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# Memorandum

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**Project:** SRRTTF

**To:** SRRTTF

**SUBJECT:** **Identification of Data Gaps - Final**

## Summary

The Spokane River Regional Toxics Task Force (SRRTTF) is developing a comprehensive plan to reduce toxic pollutants in the Spokane River, and has hired LimnoTech to serve as a technical advisor. This memorandum assesses the amount of data available describing the processes contained in the conceptual models for polychlorinated biphenyl (PCB) and polychlorinated dibenzo-*p*-dioxin and dibenzofuran (dioxin) levels in the Spokane River (LimnoTech, 2013). The conceptual models will be used as an organizing framework to identify data gaps and to guide future monitoring efforts, as well as to determine which processes are significant enough to ultimately be included in the models used to develop the comprehensive plan. This memorandum serves as the draft deliverable for Subtask 6-2: Refined Conceptual Model and Technical Memorandum Describing Data Gaps.

In summary, the Spokane watershed has the benefit of a robust PCB monitoring database, which provides a good estimate of the amount of PCBs entering the Spokane River from contributing source area categories (e.g., stormwater, WWTPs). Based upon the data presented in Figure 19 in the Department of Ecology's report entitled Spokane River PCB Source Assessment 2004 – 2007 (Serdar et al., 2011), only 43% of the PCB source loading to the Spokane River between the Stateline (RM 96.1) and Long Lake Dam (RM 33.9) could be identified. The percentage of contribution to PCB loadings referenced below for the various sources discussed below is its estimated percentage of the identified loadings. The existing data indicate that sources of PCBs are very diffuse throughout the watershed, such that more data will be needed to support development of a management plan with targeted control actions. Primary data gaps, in decreasing order of importance, consist of:

- **The magnitude of true sources contributing to stormwater loads.** A robust data set exists characterizing PCB concentration at numerous locations throughout the stormwater system; unfortunately, these data indicate that PCBs sources are very diffuse and difficult to trace back to their origin. Additional information may be able to be gleaned through the application of advanced pattern recognition techniques.
- **PCB sources upstream of the Idaho/Washington border:** PCBs entering from Idaho were estimated to represent 30% of the overall identifiable loading to the Spokane River system. The origin of these sources is currently unknown, and will need to be defined to control them.
- **The significance of loading from atmospheric and groundwater sources:** Insufficient data presently exist to define the magnitude of these source categories.

The available data are much more limited for dioxins than they are for PCBs, due primarily to lesser historical regulatory demands and ambient concentrations being very low relative to detection limits.

## Introduction

The SRRTTF is developing a comprehensive plan to reduce toxic pollutants in the Spokane River. The plan is designed to identify specific management actions that can be undertaken to control pollutant loads such that water quality objectives can be attained. LimnoTech (2013) presented draft conceptual models for PCB and dioxins depicting all of the processes believed to be potentially significant in affecting pollutant concentrations. This memorandum applies that conceptual model to serve two purposes:

- Assess data gaps: The conceptual model describes all processes that may be ultimately simulated in the final model. These processes will be cross-referenced with available data to define which processes can be accurately defined with existing data and which processes require additional data to describe them. This data gap assessment will directly inform the upcoming monitoring plan that will be subsequently developed in Task 8 of this project.
- Determine which processes should be included in the final model: The conceptual model is intended to include all processes that could potentially be important to describing pollutant concentrations. Calculations will be made with the available data to assess each individual process and to determine whether they are significant enough to be included in the final model.

The remainder of this memorandum describes the assessment of data gaps and how they relate to the initial conceptual models of PCB and dioxin behavior in the Spokane River and watershed. It is divided into sections of:

- Assessment of Data Gaps
- Updated Conceptual Models

## Assessment of Data Gaps

The data gap analysis consisted of compiling the available information that can be used to estimate the magnitude of each process contained in the draft conceptual models, and assessing whether sufficient information exists to quantify each process. Separate data gap assessments were conducted for PCBs and dioxins.

### *Assessment of Data Gaps for PCBs*

Data gap assessment is described below for each of the component groups of the draft PCB conceptual model, followed by the conclusions of the data gap assessment:

- True Sources
- Mobilization of Contained PCBs
- Delivery Pathways
- Fate and Transport in the Spokane River
- Conclusions

## True Sources

Table 1 lists the true sources of PCBs in the Spokane watershed as contained in the draft conceptual model, along with the data that have been collected to help define the magnitude of these sources.

**Table 1. Data Gap Assessment of True Sources of PCBs**

| True Source Category | Available Data | Assessment of Magnitude and Certainty |
|---|---|---|
| Fixed and non-fixed building sources | Literature values of PCB release rates. | 837 mg/day. High uncertainty. |
| Contaminated soil | Number of landfills, number of recycling facilities, existing land use, stormwater/catch basin data. | Data not available to quantify; assumed significant. |
| Aquatic sediments | 57 sediment samples.<br>Surficial sediment PCB concentrations in Spokane River.<br>Sediment cores for upper and lower Lake Spokane. | Assumed to be low upstream of Lake Spokane.<br>Data not available to assess loading rate, due to uncertainty in sediment resuspension and diffusion. |
| Electrical and hydraulic equipment | Literature estimates of PCB content and failure rates. | Data not available to quantify; assumed significant |
| Global atmosphere | Literature values for deposition rate. | 30–89 mg/day. High uncertainty. |
| Pigments/dyes in consumer products and recycled newsprint | Literature values for PCB content of pigments/dyes. | Data not available to quantify; assumed significant. |
| Motor boats | None. | Data not available to quantify; significance unknown. |
| Agricultural chemicals | Literature estimates of PCB content in agricultural and non-agricultural soils | Data not available to quantify; significance unknown. |

***Building sources***: No Spokane-specific data are available defining the amount of PCBs released from fixed and non-fixed building sources, although literature values are available from a PCB source assessment of San Francisco Bay (SFEI, 2010; LWA, 2006). Annual PCB loadings to San Francisco Bay from home remodeling and demolition were estimated from literature values of PCB levels measured in building materials; PCB levels in different waste streams from a demolished building; the number of buildings demolished in the U.S. each year; the assumed percentage of these buildings that were built, repainted or re-caulked between 1950 and 1975; and the proportion of release due to remodeling and maintenance relative to demolition. The annual load released to the San Francisco Bay watershed was estimated at 4,286 g PCBs per year. This estimate can be scaled to the Spokane watershed using a ratio of population densities. Given the 2010 census Spokane watershed population estimate of 415, 136 and the San Francisco Bay watershed population estimate of 5,820,000 (California Regional Water Quality Control Board, 2008), the magnitude of PCB load from building sources can be estimated at 306 g/year (837 mg/day). Because this number is based on literature estimates and a wide range of assumptions, it is considered highly uncertain when extrapolating to the Spokane River watershed.

***Contaminated soil sources***: Information is currently available describing the number of landfills, number of recycling facilities, and other existing land uses that could be prone to PCB contamination. Stormwater and catch basin monitoring data provide an indication of overall amount of PCBs coming from individual sub-basins, and could be subjected to additional pattern recognition analysis that may provide more indication of the nature of their source. Data are lacking describing typical soil PCB concentrations at these sites. Data describing historical land uses in the Spokane watershed have not been collected, but would be useful to defining areas that have contributed to existing soil contamination.

***Aquatic sediments***: Fifty-seven measurements of PCB concentrations in aquatic sediments are available throughout the Spokane River system. Ecology's PCB Source Assessment (Serdar et al., 2011) concluded that in-place sediments in the Spokane River upstream of Lake Spokane were a negligible contributor to ongoing contamination, because: 1) bulk fine sediments deposits are sparse in the River, except for isolated locations behind Upriver Dam, and 2) PCB concentrations in the sediments behind Upriver Dam are low due to the cleanup of historical contamination that was competed in 2007. Because most fine-grained sediments in the Spokane River are flushed out on an annual basis, sediment PCBs in the River upstream of Lake Spokane likely represent recent watershed loading as opposed to historical sources. Historical PCBs deposited in Lake Spokane provide a potential ongoing source to the Spokane River system. Monitoring by Ecology in 2003-2004 showed surficial (i.e., upper 2 cm) sediment PCB concentrations of 8-14 ng/g dw in upper Lake Spokane and 28-75 ng/g dw in lower Lake Spokane. Concentrations in deeper core sections in the Lake were as high as 51 ng/g dw in upper Lake Spokane and 1,000 ng/g dw in lower Lake Spokane. The extent to which these sources contribute to ongoing water column concentrations depends on sediment resuspension (and to some extent, pore water diffusion) rates, which are not currently well understood.

***Electrical and hydraulic equipment***: No site-specific data are available describing PCB content and/or release rates from electrical and hydraulic equipment, other than limited information on spills. Estimates are available in the literature (Versar, 1976) describing PCB content and approximate failure rates of power capacitors and transformers. This information is insufficient to generate a quantitative estimate of current loading rate for this source category.

***Atmospheric sources***: Era-Miller (2011) provided a summary from the scientific literature of atmospheric deposition rates of PCBs, and used this to estimate a range of loading rates for the Spokane River watershed of 0.13-1.60 lbs/yr (161-1,987 mg/day). The atmospheric deposition rates used for these calculations were based on values representing urban watersheds, and therefore include a mixed contribution of global and local sources. The goal of this section is to estimate true sources, i.e., sources originating from outside the watershed. Literature-reported atmospheric deposition rates for rural areas in Era-Miller (2011) can be used to provide an estimate of the contribution of PCB deposition from global atmospheric sources. These result in an estimate of 0.024–0.072 lbs/yr (30–89 mg/day). Neither of these sources provides site-specific information on PCB deposition in the Spokane watershed, and should be considered highly uncertain.

***Pigments/dyes in consumer products and recycled newsprint***: PCBs are a known inadvertent contaminant in the production of certain pigments and dyes, especially the organic pigment diarylide yellow and the inorganic white pigment titanium dioxide. The inadvertent production of PCBs is allowed under the Toxics Substance Control Act, with PCB concentrations in products restricted to average less than 25 ppm and be no higher than 50 ppm. Guo et al. (2013) documented the significance of pigment-related PCBs, showing that: 1) PCBs from TiO2 production in Wilmington, DE, contribute 61% of all PCBs in surface sediment in the Delaware River, and 2) PCB 11 concentrations in pigment may be at (or above) 125 ppm and are readily leachable from these products into the environment. PCBs are also a known contaminant in feedstock used for paper recycling. While no site-specific data are available describing the magnitude of PCBs imported into the Spokane basin from pigments/dyes, it can reasonably be concluded that these are a significant source.

***Motor boats and agricultural chemicals:*** These two true source categories were identified for inclusion at the September 25 SRRTTF meeting. A literature review found only very limited information discussing the potential significance of these sources (e.g. Armitage et al. 2006), with no quantitative description of potential source loading. The significance of these source categories is currently unknown, although the lack of published information may serve as an indication that they are likely small.

### Mobilization of Contained PCBs

The second step of the PCB conceptual model describes potential mobilization pathways of PCBs in other materials. Specifically, the mobilization pathways describe the transfer from:

| | | |
|---|---|---|
| • Building sources | | • Recycling facilities |
| • Electrical equipment | | • Landfills |
| • Hydraulic equipment | to | • Soil; and |
| • Recycled newsprint; and | | • WWTP influent |
| • Consumer products | | |

No data are presently available quantifying the magnitude of these processes, other than literature sources (Guo et al., 2013) demonstrating high rates (i.e., 6 to 81%/48 hrs) of PCB 11 leached from a range of consumer products.

### Delivery Pathways

Table 2 lists all of the potential delivery pathways of PCBs in the Spokane watershed as contained in the draft conceptual model.

***Contaminated soil to stormwater/CSO system***: Ecology's Urban Waters Initiative, along with the City of Spokane, have collected an extensive amount of data documenting PCB concentrations throughout the City's stormwater and CSO system (Fernandez, 2012). These data include measurement of PCB concentrations at outfalls representing the majority of the City's stormwater/CSO system. Parsons and Terragraphics Inc. (2007) used these PCB concentration data, in conjunction with a simple model of runoff volume, to estimate a stormwater loading rate ranging from 195 – 687 mg/day. While these data represent the amount of PCBs delivered to the Spokane River via stormwater, they also provide a surrogate measure of the amount of contaminated soil delivered to the stormwater/CSO system.

***Contaminated soil to direct urban drainage***: Ecology's PCB Source Assessment (Serdar et al., 2011) concluded that the potential for small direct drainage tributaries to deliver PCBs to the

Spokane River was inconsequential, citing previous investigations from Ecology (1995), and Golding (1996, 2001, and 2002).

***Contaminated soil to groundwater***: No data presently exist defining the extent to which PCB-contaminated soil contributes to groundwater in the Spokane watershed.

***Contaminated soil to atmosphere***: The rate at which soil-contaminated PCBs contribute to local atmospheric loading can be approximated using the results of Era-Miller (2011) discussed earlier, by assuming that the local contribution to atmosphere is the difference between total atmospheric loading to the Spokane watershed (0.13-1.60 lbs/yr, or 161-1,987 mg/day) and the amount of loading contributed from global sources (0.024–0.072 lbs/yr, 30–89 mg/day). This results in an estimate of local contribution to atmospheric sources ranging from 72-1,957 mg/day.

***Atmosphere to contaminated soil***: As discussed above, Era-Miller (2011) provided a summary of atmospheric deposition rates of PCB from the scientific literature, and used this to estimate a range of loading rates for the Spokane River watershed of 0.13-1.60 lbs/yr (161-1,987 mg/day).

***Direct drainage to river***: As discussed previously, Ecology's PCB Source Assessment (Serdar et al., 2011) concluded that the potential for small direct urban drainage to deliver PCBs to the Spokane River was inconsequential.

***Stormwater system to river***: As discussed previously, Parsons and Terragraphics Inc. (2007) estimated a stormwater loading rate to the Spokane River ranging from 195 – 687 mg/day.

***Nonpoint source runoff:*** Nonpoint source runoff can deliver PCBs to the Spokane River and Lake Spokane, primarily via tributaries. Ecology's PCB Source Assessment (Serdar et al., 2011) estimated a total PCB loading from the Little Spokane River of 97 mg/day. PCB loading rates for other tributaries are not available, but can be assumed to be similar in magnitude. While some tributaries contain small wastewater treatment plants, the majority of the PCB loading is presumed to come form nonpoint source runoff.

***Groundwater to river***: Groundwater monitoring was conducted as part of a remedial investigation (RI) and feasibility study (FS) of contamination at Upriver Dam. Monitoring wells located down-gradient of the dam showed PCB concentrations in the range of associated field and laboratory blanks, suggesting very low actual PCB concentrations in groundwater (Anchor, 2004). The spatial extent of this monitoring was too limited to make broad statements about the significance of groundwater as a significant pathway of PCBs to the Spokane River.

***Atmosphere to river***: No data presently exist defining the extent to which atmospheric PCBs contribute directly to surface water in the Spokane.

***Aquatic sediments to river***: As discussed in the true source section, several measurements of PCB concentrations in sediments are available throughout the Spokane River system. The extent to which these sources contribute to ongoing water column concentrations depends on sediment resuspension (and to some extent, pore water diffusion) rates, which are not currently well understood.

***WWTP to river***: PCB loading from wastewater treatment plants was calculated in Serdar et al. (2011) as 307 mg/day. This estimate was based upon data collected from 2001 to 2004 and may not exactly represent present-day conditions, but provide a reasonable estimate of loading for purposes of refining the conceptual model. More recent effluent results are available. The loading estimate may be updated, if needed.

**Table 2. Data Gap Assessment of PCB Delivery Pathways**

| Delivery Pathway | Available Data | Assessment of Magnitude and Certainty |
|---|---|---|
| Contaminated soil to stormwater and CSO system | 118 water samples; 180 sediment samples. | 195 – 687 mg/day. |
| Contaminated soil to direct drainage | Historical estimate of significance. | Assumed to be negligible. |
| Contaminated soil to groundwater | None. | Data not available to assess. |
| Contaminated soil to atmosphere | None. | 72-1,957 mg/day. Highly uncertain. |
| Atmosphere to contaminated soil | Literature estimates. | 161-1,987 mg/day. Highly uncertain. |
| Direct urban drainage to river | Historical estimate of significance. | Assumed to be negligible. |
| Stormwater system to river | 118 water samples; 180 sediment samples. | 195 – 687 mg/day |
| Nonpoint source runoff | Loading estimate for Little Spokane River. | > 100 mg/day. Assumed to be significant. |
| Groundwater to river | 4560 groundwater samples; majority non-detect. Groundwater flow model. | Data not available to assess. |
| Atmosphere to river | None. | Data not available to assess. |
| Aquatic sediments to river | 57 sediment samples.<br>Surficial sediment PCB concentrations in Spokane River.<br>Sediment cores for upper and lower Lake Spokane. | Assumed to be low upstream of Lake Spokane.<br>Data not available to assess loading rate, due to uncertainty in sediment resuspension and diffusion. |
| WWTP to river | 21 effluent concentration measurements from 2001-2004 source assessment; 34 effluent concentration measurements from 2010 to 2012. | 307 mg/day. |

## Fate and Transport in the Spokane River

Table 3 lists all of the potential delivery pathways of PCBs in the Spokane watershed as contained in the draft conceptual model.

**Table 3. Data Gap Assessment of PCB Fate and Transport in the Spokane River**

| Fate and Transport Pathway | Available Data | Assessment of Magnitude and Certainty |
|---|---|---|
| Upstream/downstream transport | 24 water column measurements. | 480-3,664 mg/day. Known to be significant. |
| Volatilization to atmosphere | No direct measurements; can be estimated from water quality model. | Up to 1,800 mg/day. Highly uncertain. |
| Settling of sorbed pollutant | No direct measurements; can be estimated from water quality model. | 1.4 mg/day. Highly uncertain. |
| Loss to groundwater | 4,560 groundwater samples. Groundwater flow model. | Assumed to be significant on a localized basis. |
| Biodegradation in sediments | No direct measurements; can be estimated from water quality model. | Assumed to be significant. |

***Upstream/downstream transport***: Twenty-four measurements of water column PCBs exist throughout the Spokane River system. These data, in conjunction with existing data on harmonic mean river flow, can be used to define the amount of PCBs carried along the length of the Spokane River. Serdar et al. (2011) used water column concentrations from 2003-2004 monitoring in conjunction with calculated harmonic mean flows to estimate downstream transport of 480 mg/day. These loading estimates were based on data collected from October 2003 to May 2004. The data are certainly adequate to provide an estimate of the overall magnitude of this process, but additional data will be needed to provide more refined estimates of current conditions.

***Volatilization to atmosphere***: Volatilization describes the process where a dissolved material is converted into a vapor state. Volatilization has been shown to be an important transport process for PCBs. While no direct measurements have been made for volatilization in the Spokane system, the significance of this process can be estimated from existing water quality modeling efforts. A simple volatilization model developed using a Henry's Constant of $5.60 \times 10^{-4}$ atm $m^3$/mol indicates that up to half of the PCBs passing through Lake Spokane could be lost to volatilization.

***Settling of sorbed pollutant***: PCBs have low water solubility and therefore can adsorb to particulate matter in the water column. This means that PCB transport can be affected by the movement of solids, and that settling of solids from the water column can be an important transport mechanism for PCBs. While no direct measurements have been made for settling of sorbed PCBs in the Spokane system, the significance of this process can be estimated from existing water quality modeling efforts. A simple spreadsheet model was developed using results from CE-QUAL-W2 for inorganic and organic solids settling rates and velocities, along with a representative organic carbon partition coefficient. Results from this model indicate that loss through settling is approximately 1.4 mg/day.

***Loss to groundwater***: Monitoring data have indicated that the Spokane River is hydraulically connected to the local groundwater, with different reaches of the river either losing water to groundwater or gaining water from groundwater. Because transport of dissolved PCBs is directly related to the movement of water, the interaction between groundwater and surface water can be assumed to be important to PCB movement. No direct measurements are available describing the rate at which PCBs move between groundwater and surface water, although a groundwater flow model exists which may assist in quantifying this process.

***Biodegradation in sediments***: Biotic processes have been shown to dechlorinate PCBs in bedded sediments. No data currently exist describing PCB degradation in bedded sediments. The reaction time for this process is typically very slow, but the long residence time of PCBs in bedded sediment can make this a loss process worth considering.

### Conclusions

The Spokane watershed has the benefit of a robust PCB monitoring database, which provides a good estimate of the amount of PCBs entering the Spokane River from contributing source area categories (e.g., stormwater, WWTPs). The existing data indicate that sources of PCBs are very diffuse throughout the watershed, such that more data will be needed to support development of a management plan with targeted control actions. Primary data gaps, in decreasing order of importance, consist of:

- **The magnitude of true sources contributing to stormwater loads.** A robust data set exists characterizing PCB concentration at numerous locations throughout the stormwater system; unfortunately, these data indicate that PCBs sources are very diffuse and difficult to trace back to their origin. Additional information may be able to be gleaned through the application of advanced pattern recognition techniques.
- **PCB sources upstream of the Idaho/Washington border:** PCBs entering from Idaho were estimated to represent 30% of the overall loading to the Spokane River in Washington. The origin of these sources is currently unknown, and will need to be defined to control them.
- **The significance of loading from atmospheric and groundwater sources:** Insufficient data presently exist to define the magnitude of these source categories.

In addition to the primary data gaps defined above, additional data will be required to supplement the understanding of key source areas. While the existing PCB Source Assessment provides a strong initial understanding of the sources delivering PCBs to the river, there is still a mismatch between estimated loads to the river and observed instream loads. In addition, some of the data used to support the Source Assessment are nearly ten years old, and new data will be needed to better represent current conditions.

### *Assessment of Data Gaps for Dioxins*

The quantity of dioxin data for the Spokane watershed is much less than the amount of PCB data, as PCB assessment has been a priority due to regulatory requirements. The Urban Waters Initiative has done some recent assessment of dioxins/furans in stormwater, identifying a source along the Crestline-Springfield branch within Union Basin. High OCDD concentrations found at this site imply that atmospheric sources are significant, as OCDD is a dominant form of dioxin by-product formed during incomplete combustion. In addition, the Urban Waters Initiative identified an association between 2,3,7,8 TCDD TEQ and TOC in sanitary sewer wastewater (Fernandez, 2012).

## Updated Conceptual Models

This section describes refinements to the initial conceptual models that can be made based on a review of the available data. The intent of the initial conceptual models was to describe all processes that were potentially contributing to impairment. The purpose of the update is to use available site information to eliminate those components of the initial model that can reasonably be assumed to be insignificant. "Significance" of a source/process can be estimated relative to the overall loading capacity of the pollutant. The update of the conceptual models provided here will assume that any source/process that contributes more than one percent of the loading capacity will be kept in the updated conceptual model.

For the conceptual PCB model, the loading capacity depends upon the location in the system (because stream flow generally increases over the length of the river) and the water quality target of interest. The lowest loading capacity occurs at the State line using the Spokane Tribe water quality standard of 3.37 pg/l, and is 15 mg/day. The highest loading capacity occurs in lower Lake Spokane (and locations downstream) using the National Toxics rule standard of 170 pg/l, and is and is 1,562 mg/day. The smallest of the processes quantified in the above analysis was 1.4 mg/day, which is nearly 10% of the loading capacity required to attain the Tribal water quality standard. For this reason, none of the quantified processes can be dropped from the revised conceptual model. The majority of the processes that could not be quantified during the data gap assessment also remain in the final conceptual model, because insufficient evidence exists to exclude them. The components that can be dropped from the initial conceptual model based on this assessment are:

- Historical in-place sediments in the Spokane River upstream of Lake Spokane, and
- Direct urban drainage of Spokane stormwater to the Spokane River.

In-place sediments are excluded as a true source because : 1) bulk fine sediment deposits are sparse in the River, except for isolated locations behind Upriver Dam; 2) PCB concentrations in the sediments behind Upriver Dam are low due to the cleanup of historical contamination; and 3) most fine-grained sediments in the Spokane River are flushed out on an annual basis, such that sediment PCBs in the river upstream of Lake Spokane likely represent recent watershed loading as opposed to historical sources. Direct drainage of Spokane stormwater to the Spokane River is excluded as a pathway due to the conclusions from previous studies that this pathway is insignificant, with the overwhelming majority of stormwater being captured by Spokane's stormwater system.

The quantity of information available on dioxins/furans is too limited to exclude any processes from the initial conceptual model, so the updated conceptual dioxin model remains unchanged from the initial conceptual model.

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