

Sources and Pathways of PCB-11: Scoping of Phase II

**TTWG Meeting
December 1, 2021**

Background

- Phase I mass balance on observed PCB-11 loads suggests presence of previously unidentified sources during dry weather
 - Next step was to develop scope(s) of work to help identify sources and pathways
 - November TTWG Meeting obtained consensus on which specific scopes should be considered
- December TTWG Meeting intended to review scopes/budgets for recommendation to the full task force.

Discussion Topics

- Sensitivity of Phase I mass balance calculations to blank correction assumption
- Scopes of work

Blank Correction Sensitivity

- Initial PMF-based mass balances being conducted by Dr. Rodenburg show lesser amounts of unexplained PCB-11 loading than our analysis
 - Differences in results traced to different methods used to blank-correct samples
- What is blank correction?
 - Adjustment of laboratory reported PCB concentrations to account for observed contamination in blank samples
 - Many options exist for blank correction

Blank Correction Options: Censoring and Subtraction

- Censoring
 - Set to zero any concentration measurement that is not a given level above the laboratory blank, otherwise leave unchanged
 - 3x censoring has been used for SRRTTF mass balances, i.e., any environmental sample concentration $< 3 \times$ laboratory blank concentration is treated as zero
- Subtraction
 - Subtract reported blank concentration from reported environmental sample concentration
- There is no definitively “right” or “wrong” method of blank correction
 - Common practice is to perform analyses using multiple methods to estimate uncertainty caused by blank contamination

Blank Correction Examples Using Spokane River Data

- Field sample = 32.7 pg/l, blank sample = 11.4 pg/l
 - Censoring: 0 (because $32.7 < 3 \times 11.4$)
 - Subtraction: 21.3 ($32.7 - 11.4$)
- Field sample = 34.3 pg/l, blank sample = 10.6 pg/l
 - Censoring: 34.3 (because $34.3 > 3 \times 10.6$)
 - Subtraction: 23.7 ($34.3 - 10.6$)

Ramification of Blank Correction Sensitivity

- Results of mass balances on total PCBs were relatively insensitive to the choice of blank correction method used
- Results of mass balances on PCB-11 are much more sensitive to the choice of blank correction method
 - PCB-11 more prevalent in blank samples than most other congeners
 - Unexplained PCB loads using subtraction method are approximately half that from using the 3x censoring method
- The certainty that there are unexplained sources of PCB-11 in Spokane is much less than originally assumed

Scopes of Work

- Given the uncertainty in PCB mass balance, only screening level assessments (if any) are recommended at this time
- Screening level is likely sufficient to rule out many pathways
 - e.g., an estimated pathway load of 0.001 to 0.01 mg/day, while uncertain, can be ruled out as an explanation of 10 mg/day load
- Pathways scoped
 - Atmospheric loading
 - Breakdown of higher-level congeners to PCB-11
 - In-place sources
 - Stormwater loads to dry wells
 - Fertilizer application loads

Scope: Atmospheric Loading

- Objective
 - Screening-level assessment of the significance of atmospheric loading of PCB-11 to the Spokane R.
- Scope
 - Merge national level research with Spokane-specific data to quantitatively assess the magnitude of PCB-11 loading from the following pathways
 - Dry deposition
 - Wet deposition
 - Gas-phase transfer
 - Convert previous calculations on total PCB flux to PCB-11 specific values
 - Determine magnitude of deposition necessary to explain observed increases in PCB-11 in Spokane

Scope: Atmospheric Loading

- Source materials
 - Atmospheric deposition of PCBs in the Spokane River watershed (Ecology, 2019)
 - Air deposition as a source of polychlorinated biphenyls to the Spokane River watershed (Hope, 2012)
 - Total maximum daily loads for PCBs from atmospheric sources
 - San Francisco Bay atmospheric deposition pilot study
- Outcome
 - Technical memorandum characterizing likelihood that atmospheric loading is a significant source of PCB-11 to the Spokane River
- Cost: \$4000

Scope: Breakdown of Higher-Level Congeners

- Objective
 - Screening-level assessment of the significance of the breakdown of higher-level congeners as a loading source of PCB-11 to the Spokane R.
- Scope
 - Identify range of congeners most likely to degrade to PCB-11
 - Calculate concentration of those congeners in Spokane River
 - Determine worst-case PCB-11 load, i.e., complete and instantaneous degradation of parent compounds to PCB-11
 - If necessary, determine breakdown rate necessary to explain expected PCB-11 mass load increase in Spokane River

Scope: Breakdown of Higher-Level Congeners

- Source materials
 - SRRTTF database of Spokane River PCB concentrations
 - Photodechlorination pathways of non-ortho substituted PCBs by ultraviolet irradiation in alkaline 2-propanol (Yao, 1997)
 - Degradation of polychlorinated biphenyls by UV-catalysed photolysis (Wong, 2006)
- Outcome
 - Technical memorandum characterizing the likelihood that breakdown of higher-level congeners is a significant source of PCB-11 to the Spokane River
- Cost: \$3000

Scope: In-Place Sources

- Objective
 - Screening-level assessment of the magnitude of PCB-11 loading to the Spokane River from sources located within the river
- Scope
 - Identify range of in-place objects potentially containing PCB-11
 - Bedded sediments, dams, painted fixtures, buoys, dock bumpers, kayaks
 - Estimate quantity of each identified object in the Spokane River
 - Estimate PCB-11 concentration in each object
 - Estimate release rate (diffusion from bed sediments, leaching from other objects)
 - Calculate PCB-11 loading rate from object mass and release rate

Scope: In-Place Sources

- Source materials
 - SRRTTF and Ecology PCB and organic carbon measurements in bed sediment
 - Global distribution and local impacts of inadvertently generated polychlorinated biphenyls in pigments (Guo et al, 2019)
 - Scientific literature for partition coefficients and pore water diffusive flux rate
- Outcome
 - Technical memorandum characterizing likelihood that in-place sources are a significant contributor of PCB-11 to the Spokane River
- Cost: \$5000

Scope: Stormwater Loads to Dry Wells

- Objective
 - Screening-level assessment of stormwater PCB-11 loading to dry wells
- Scope
 - Calculate quantity of stormwater volume delivered to dry wells
 - Calculate average PCB-11 concentration of stormwater
 - Determine PCB-11 loading rate from volume and concentration
- Source materials
 - City and County stormwater data
- Outcome
 - Technical memorandum characterizing stormwater PCB-11 loading to dry wells
- Cost: \$2500

Scope: Fertilizer Application Loads

- Objective
 - Screening-level assessment of PCB-11 loading to Spokane watershed via fertilizer application
- Scope
 - Estimate fertilizer application rate
 - Biosolids and commercial fertilizer
 - Determine average PCB-11 concentration for each type of fertilizer
 - Determine PCB-11 loading rate from volume and concentration

Scope: Fertilizer Application Loads

- Source materials
 - City and County biosolids data
 - Literature for commercial fertilizers
- Outcome
 - Technical memorandum characterizing PCB-11 loading from fertilizer application
- Cost: \$2500

Summary of Scopes and Costs

	Cost
Atmospheric loading	\$4000
Breakdown of higher-level congeners	\$3000
In-place sources	\$5000
Stormwater loads to dry wells	\$2500
Fertilizer application loads	\$2500
Wait for results of 2022 synoptic survey to better assess potential for existence of unexplained sources of PCB-11	\$0