poor for sustainability.

Cost

Solid phase passive devices require time for both deployment and subsequent retrieval Overall, the cost of solid phase passive devices is rated as moderate/fair.

ELISA

Temporal Representativeness

Sediments as a medium have an uncertain period of integration, because the period of contaminant exposure varies depending upon location-specific resuspension and deposition characteristics. Because exposure times could be more than one year, ELISA is rated fair for temporal representativeness.

Spatial Representativeness

Locations with bottom sediments are rare in the Spokane River, such that selection of a location that is known to representative of broad spatial conditions is unlikely. Due to the risk that a given sediment deposit reflects localized conditions that are not representative of the systems as a whole, ELISA is rated fair for spatial representativeness.

Physical Representativeness

Sediment pore water PCB concentrations are driven by the solids-bound portion of PCBs, and do not represent total PCB concentrations. To the extent that it can be assumed that the fraction of total PCBs in solids-bound form remains relatively constant, changes in solids-bound PCB concentrations over time should accurately reflect changes in total PCBs concentrations. Because this assumption is somewhat uncertain, ELISA is rated fair for physical representativeness.

Trend Discerning (Variability)

No data exist defining the variability, either replicate or seasonal, for the use of ELISA to measure PCBs in Spokane. Given the large variability observed in sediment grab samples, it is expected that ELISA would be rated no better than fair.

Low-Level Capability

No Spokane data are available by which to judge the signal to blank ratio for ELISA. Because sediment pore water serves to concentrate environmental PCB levels, it is expected that ELSIA would rate as high in terms of low level capability.

Sustainability

The use of various ELISA methods for the determination of PCBs in sediments dates back to the 1990s (Franek et al, 1997). As such, ELISA is rated good for sustainability.

Cost

ELISA is designed to be a rapid characterization tool and is consequently inexpensive to implement, resulting is a rating of good for cost.

Fish

Temporal Representativeness

The period of integration of PCB concentrations by fish depends upon both the rate that fish accumulate PCBs from their food source and the rate that fish eliminate accumulated PCB from their bodies. These rates depend somewhat on the species and age of fish. Younger fish, whose PCB concentrations are dictated by uptake, can be expected to integrate concentration on the order of months. Older fish, who may have been exposed to historically higher PCB concentrations, integrate concentrations over a period of months to years. The temporal representativeness of year-old fish is therefore rated as good; the temporal representativeness of fish older than one year is rated as fair.

Spatial Representativeness

The spatial representativeness of fish tissue is potentially problematic, as fish are mobile and there is no way of knowing the exact location from where they received their PCB exposure. The presence of multiple dams throughout the Spokane area limits the extent of migration. On the other hand, fish are able to roam freely between dams, and could theoretically spend a disproportionate amount of time in areas of atypical PCB concentrations. The spatial representativeness of fish tissue PCBs in the Spokane River is rated as fair.

Physical Representativeness

PCB in fish tissue are an indirect measure of water column PCB concentration. While the conceptual relationship between water column and fish tissue PCB concentration is well understood, the site-specific relationship depends on several factors such as diet. For fish species with a significant benthic component to their diet, fish tissue PCBs will reflect sediment PCB concentrations, which may be a lagging indicator of water column concentrations. In this regard, species with a primarily pelagic diet such as rainbow trout may be more representative of water column concentrations than species with a primarily benthic diet such as suckers. In addition, for year old salmonids such as rainbow trout, a significant portion of their PCB body burden is derived from their mother rather than from environmental exposure. This becomes important for systems where hatchery-raised fish are stocked, as the maternally driven PCB signal in their tissue may not be reflective of the location where they were captured. Considering all of the above, fish tissue is rated as fair for physical representativeness.

Trend Discerning (Variability)

Existing fish tissue data allow the variability in tissue PCB concentrations to be estimated. Spokane River fish tissue monitoring conducted by Ecology in 2005 (Serdar and Johnson, 2006) and 2012 (Seiders et al,

2014) collected composite samples of five fish apiece for multiple species throughout the Spokane River study area. Pre-QAPP trend monitoring conducted by the Washington State Toxics Monitoring Program (Seiders, 2003) examined tissue PCBs in individual rainbow trout captured at Ninemile Dam in 2003.

Serdar and Johnson (2006) analyzed duplicates from five samples to obtain an estimate of laboratory precision. Relative percent differences averaged for the five duplicate pairs were 7%-38%.

Coefficients of variation were calculated by station and by species for the fish data collected in 2012 and 2015, and shown in Table 7. The 2012 results show that the average relative standard deviation across stations ranged from 29 to 35% for rainbow trout, from 25 to 57% for rainbow trout, and 40 to 50% for mountain whitefish. Seiders er al, (2014) state "The high variability associated with fish contaminant data makes it difficult to detect small differences among locations or over time".

Table 7. Station-Specific Relative Standard Deviation in Fish Tissue PCB Concentrations by Species, 2012 and 2015

	Rainbow Trout			Large Scale Sucker			Mountain Whitefish		
	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
2005	21%	34%	29%	54%	63%	57%	24%	93%	50%
2012	21%	49%	35%	5%	36%	25%	6%	65%	40%

The coefficient of variation for all year old rainbow trout collected in 2003 at Ninemile Dam was 0.59. As shown in Table 8, there are large differences in average PCB concentrations and variability between hatchery-reared and wild fish. Hatchery reared fish has less than half the average PCB concentration of wild fish, and three times the coefficient of variation.

Table 8. Average PCB and Relative Standard Deviation in Fish Tissue PCB Concentrations in Year Old Rainbow Trout at Ninemile Dam, 2003

	Avg. PCB ng/kg	RSD
All fish	19910	59%
Hatchery	15651	0.57%
Wild	34815	0.19%

Given the variability presented above, hatchery raised fish and fish from multiple age classes are rated fair for trend discerning, while year-old rainbow trout are rated as good.

Low-Level Capability

The use of fish tissue as a sampling medium presents excellent low level capabilities, because fish bioaccumulate PCBs from their ambient environment. No PCBs were detected in method blanks analyzed by Serdar and Johnson (2005). Seiders et al (2014) did not report method blank results, but did indicate that quality control procedures included method blanks, and that the data met measurement quality objectives. For these reasons, fish tissue is rated good for low-level capability.

Sustainability

Measurement of fish tissue PCBs dates back to 2003 in the Spokane River (and 2001 in Lake Spokane), and standard operating procedures exist. Routine fish tissue monitoring is expected to continue indefinitely in the Spokane System and part of Ecology's Freshwater Fish Contaminant Monitoring Program. For these reasons, fish tissue is rated good for sustainability.

Cost

The cost of fish tissue collection and analysis is rated as good.

Osprey Eggs

Temporal Representativeness

Because osprey receive their PCBs from fish tissue, which has an integration period of months to years, the integration period of osprey eggs is expected to be on the order of several months to years. This corresponds to a rating of fair for temporal representativeness.

Spatial Representativeness

The spatial representativeness of osprey eggs cannot be explicitly determined, because the specific location of the fish from which they obtain their PCBs (and hence the spatial representativeness of their food source) is unknown. This corresponds to a rating of fair for temporal representativeness.

Physical Representativeness

PCB in osprey eggs are an indirect measure of water column PCB concentration. That said, the facts that:

1. The overwhelming majority of their PCB exposure comes from eating fish, and
2. Their feeding range is localized to the extent that nests located near the Spokane River strongly suggest that the fish being eaten come from the Spokane River

indicate that PCBs in osprey eggs are likely highly correlated to water column PCB concentrations. This corresponds to a rating of fair for physical representativeness.

Trend Discerning (Variability)

No data currently exist for PCBs in Spokane-area osprey eggs from which to define variability. Osprey eggs are not rated for trend discerning.

Low-Level Capability

No data currently exist for assessing the low level capability of osprey egg PCB concentration, but the expectation is that the degree of bioaccumulation involved should make them a good indicator in this regard.

Sustainability

The use of osprey eggs to estimate PCB concentrations dates back more than 30 years (e.g. Johnson et al, 1975). This corresponds to a rating of good for sustainability.

Cost

Collection of osprey eggs is relatively simple, although multiple permits must be obtained prior to sample collection and analysis. This corresponds to a rating of good for costs.

Point Source Discharges

Period of Integration

Point source discharge samples are commonly collected as daily composite samples or individual grabs, such that the period of integration is one day or less. Because integration times are less than one year, point source discharges are rated good for temporal representativeness.

Spatial Representativeness

A measurement from any individual wastewater treatment plant is not representation of spatial average conditions in the river, but measurement from all treatment plants provide relevant spatial information. For example, cumulative point source loading at any location in the river can be estimated by summing all wastewater loads upstream of that location. For these reasons, point source discharges are rated fair for spatial representativeness.

Physical Representativeness

PCBs in wastewater discharges are an indirect measure of water column PCB concentration. Cumulative wastewater loading should correlate strongly to the increase in Spokane River concentrations above the background being delivered from Lake Coeur d'Alene. Point source discharges are rated fair for physical representativeness.

Trend Discerning (Variability)

Review of wastewater data collected by SRRTF for the Comprehensive Plan show relative standard deviations of daily load ranging across facilities of 27 to 83%, with an average of 56%. This corresponds to a rating of fair for trend discerning.

Low-Level Capability

Signal to blank ratios for existing treatment plants range from approximately 3 for facilities that have installed tertiary treatment to greater than 45 for facilities that have not. This corresponds to a rating of good for facilities that have not yet installed tertiary and fair for those that have.

Sustainability

Direct measurement of wastewater discharges has been in place for more than fifteen years at several discharges, and is an ongoing permit requirement for all of the dischargers. For this reason, point source discharges are rated good for sustainability.

Cost

Because monitoring requirements are currently in place in NPDES permits, there is no additional cost associated with point source discharge measurement. This corresponds to a rating of good for cost.

Recommendations

The results of the above assessment are summarized below in Table 9. Based upon the evaluations, recommendations are provided via the following tiers:

- Highest consideration
- Secondary consideration
- Recommended opportunistically
- Not recommended

***Table 9**. Summary of Attributes*

Medium/Methodology	Temporally Representative	Spatially Representative	Physically Representative	Trend Discerning	Low-Level Capability	Sustainability	Cost
Water Column							
• Small volume grab samples	Good	Good	Good	Fair/Poor	Fair/Poor	Good	Good
• Large volume composite	Good	Good	Good	Fair/Poor	Fair	Good	Good
• In situ solid phase extraction	Good	Good	Good	Good	Good	Good	Fair
• Passive sampling: SPMD	Good	Good	Fair	Good	Good	Good	Fair
• Solid-phase passive devices	Good	Good	Fair	Insufficient Data	Good	Poor	Good
• Particulates (sediment trap)	Good	Good	Fair	Fair	Good	Good	Fair
• Particulates (centrifugation)	Good	Good	Good/Fair	Good	Good/Fair	Good	Poor
• Biofilm	Good	Good	Fair	Fair	Good	Fair	Poor
Sediments							
• Grab samples	Fair	Fair	Fair	Fair	Good	Good	Good
• ELISA	Fair	Fair	Fair	Insufficient Data	Good	Good	Good
• Solid-phase passive devices	Fair	Fair	Fair	Insufficient Data	Good	Poor	Good
Fish							
• Multi-age composites	Fair	Fair	Fair	Fair	Good	Good	Good
• One year old rainbow trout	Good	Fair	Fair	Good/Fair	Good	Good	Good
Other							
• Osprey Eggs	Fair	Fair	Fair	Insufficient Data	Good	Good	Good
• Point Source Discharges	Good	Fair	Fair	Fair	Good/Fair	Good	Good

Key:

(green)	(yellow)	(red)	(grey)
Good	Fair	Poor	Insufficient Data

Highest Consideration

Two media/methodologies are recommended for highest consideration: *in situ* solid phase extraction and year-old trout. *in situ* solid phase extraction rates good on all technical assessment categories, with cost being the only category rated fair. Year old wild rainbow trout are the only other media/methodology rated good in terms of trend assessment, without posing serious concerns in other assessment categories.

Secondary Consideration

Four media/methodologies are recommended for secondary consideration: passive sampling with SPMDs, solid-phase passive devices, particulates (sediment trap), and osprey eggs. Passive water column sampling provides significant benefits, but the technology is evolving and efforts may be shifting from SPMDs to solid-phase passive devices. Particulates (sediment trap) and osprey eggs also have desirable attributes, but concerns about their trend-detection capabilities prevent them from receiving the highest recommendation.

Recommended Opportunistically

Three media/methodologies, although each possessing significant limitations, provide enough benefit that they merit consideration to the extent that they continue to be conducted for other purposes. Small volume grab samples are rated poor in terms of trend detection and low level capability, but are likely to serve as the basis for future Ecology determinations of compliance with water quality standards. Multi-age fish tissue are rated only fair in terms of temporal representativeness and trend detection, but are likely to serve as the basis for future fish contaminant monitoring to support development of consumption advisories. Point source discharges do not reflect in-river concentrations, but will continue to be monitored into the future as part of NPDES permit requirements. While the Task Force may not explicitly include these media/methodologies as part of their long term monitoring program, they should make use of the data generated by others to facilitate future trend detection activities.

Not Recommended

The following media/methodologies, while worthwhile for supporting other monitoring objectives, are not recommended for purposes of this long term monitoring program:

- Sediment grab samples
- ELISA
- Solid-phase passive devices in sediment
- Particulates (centrifugation)
- Large volume water column composite
- Biofilm

The sediment-based methodologies are not recommended due to the potential for sediments to be non-representative of current conditions (both from a temporal and spatial perspective) as well as for high variability confounding trend detection. Particulates (centrifugation) are not recommended due to the large cost relative to information provided. Large volume water column composites are not recommended due to their inability to discern trends as water column concentrations decrease. Biofilm is not recommended due to the potential for high variability to obscure trend detection.

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