

2020-2021 Spokane River PCB Concentration Monitoring Using Semi-Permeable Membrane Devices in Support of a Long-Term Monitoring Program

TTWG Meeting
November 3, 2021

Summary

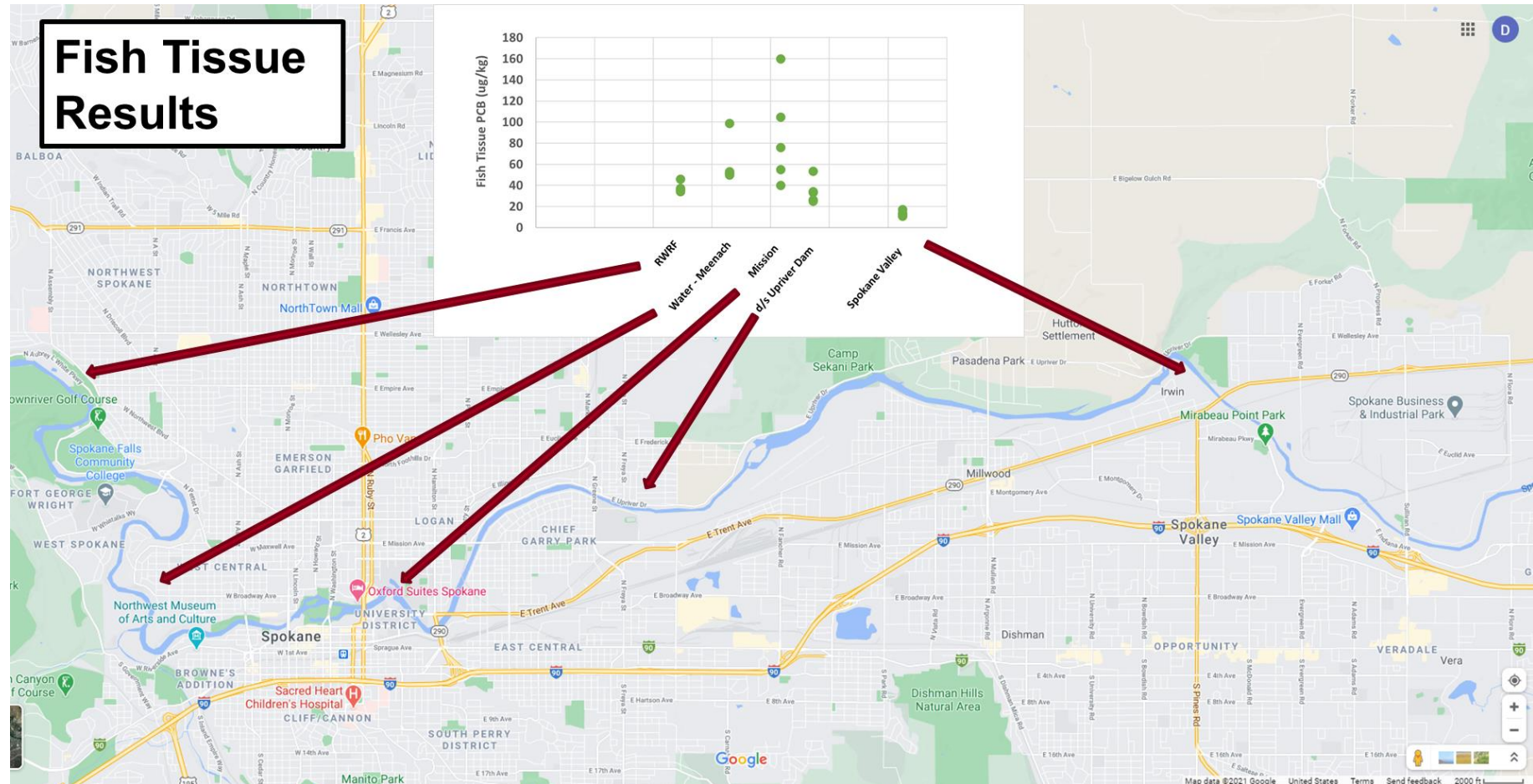
- SPMDs successfully deployed in Spokane River
 - PCB concentrations measured at four locations for three different flow conditions
- Elevated PCB concentrations were observed in Mission Reach during low flow
 - Lends support to the theory of a previously un-defined source
- Use of SPMDs poses some challenges for long-term trend assessment

Background

- Task Force must make measurable progress toward meeting applicable water quality criteria for PCBs
- Demonstration of progress requires a long-term monitoring program
- Task Force initiated a long-term monitoring program starting in 2020
 1. Analysis of PCB concentrations in year-old Redband Trout
 2. Analysis of PCB concentrations in the water column via semi-permeable membrane devices (SPMDs)

Fish Tissue Findings

- Sampling conducted in fall of 2020
- Five reaches sampled
 - 25 fish per reach
- Report completed and approved



SPMD: Semi-Permeable Membrane Device

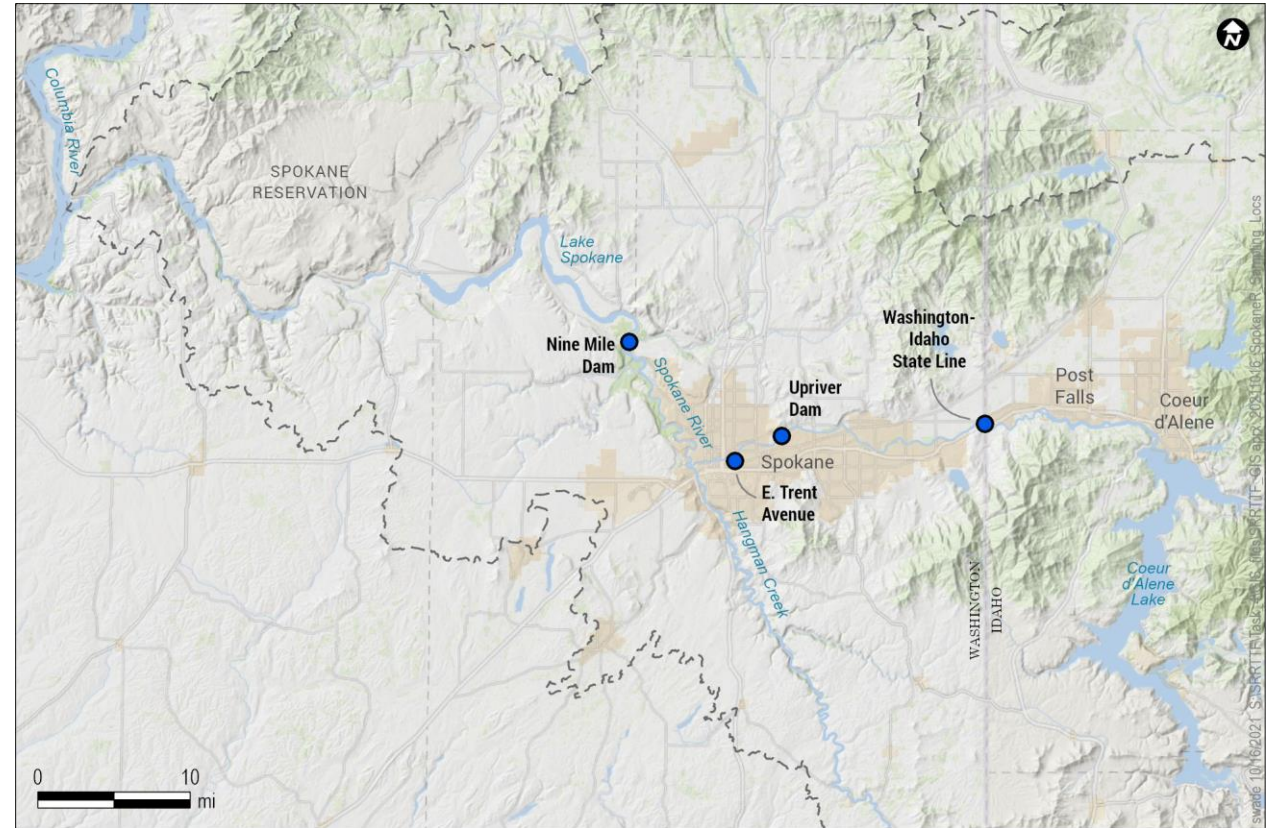
- Passive sampler
 - Low-density polyethylene tube filled with a highly purified lipid
 - PCBs from the water column diffuse through tube walls and concentrate in the lipid
- Deployed in field for ~28 days
 - Provides integrated estimate of dissolved phase water column PCB concentration



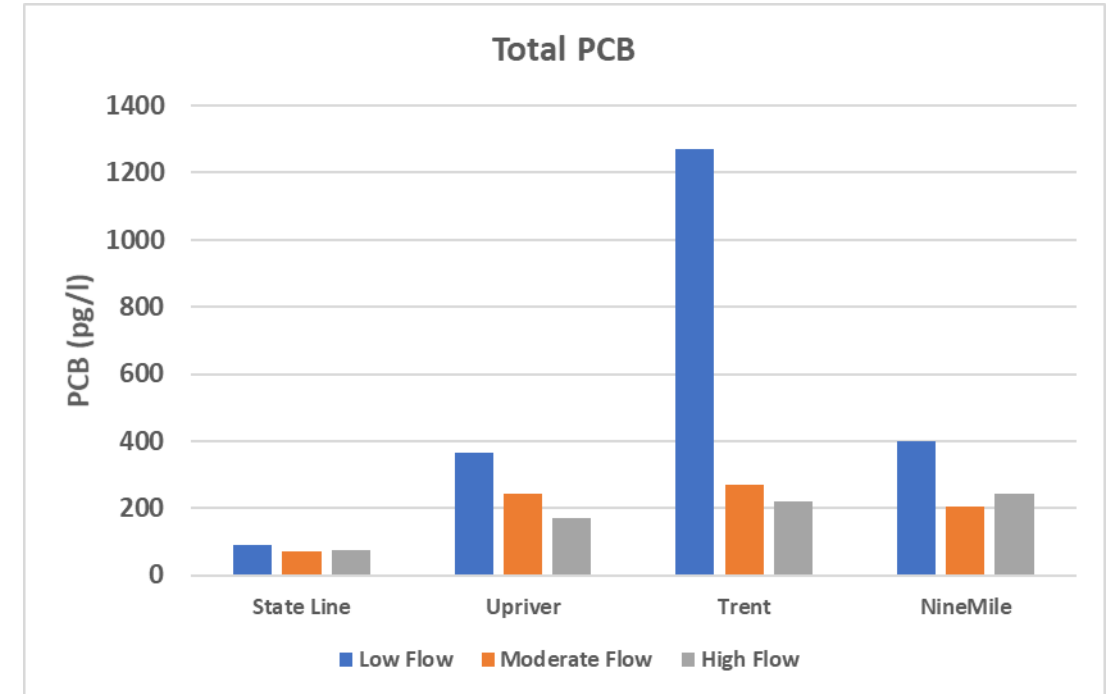
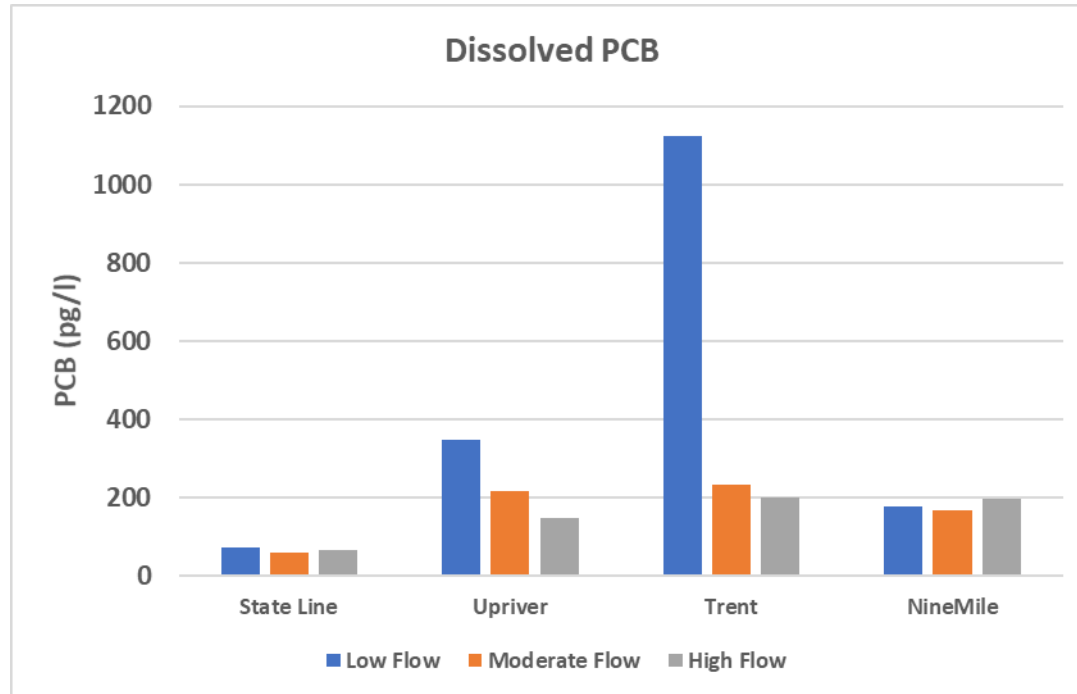
Pictures from Ecology (2019) SOP

Deployment Details

- Four locations
 - WA/ID State Line
 - Downstream of Upriver Dam
 - Downstream of E. Trent Avenue (i.e., Mission Reach)
 - Nine Mile Dam
- Three deployment periods
 - Low flow (Aug/Sept, ~1000 cfs)
 - Moderate flow (Feb/Mar, ~4000 cfs)
 - High flow (Apr/May, ~10,000 cfs)



Observed Concentrations



Location	Low Flow		Moderate Flow		High Flow	
	Dissolved	Total	Dissolved	Total	Dissolved	Total
Stateline	72.4	91.7	58.7	69.9	67.3	76.8
Upriver	347.2	367.1	216.2	243.8	149.8	169.1
Trent	1122.9	1272.1	234.0	271.0	201.4	220.2
Nine Mile	179.1	397.8	167.2	205.7	196.3	241.7

Challenges of SPMDs for Long-Term Trend Assessment

- Comparability to grab sample results
- Calculation of total PCB concentration
- Quality control issues

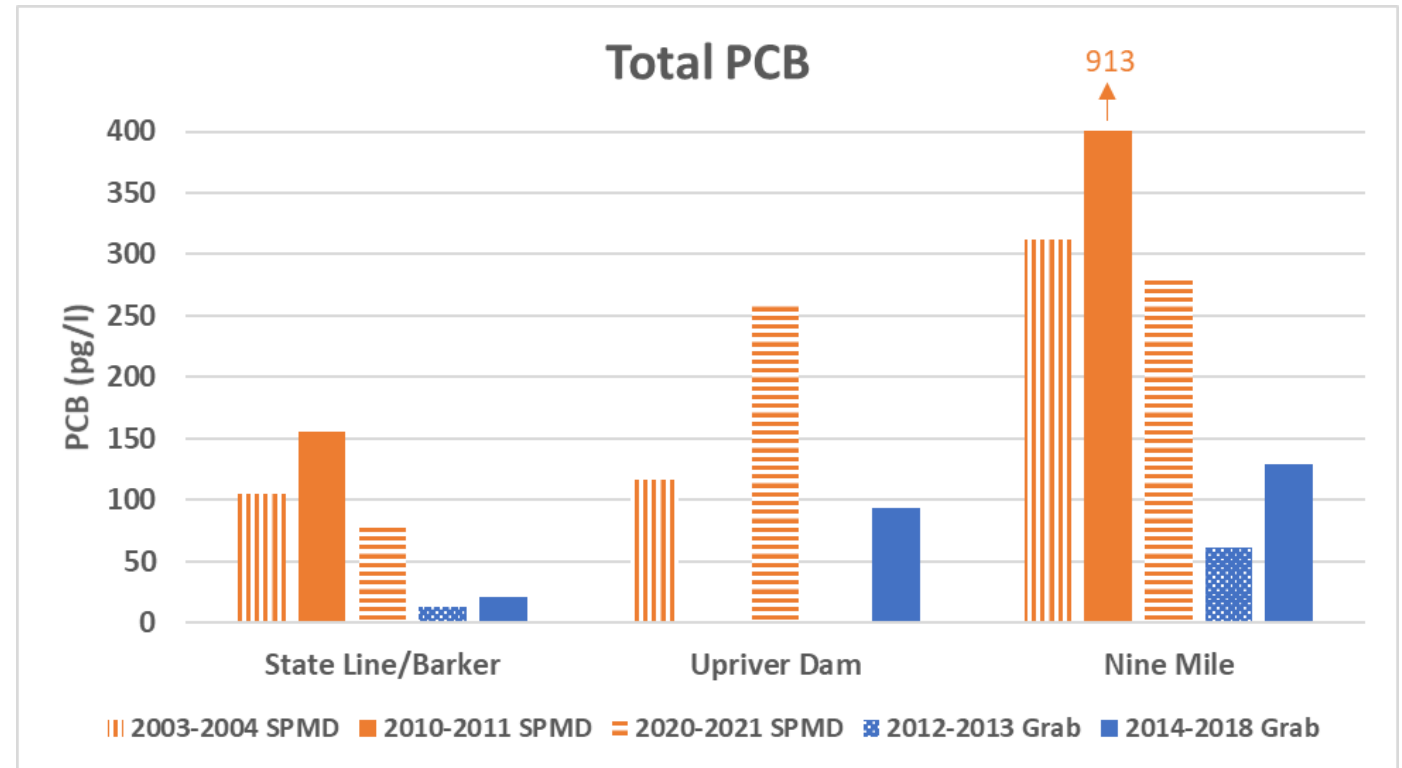
Comparison to Historically Observed Concentrations

Five studies exist measuring PCB concentration via SPMD or grab samples at similar locations

- Ecology 2003-2004
 - SPMDs at State Line, Upriver Dam, and Nine Mile
- Ecology 2010-2011
 - SPMDs at State Line and Nine Mile
- Ecology 2012-2013
 - Grab samples at State Line and Nine Mile
- SRRTTF 2014-2018
 - Grab samples at Barker Road, Upriver Dam, and Nine Mile
- SRRTTF 2020-2021
 - SPMDs at State Line, Upriver Dam, and Nine Mile

Comparison to Historically Observed Concentrations

- Concentrations measured by SPMDs are always greater than measured by grab sampling
 - Not a statistically verified generalization
 - Worthy of further consideration before assuming results from the two methods are directly comparable



Calculation of Total PCB Concentrations

- PCB in the aquatic environment can be categorized as occurring in three different phases:
 1. Freely dissolved
 2. Sorbed (i.e., bound) to dissolved organic matter
 3. Sorbed to particulate organic matter
- SPMDs measure only the freely dissolved PCB concentration
- Translation method required to convert SPMD results to total PCBs

Calculation of Total PCB Concentrations

- Translation method converting SPMD results to total PCBs

- $C_t = C_d / (1 + K_{oc,p}[POC] + K_{oc,d}[DOC])$

C_t = water column total PCB concentration

C_d = water column dissolved phase PCB concentration

$K_{oc,p}$ = organic carbon partition coefficient to particulate organic carbon (l/mg)

[POC] = particulate organic carbon concentration (mg/l)

$K_{oc,d}$ = organic carbon partition coefficient to dissolved organic carbon (l/mg)

[DOC] = dissolved organic carbon concentration (mg/l)

- Two issues with translation method

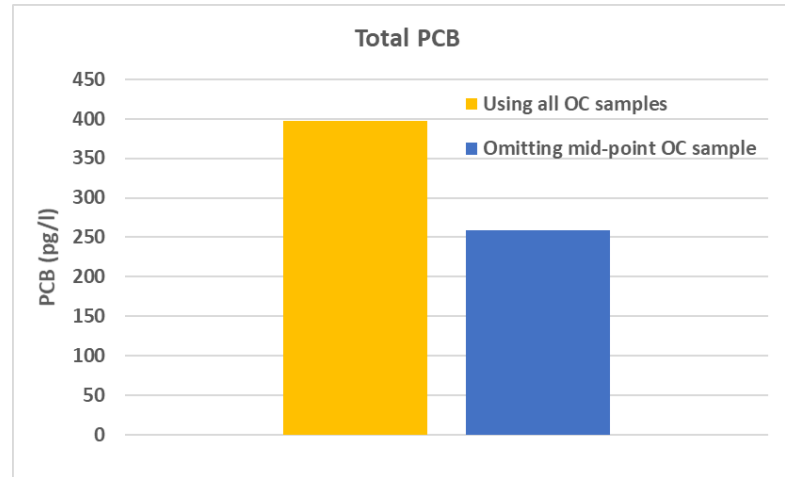
- Translation results are sensitive to variability in POC

- Partitioning to dissolved organic carbon can vary widely on a site-specific basis

Calculation of Total PCB Concentrations

- Translation results are sensitive to variability in organic carbon concentration

- Exclusion of single organic carbon sample changes predicted total PCB concentration by 140 pg/l



- $K_{OC,d}$ can vary widely on a site-specific basis
 - 95% confidence limit on the sorbing efficiency of DOC varies by a factor of 10
 - The majority of organic carbon in the Spokane River is in dissolved form

Quality Control Issues

- Majority of PCB concentration measurement arising from this study are flagged as “estimated” values
 - Percent recovery of performance reference compounds for many samples outside of the desired range
 - Failure of continuous temperature probes on two SPMDs
 - Shipping delays resulted in high flow samples exceeding recommended holding temperatures

Considerations Moving Forward

1. Calculation of total PCB concentration
2. Quality control
3. SPMDs versus grab sampling

Considerations Moving Forward

1. Calculation of total PCB concentration

- Measurement of dissolved PCB concentrations is more precise than measurement of total PCBs
- Conduct trend assessment using dissolved concentrations?
 - Advantages
 - More precise measurement
 - Generally proportional to total PCB concentrations
 - Dissolved concentrations are the most bioavailable form to fish
 - Disadvantages
 - Water quality standard expressed as total PCB
 - Not proportional to total PCBs in the (unlikely) occurrence that river organic carbon content or homolog distribution changes significantly

Considerations Moving Forward

1. Calculation of total PCB concentration
 - Conduct trend assessment using dissolved concentrations?
2. Quality control
 - Selection of performance reference compounds can be improved going forward
 - SPMDs will always provide the opportunity for more things to go wrong
3. SPMDs versus grab sampling
 - Grab sampling likely the more precise measure when concentrations are high
 - SPMDs will outperform grab sampling as concentrations decrease in the future
 - Parallel sampling for near term trend assessment?