Watershed Wide Management Issues and Candidate Studies

SRRTTF-TTWG Data Synthesis Workshop

February 1, 2022

Key Issues

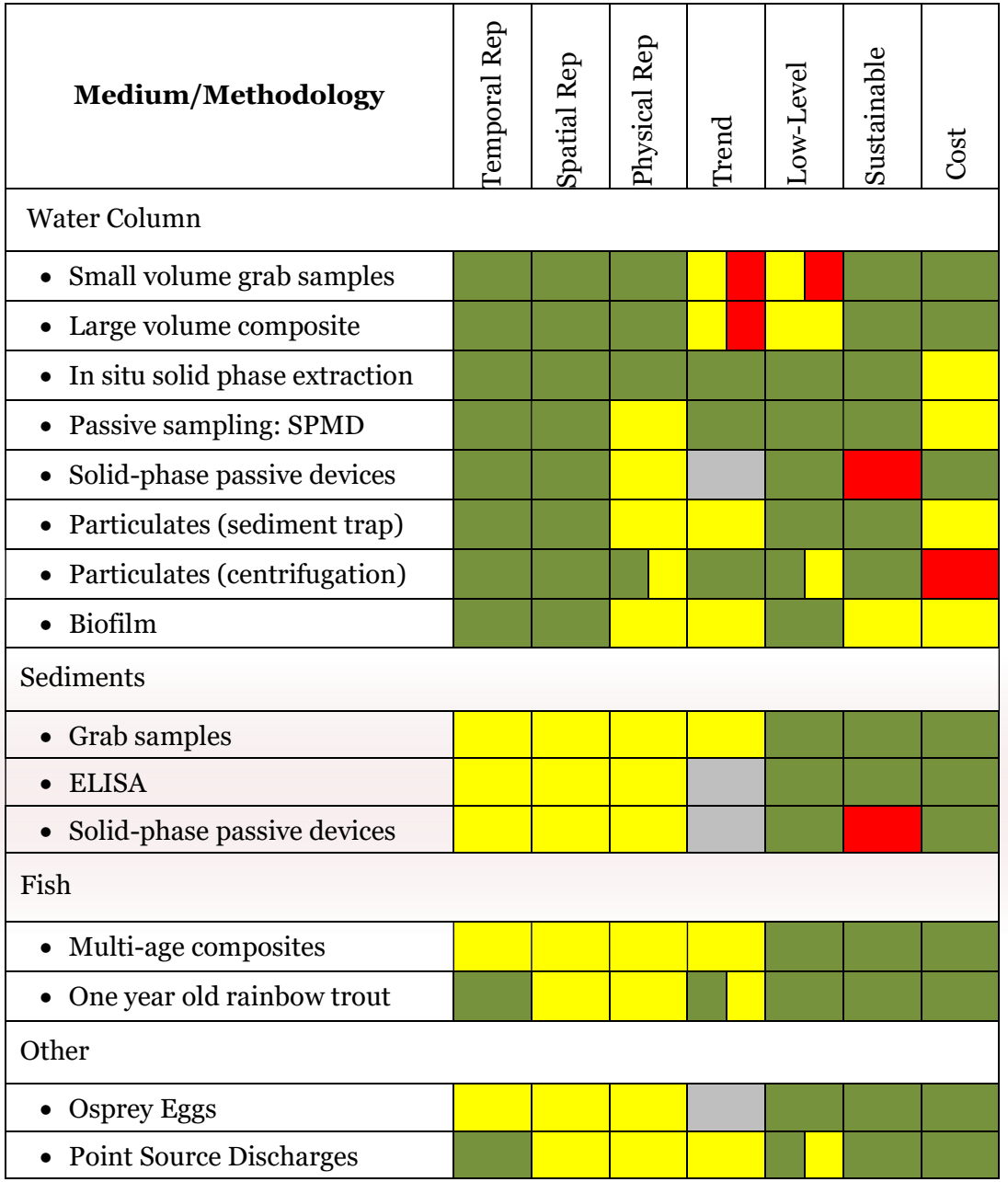
- Are we making measurable progress?
- Do currently undefined sources exist?
- From what pathway(s) are fish receiving the majority of their PCBs?

Background: Measurable Progress

- Task Force must make measurable progress toward meeting applicable water quality criteria for PCBs
  - Demonstration of progress requires a long-term monitoring
- Task Force identified need for long-term monitoring program starting in 2020
  - Designed to provide baseline year of data against which future years' concentrations could be measured
  - Key question "What sampling method(s) are most appropriate to support this assessment?"

Background: Measurable Progress

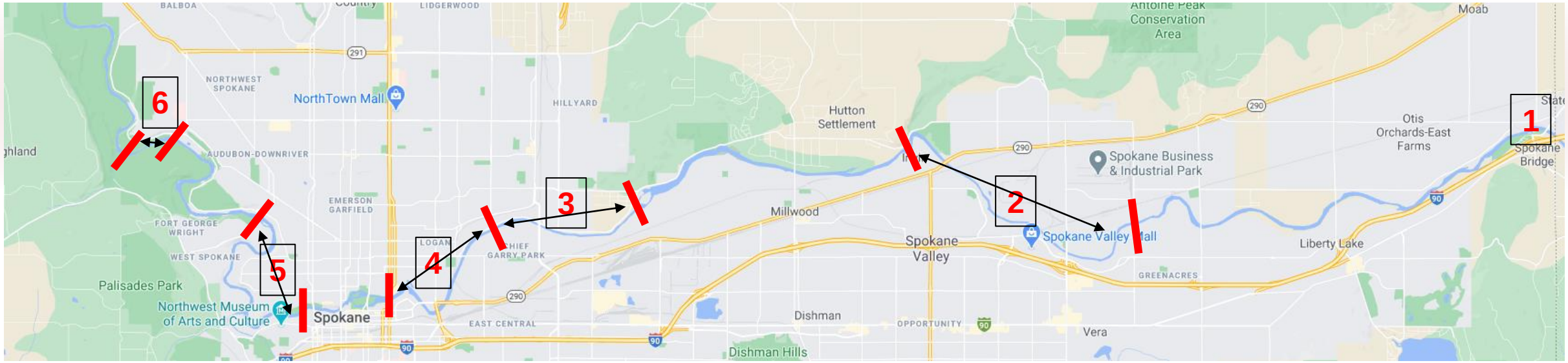
- Task Force reviewed 16 different candidate methods and selected two for implementation
  1. PCB concentrations in year-old Redband Trout
  2. Water column PCB concentrations via semi-permeable membrane devices (SPMDs)
- Monitoring was initiated in 2020
  - Today's objective is to review results and decide if adjustments need to be made



Fish Sampling

- Sampling conducted in fall of 2020 by WDFW
- Five reaches sampled
  - 25 fish per reach
  - Analyzed as composites of five fish apiece

- Sampling reaches planned
  1. State Line
  2. Spokane Valley
  3. Downstream of Upriver Dam
  4. Mission Reach
  5. Water St. to TJ Meenach
  6. Riverside Water Reclamation Facility (RWRF)



Fish Tissue Results

Future Fish Tissue Monitoring

- Program implementation proceeded as planned, except for one issue
  - Lack of fish in the target size range at the State Line location
  - Suitable sized fish not expected to be present at that station in future years
- Future steps
  - Confirm WDFW's willingness to continue sampling support
  - Resolve lack of suitable trout numbers at State Line
    - Continue existing monitoring program into the future without data from State Line?
    - Adjust monitoring program to include new species at State Line?
- How important is it to conduct a trend assessment upstream of Spokane Valley?

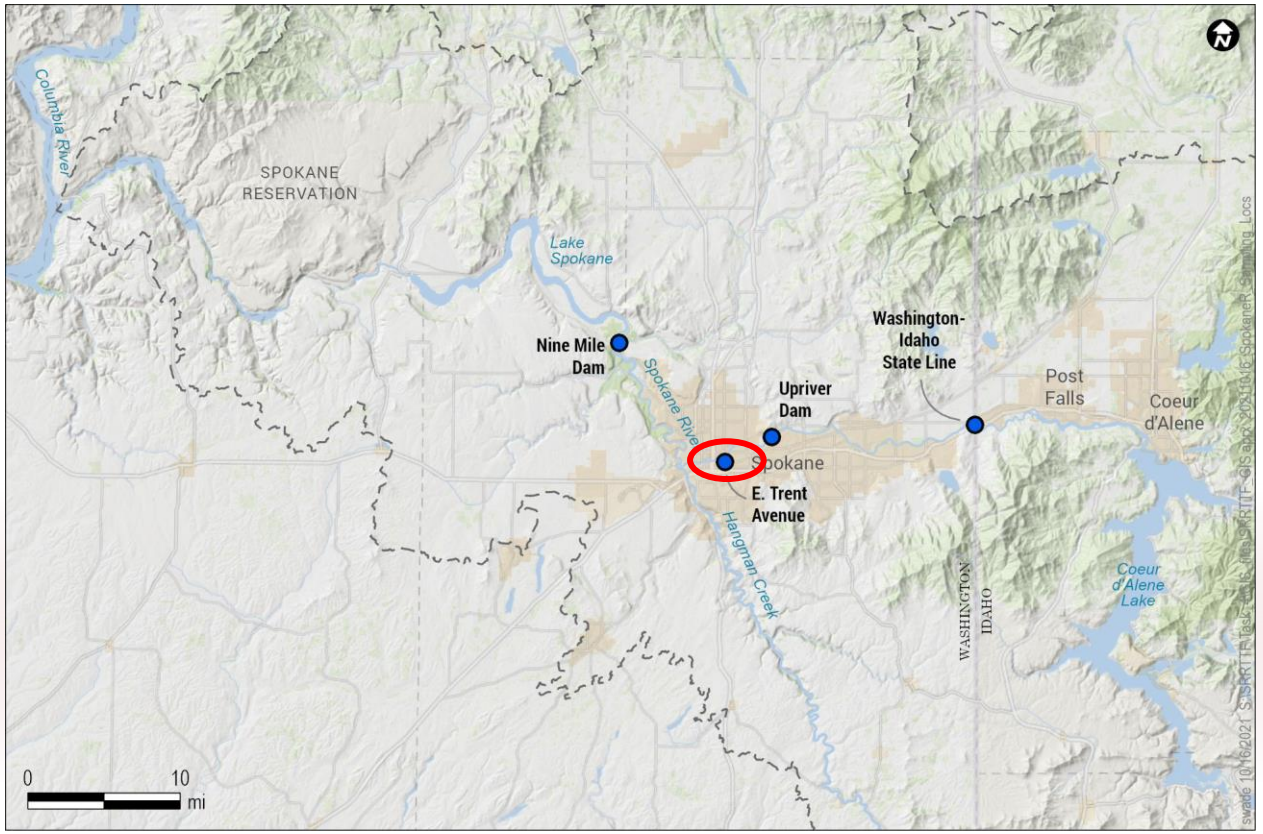
Water Column Monitoring

- Selected methodology was SPMDs: semi-permeable membrane devices
- 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

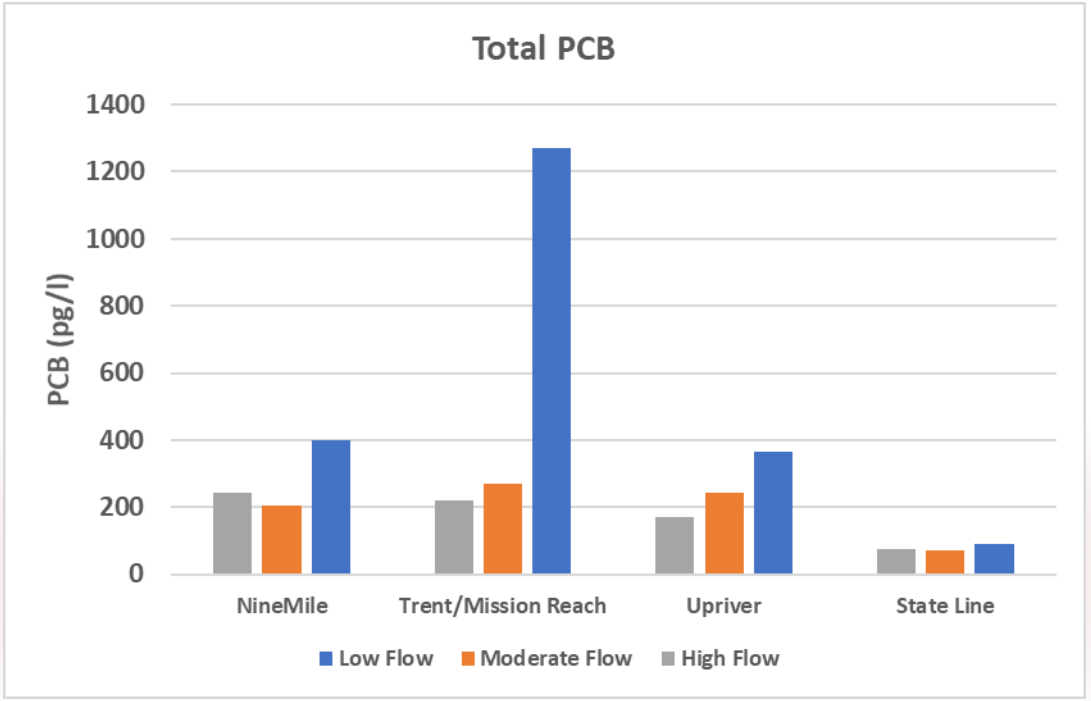
Deployment Details

- Four locations
  - WA/ID State Line
  - Downstream of Upriver Dam
  - E. Trent Avenue/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

- Results generally consistent with prior observations
  - Elevated concentration observed at Trent/Mission Reach during low flow condition



Direction of flow

Future Water Column Monitoring

- Continued use of SPMDs poses some challenges for long-term trend assessment
  - Indirect calculation of PCB concentration
  - Quality control issues
  - Comparability to grab sample results

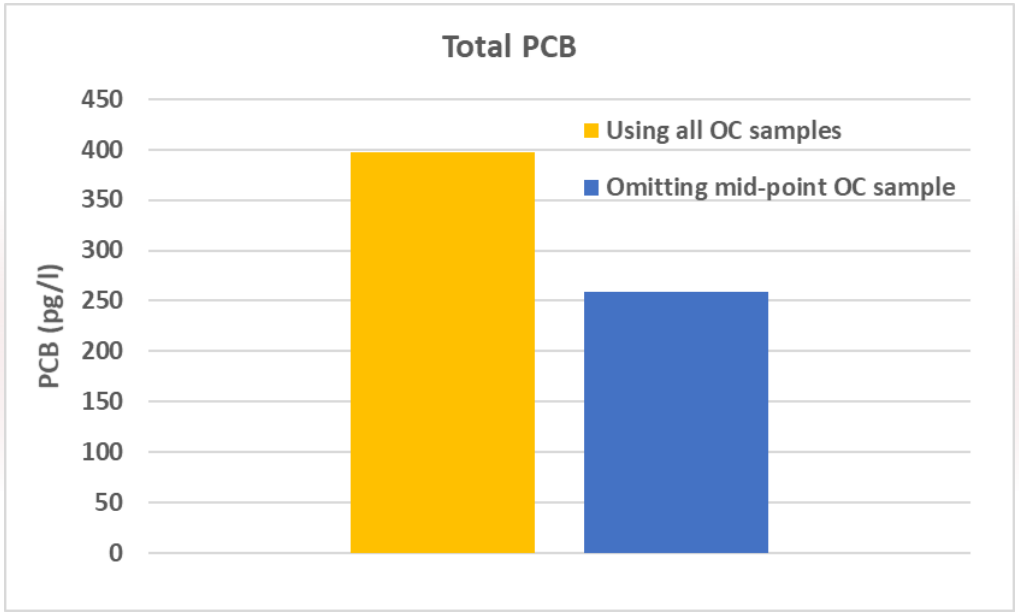
Indirect Calculation of PCB Concentrations

- SPMDs do not directly measure water column PCB concentrations
  - PCB concentration measured in the sampling device requires two conversion steps to estimate water column total PCB concentrations
    1. Mathematical calculation of dissolved water column PCB concentration based upon PCB concentration in the sampler
    2. Mathematical calculation of total water column PCB concentration based dissolved water column PCB and organic carbon concentration

- Ecology does not accept SPMD results in EIM, because concentrations are modeled and not directly observed

Indirect Calculation of Total PCB Concentrations

- While the limitations caused by indirect calculation were known in advance, recent Spokane sampling highlights the issue
  - Estimated total PCB concentrations are sensitive to variability in organic carbon concentration
    - Example: Exclusion of a single organic carbon sample changes predicted total PCB concentration at Nine Mile by 140 pg/l
- Issue of converting to total PCBs could be avoided by conducting trend analysis using only dissolved PCBs

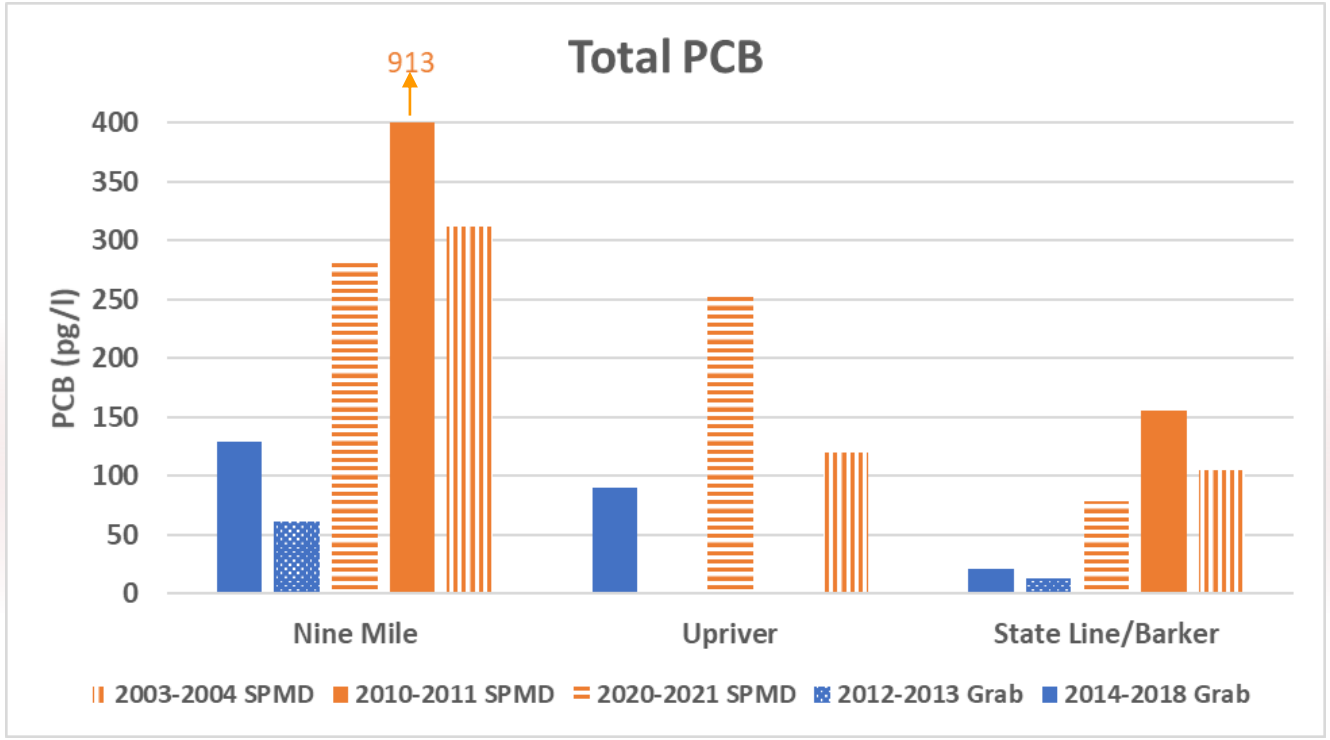


Quality Control Issues

- 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
  - Higher than expected variability among replicates
  - Failure of continuous temperature probes on two SPMDs

Comparability to Concentrations from Grab Samples

- Comparison conducted between historical concentrations measured by SMPDs and grab sampling at similar locations
  - Concentrations measured by SPMDs are consistently greater than those measured by grab sampling
- Not necessarily a reason to discontinue use of SPMDs
  - Worthy of further consideration prior to mingling both sets of data in trend analysis



Direction of flow

Post-Audit of SPMD Suitability

- What we knew

Advantages

- Less susceptible to blank contamination than grabs
- Provides integrated concentration over a month-long period

Disadvantages

- Provides indirect estimate of water column PCB concentration

- What we've learned

Advantages

- Confirmed superior performance relative to blank contamination

Disadvantages

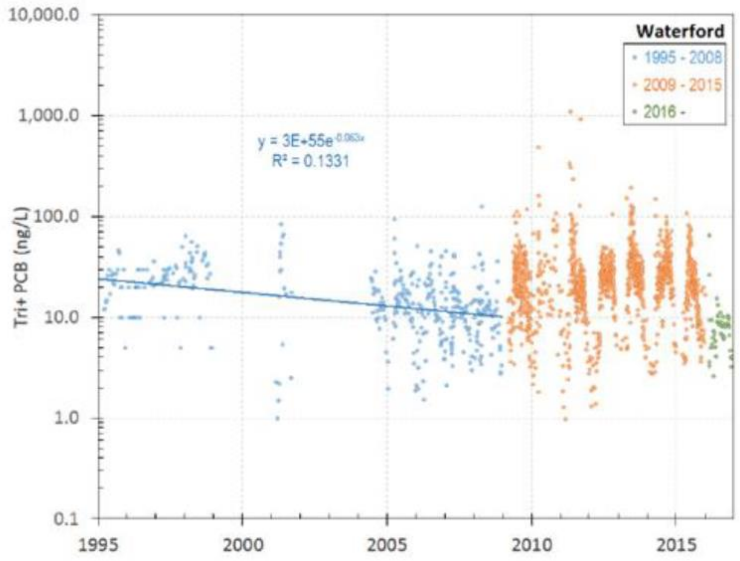
- Estimates of total PCB concentration can be sensitive to variability in water column organic carbon concentration
- Results may not be directly comparable to those from grab samples

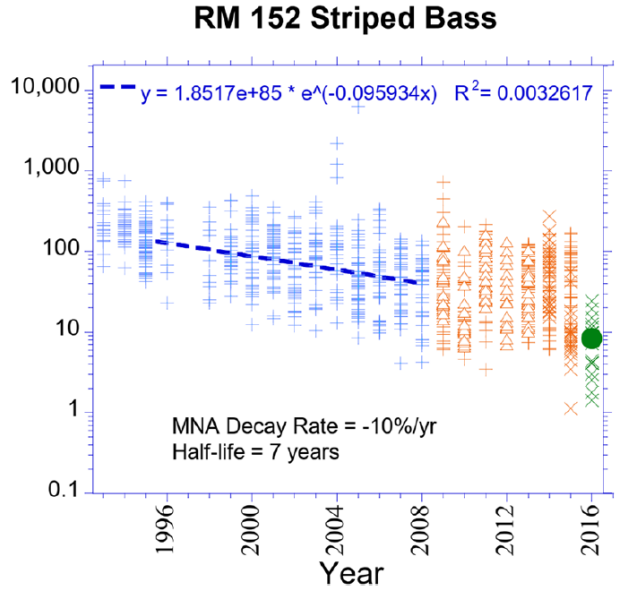
Alternatives to SPMDs

- *in situ* solid phase extraction (CLAMs)
  - Only method rated good in all key aspects of initial review
  - Has had historical issues, presumably now addressed
    - Ecology (2019) "A follow-up laboratory study should be conducted to test the accuracy of the SPE-CLAM device."
- Solid phase passive samplers
  - Similar to SPMDs but easier to implement
  - Also provide indirect estimate of dissolved phase PCB concentration
  - Less of a track record
- Water column grab samples
  - Currently being used as basis for trend assessment in Spokane
  - Blank contamination will become more problematic as concentrations decrease in the future

PCB Trend Assessment Will Not Be Easy

- "Because of natural variability, you need a LOT of data to be able to see trends in the water data (and they don't have blank issues)"
  - Rodenburg (2022) presentation to SRRTTF discussing Hudson River





Summary

- SPMDs are an imperfect measurement technique
- No clearly superior alternative exists
- PCB trends not easy to detect

Discussion

- Straw man for discussion
  - Continue use of SPMDs
    - Focus on dissolved phase concentration for trend assessment, recognizing that this doesn't allow direct comparison to the water quality standard
  - Supplement future water column trend assessments with grab samples collected for other purposes

- Other options?
  - Begin trial investigation of CLAMs?

Do Currently Undefined Sources Exist?

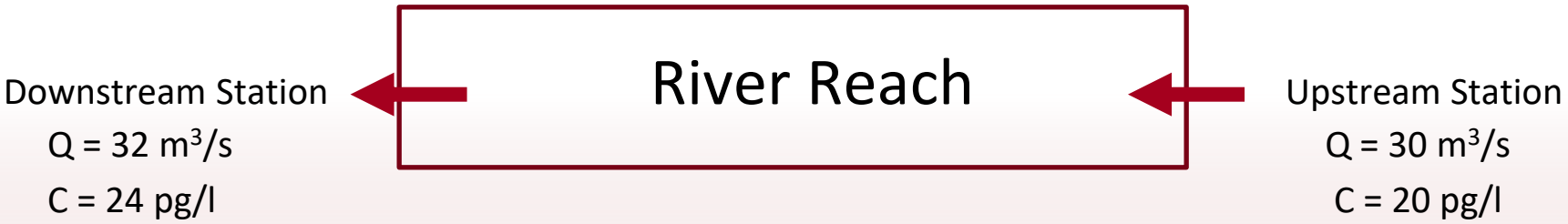
- The mission of the Task Force is to characterize the sources of toxics (PCBs) in the Spokane River and identify and implement appropriate control actions
- Problem Statement
  - Have we identified all important sources?

Activities Taken to Identify Undefined Sources

- The primary activity taken to identify undefined sources has been a mass balance approach
  - Measure all known loads of PCBs to the river
  - Measure PCB load in the river
  - Determine whether observed load in river is larger than the sum of all known loads
- Assessed via three synoptics surveys

Mass Balance Approach

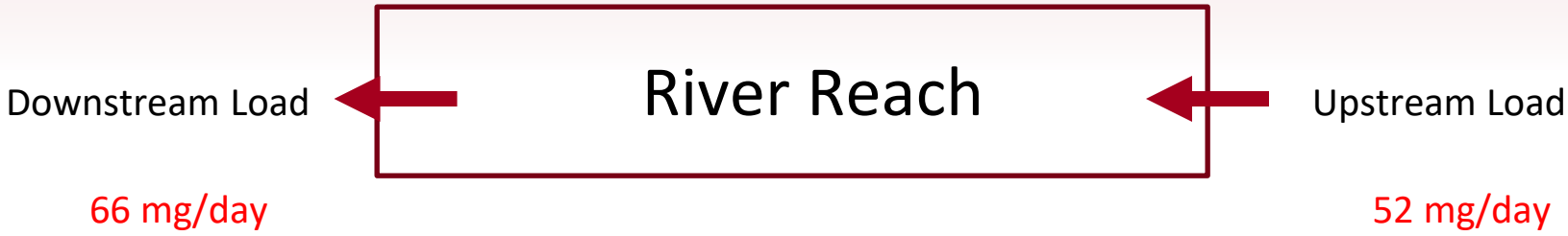
- Calculate load of PCB (mass per time) at individual river reaches
  - Load = River flow x River PCB concentration
- Example



  - Upstream Load = 30 m^3/sec x 20 pg/l = 52 mg/day
  - Downstream Load = 32 m^3/sec x 24 pg/l = 66 mg/day

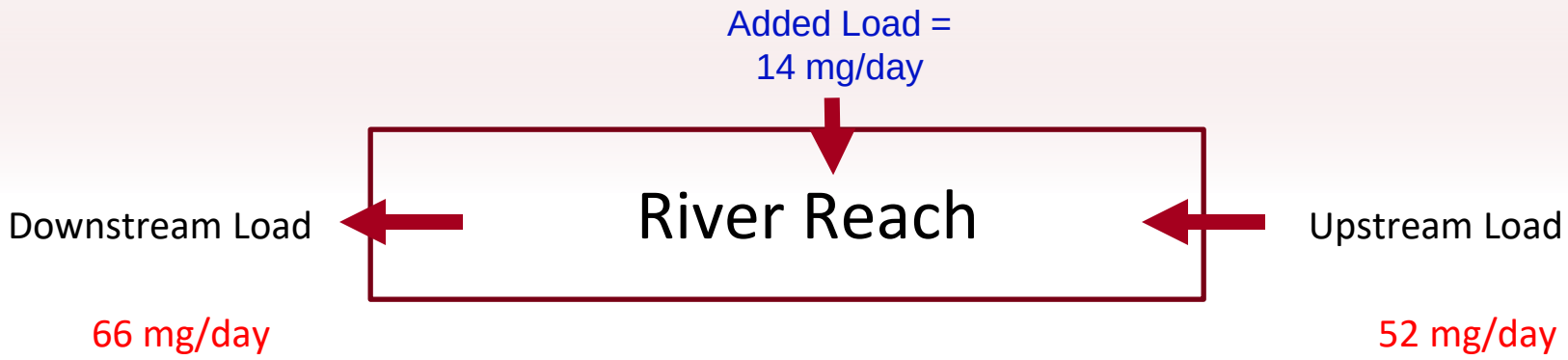
Mass Balance Approach

- Calculate load of PCB (mass per time) in river at several locations
  - Load = River flow x River PCB concentration
- Determine load of PCB added to river between two monitoring stations by comparing upstream and downstream load



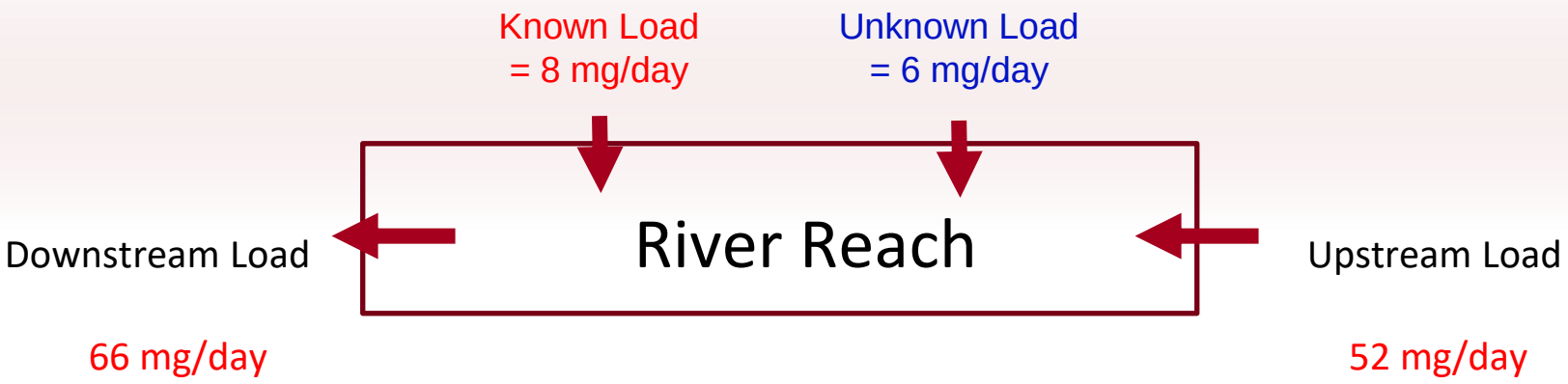
Mass Balance Approach

- Calculate load of PCB (mass per time) in river at several locations
  - Load = River PCB concentration x River flow
- Determine load of PCB added to river between two monitoring stations by comparing upstream and downstream load
  - Added load = Downstream load (66) – upstream load (52) = 14



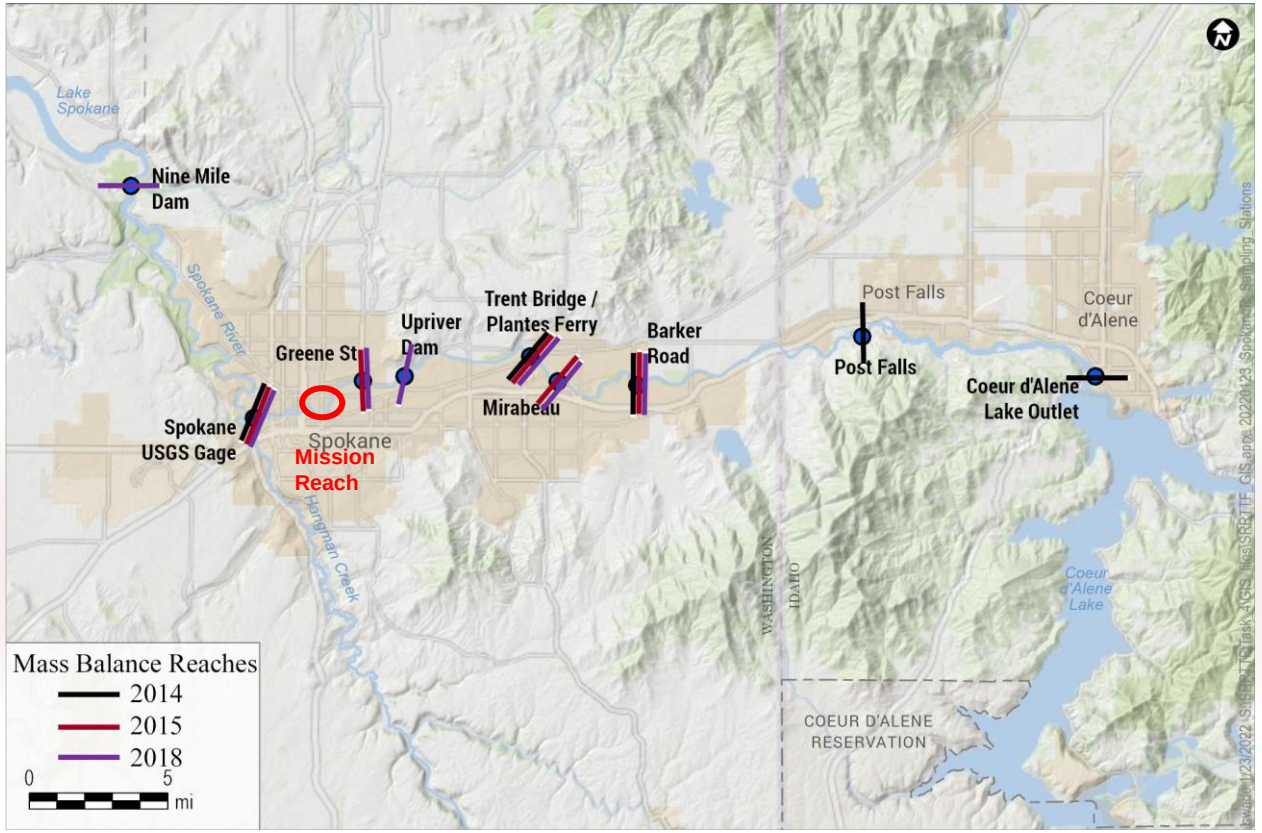
Mass Balance Approach

- Added load can be divided into known (e.g., point sources) and unknown components
  - Assume a known load of 8 mg/day exists in our reach
  - Unknown load = Downstream load (66) – upstream load (52) – known load (8) = 6



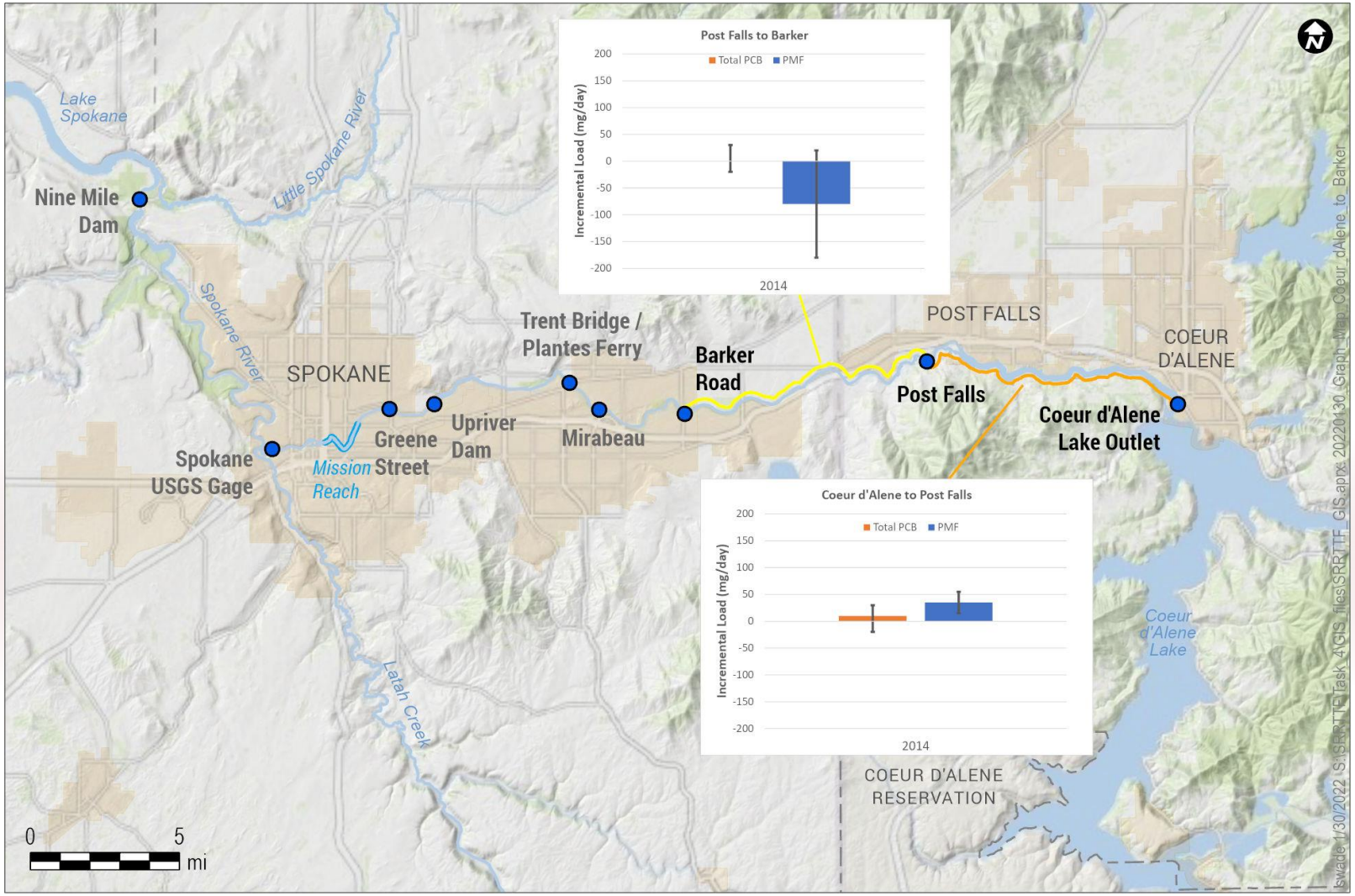
Mass Balance Assessments Conducted to Date

- Three synoptic low flow/dry weather surveys
  - August of 2014, 2015, and 2018
- Different spatial coverage each survey
- Different methods used to assess concentrations
  - Total PCBs, homologs, and PMF factors
  - Different blank correction approaches



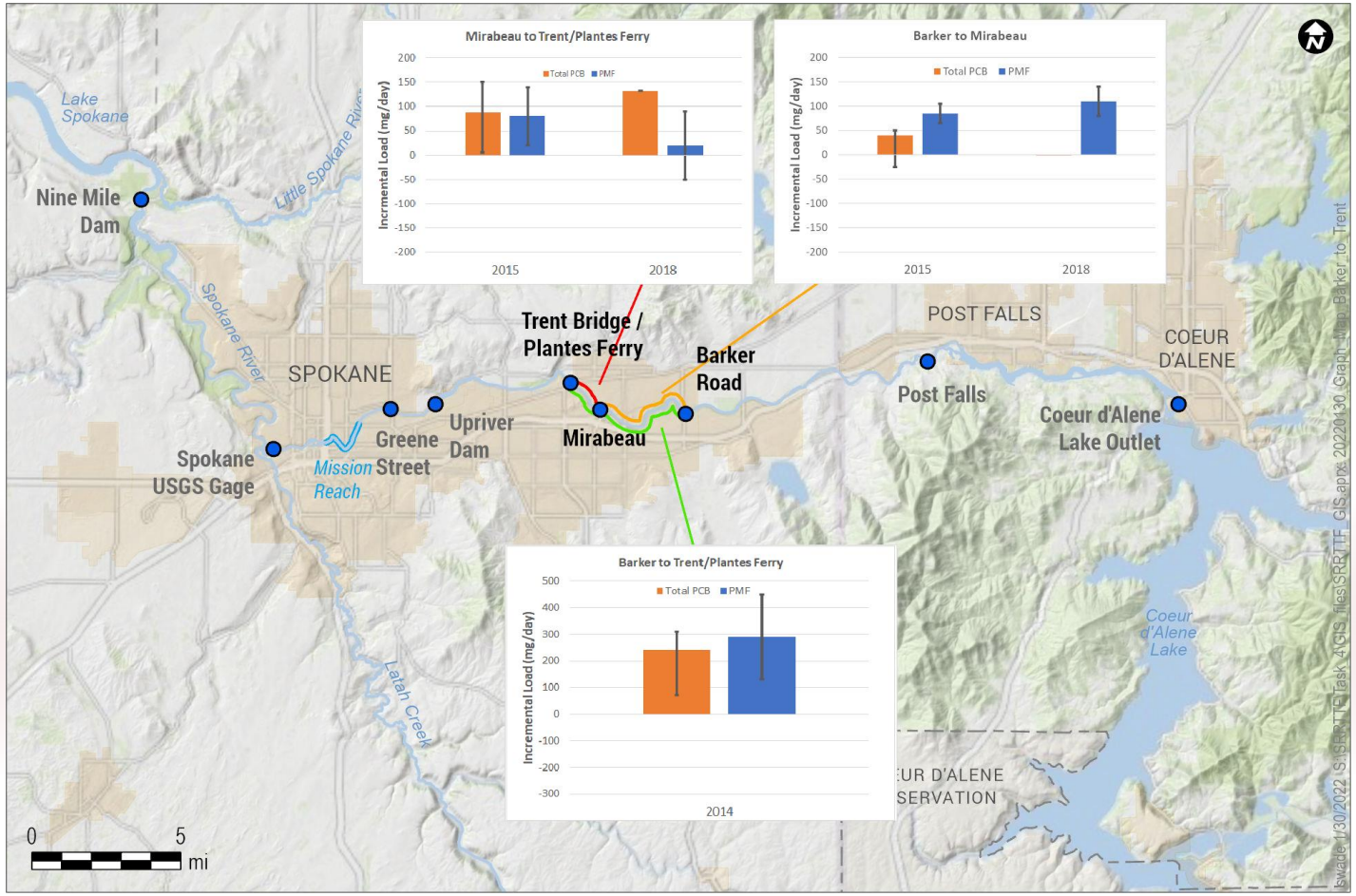
Coeur d'Alene to Barker Road

- Only sampled in 2014
- No unidentified loads of any significance observed



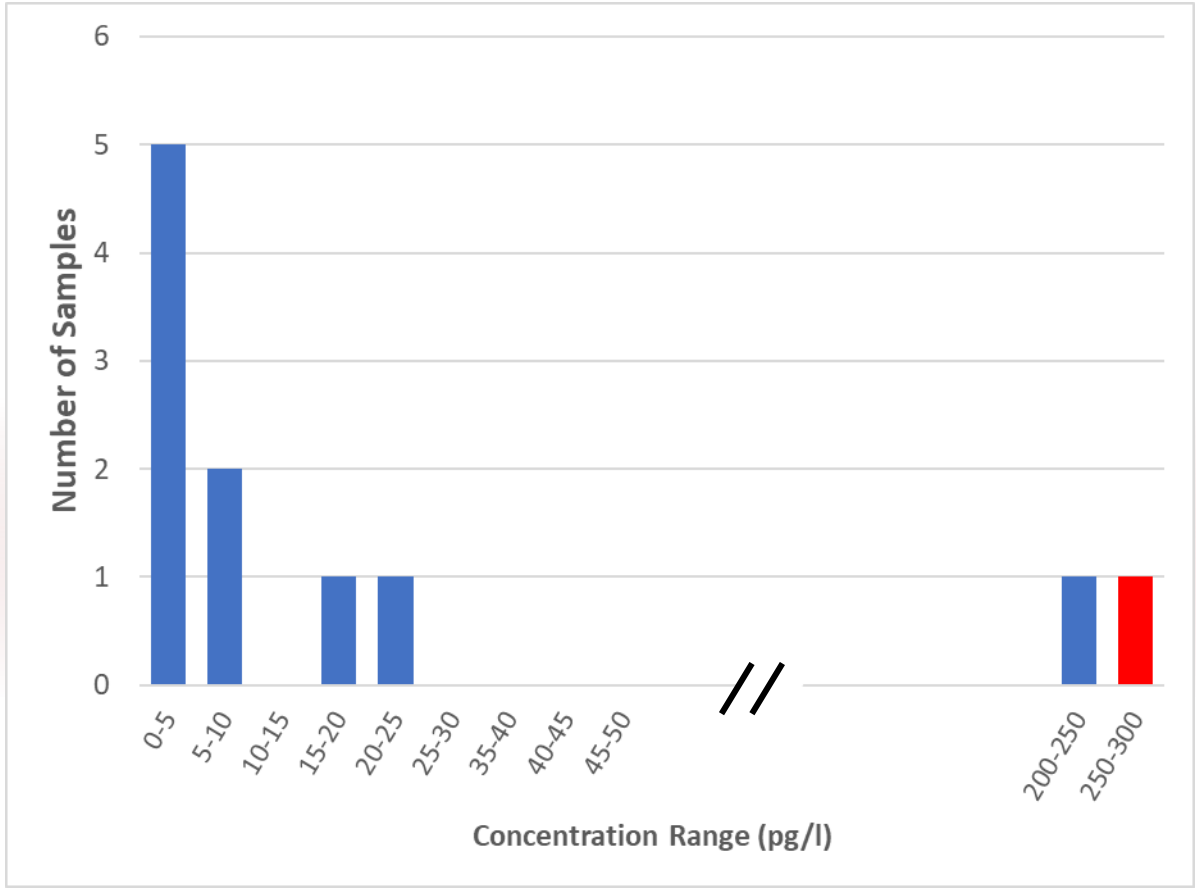
Barker to Trent/Plantes Ferry

- Large (>100 mg/day) incremental load consistently observed between Barker and Trent/Plantes Ferry
- 2018 results differ between approaches in terms of the portion of that load enters upstream of Kaiser site at Mirabeau



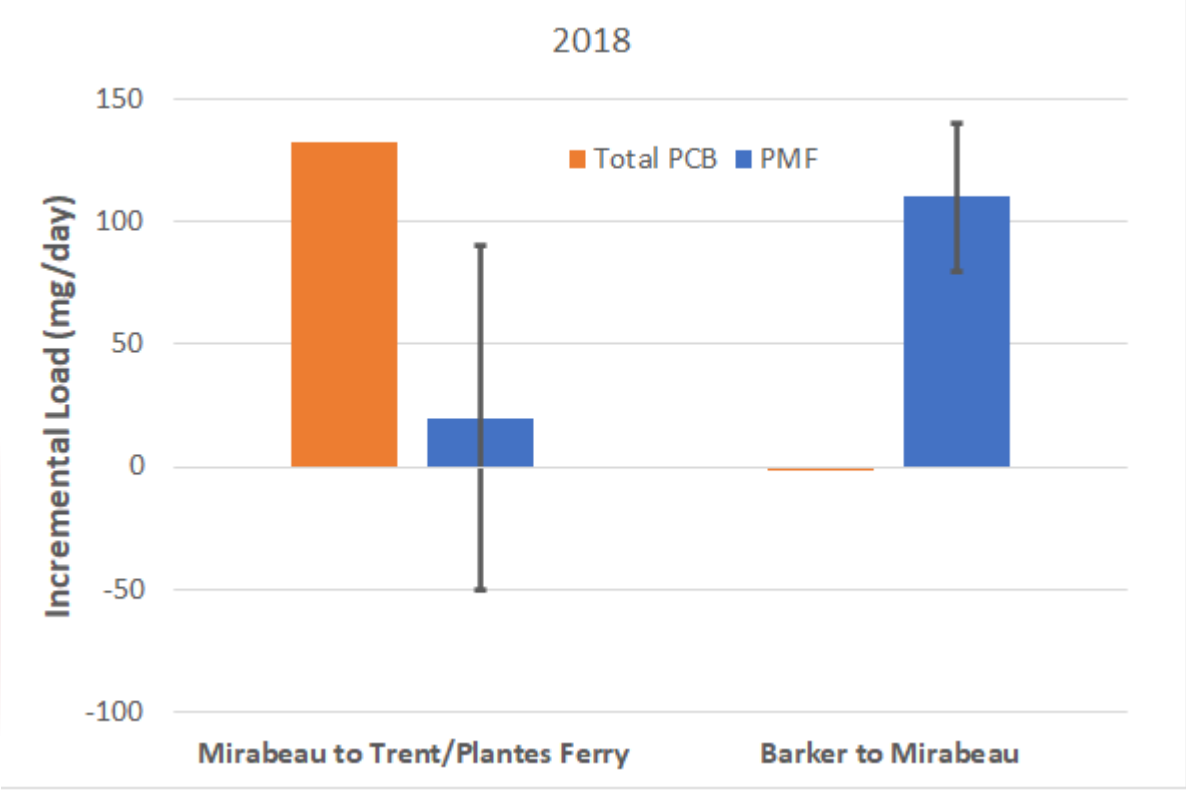
Concentration Distribution at Mirabeau

- Large majority of observed concentrations are <25 pg/l
  - Occasional value(s) above 200 pg/l
- Discrepancy in results between methods is due to how the 260 pg/l sample was handled
  - Total PCB approach rejected that sample due to 200 pg/l seen in the mono- and di-chloro homologs
  - PMF approach considered the non-anomalous portion of the sample



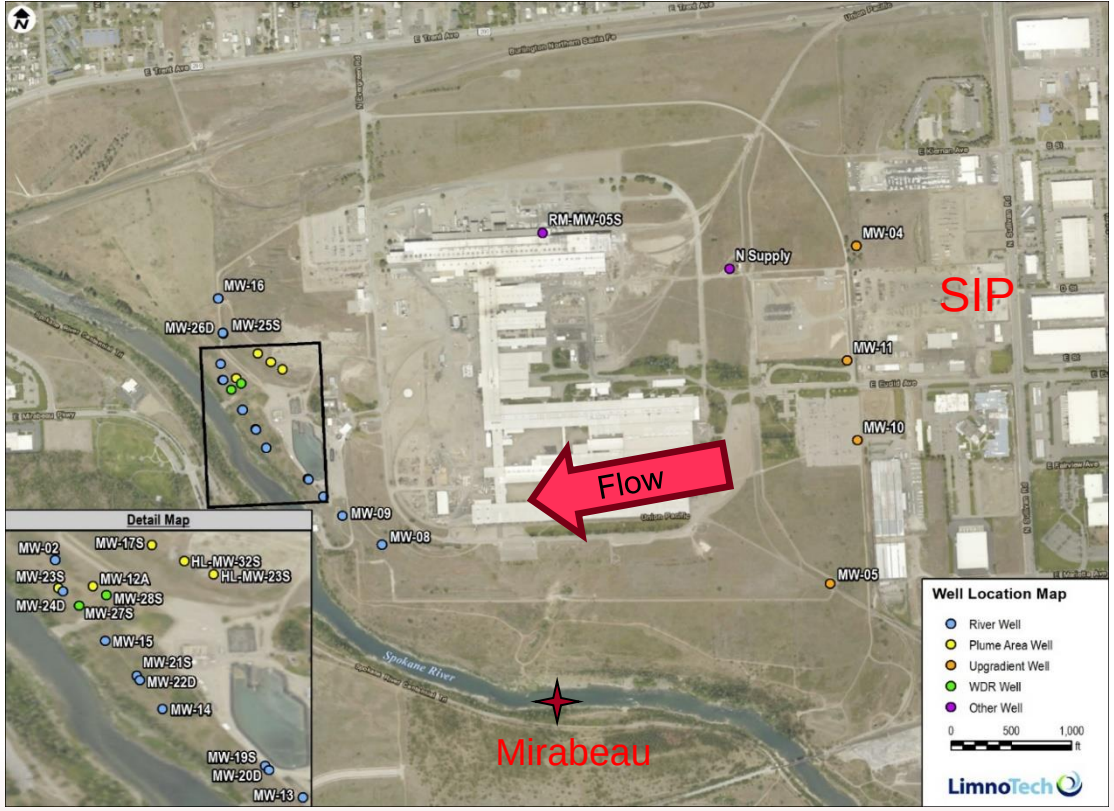
Barker to Trent/Plantes Ferry: 2018

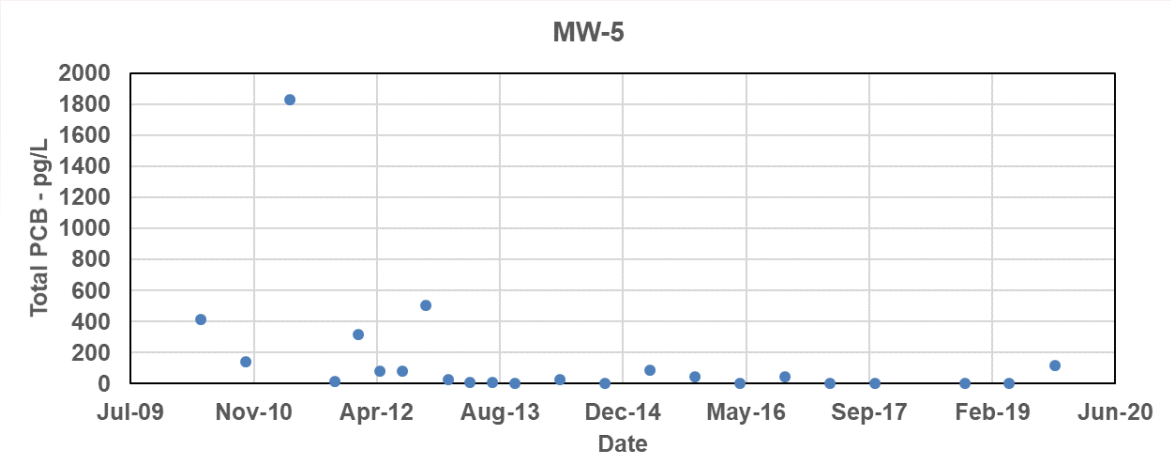
- Total PCB approach ignores anomalous sample and concludes that the load all comes from below Mirabeau (i.e., from Kaiser)
- PMF approach gives credence to anomalous sample and concludes that the majority of load enters upstream from Mirabeau



Potential Sources to Mirabeau

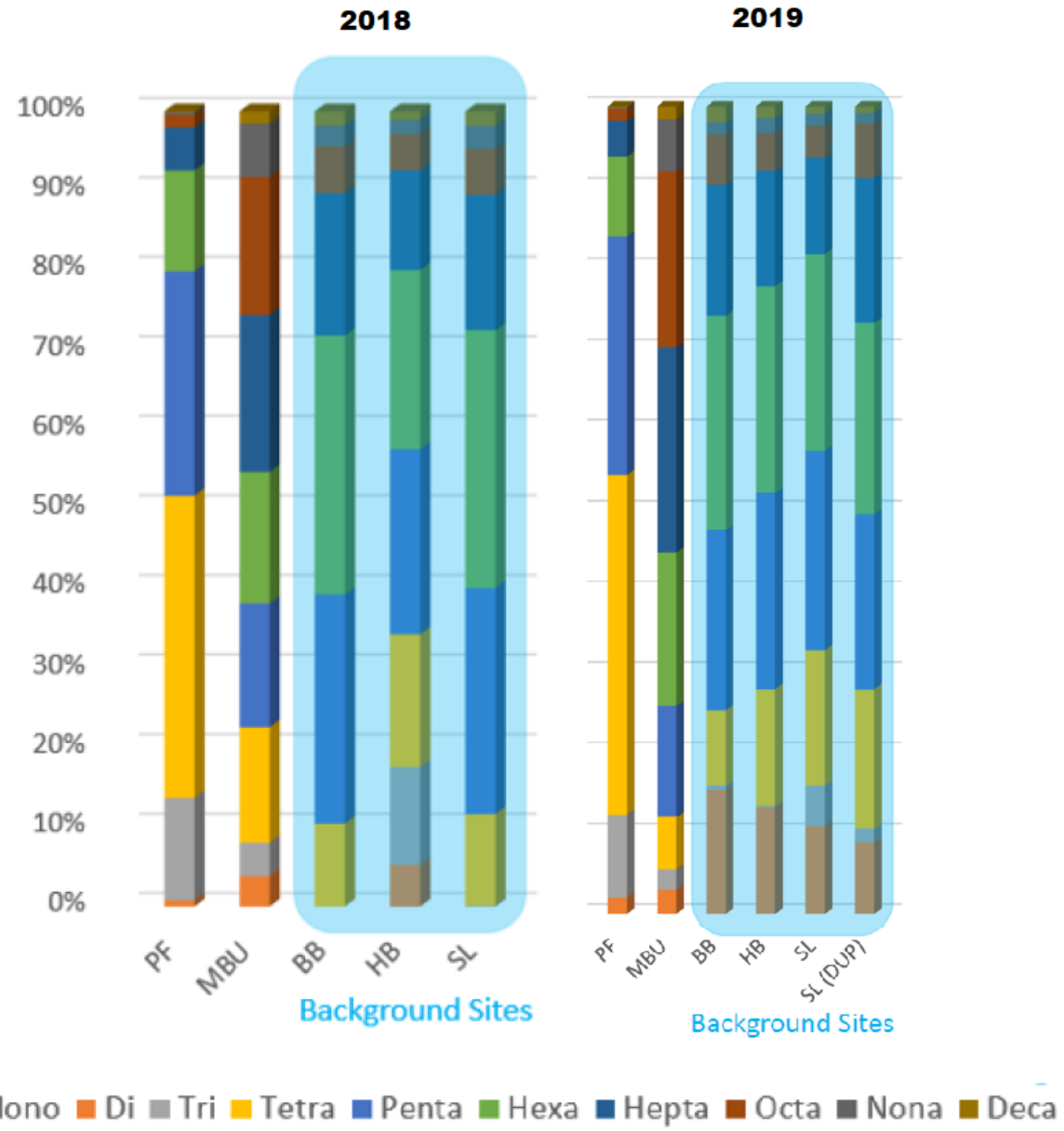
- Spokane Industrial Park (SIP), near Mirabeau, had historically used PCBs
  - PCBs >10,000 ppb found in 1994 in sludge from SIP's oxidation ditch
- Groundwater monitoring upgradient of Kaiser has shown high PCBs:
  - Kaiser upgradient well locations are not necessarily reflective of groundwater loading to Mirabeau
  - PCB concentrations in upgradient wells have been decreasing over time
  - Elevated PCBs in upgradient wells and at Mirabeau are spotty in frequency





Mirabeau Biofilm

- Biofilm homologue fingerprints imply presence of a unique source entering above Mirabeau
  - Mirabeau (MBU) fingerprint looks distinctly different than those from background sites
- Strongly indicates presence of some new source of PCBs, but doesn't say much about load
  - Near-bank biofilm samples may be reflecting a highly localized source
  - Mid-channel water column measurement may be missing a load that has not mixed laterally across the stream

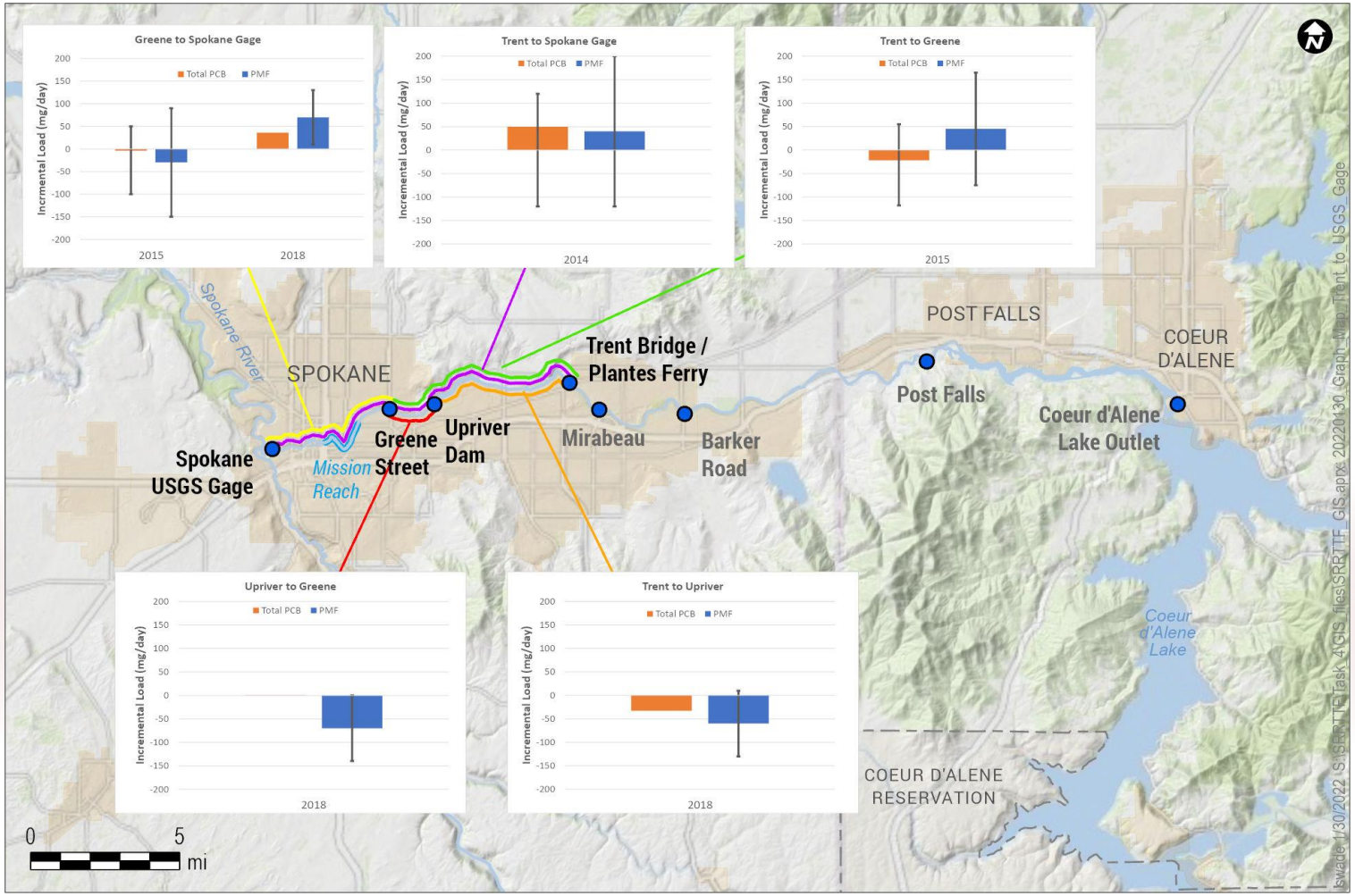


Barker to Trent/Plantes Ferry Summary

- Mass balance assessment shows consistent evidence of a large load entering somewhere in that segment
  - Much of the load comes from Kaiser
- Amount of load entering upstream of Kaiser confounded by infrequent high concentrations at Mirabeau
  - Biofilm data imply presence of a unique source above Mirabeau
  - Historical PCB contamination located in the vicinity
- Presence of previously undefined load merits future consideration

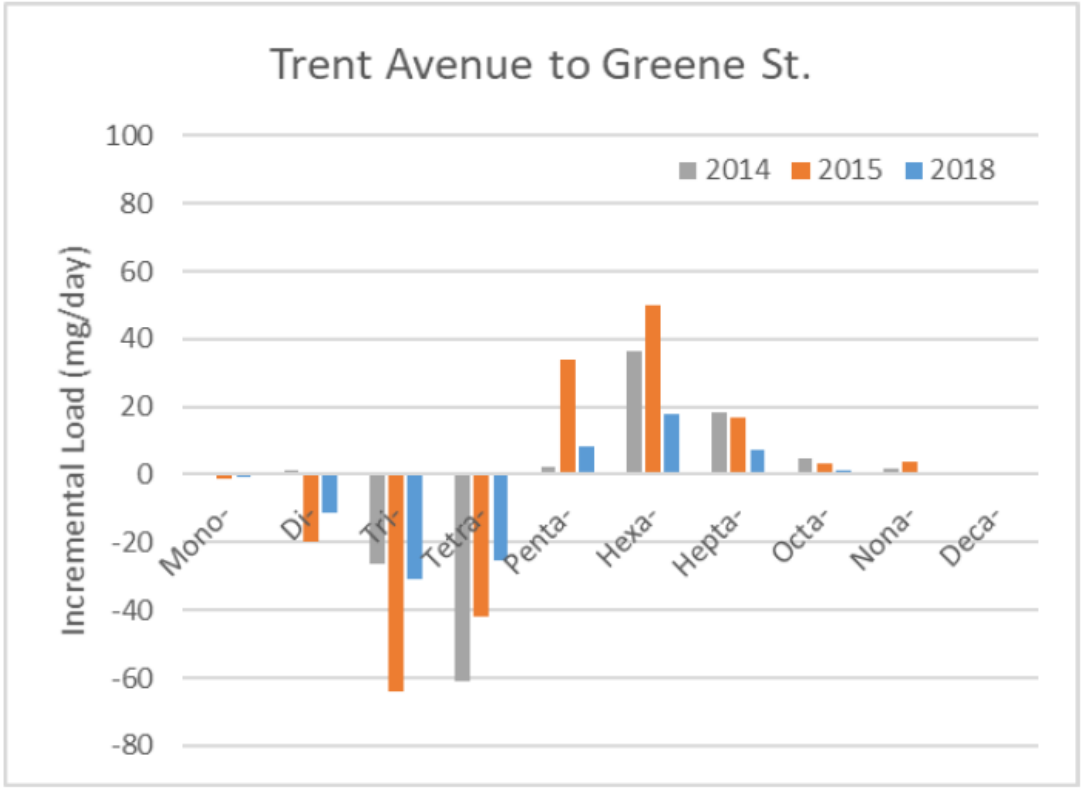
Trent to USGS Gage

- Potential for additional load entering between Greene and USGS gage
  - very uncertain



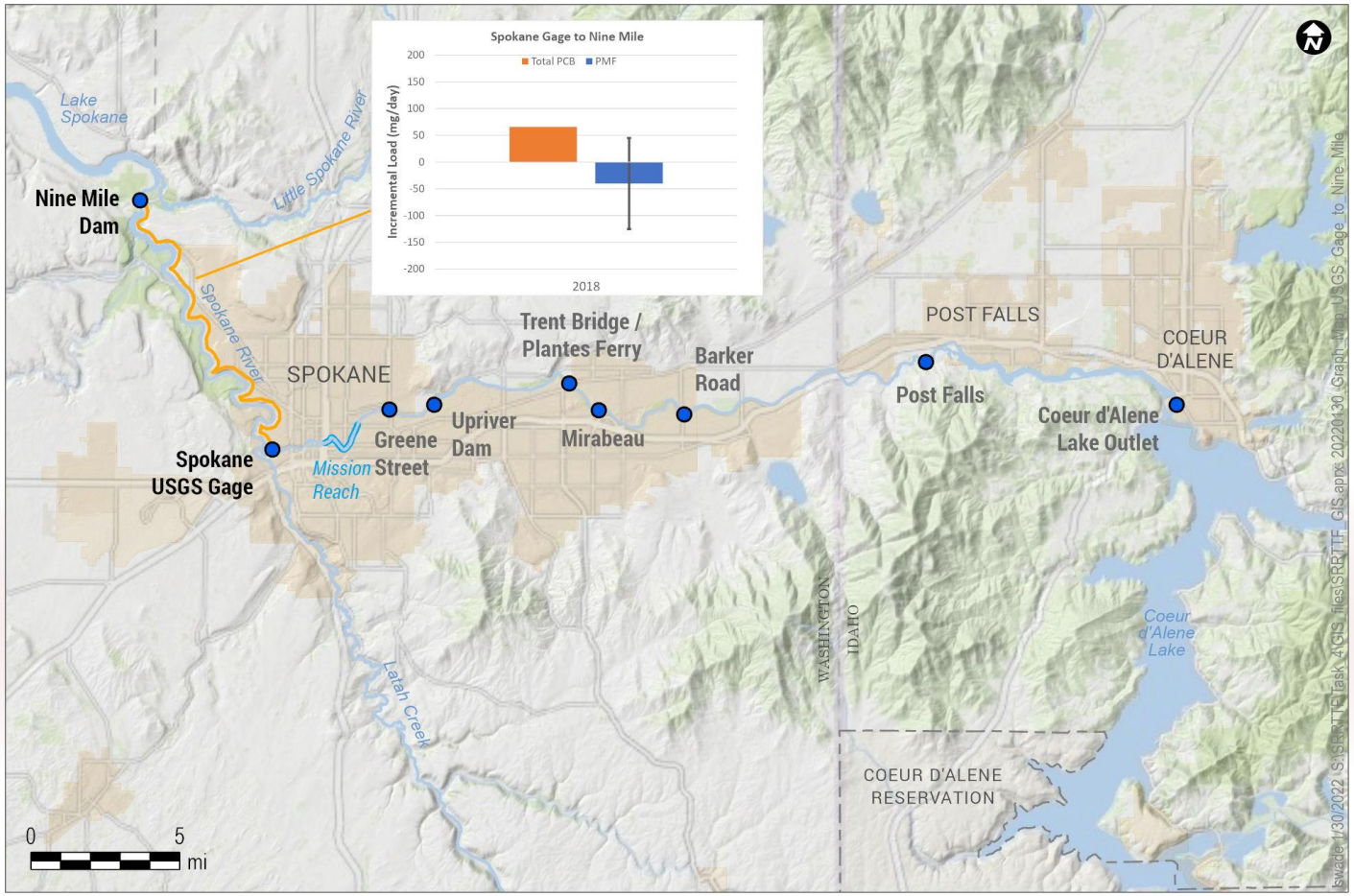
Trent/Plantes Ferry to Greene St. Homologs

- Loading of higher-chlorinated homologs appears likely
  - Balanced by loss of lower-chlorinated homologs
- Three theories have been proposed
  - Preferential loss of lower-chlorinated homologs
    - Transport to groundwater
    - Volatilization at Upriver Dam
  - Groundwater interaction more complicated that currently assumed



USGS Gage to Nine Mile

- Only one survey – 2018
  - Apparent inconsistency between models, although error bars would likely have significant overlap
- No definitive answer on presence of unidentified load



Conditions Other Than Dry Weather?

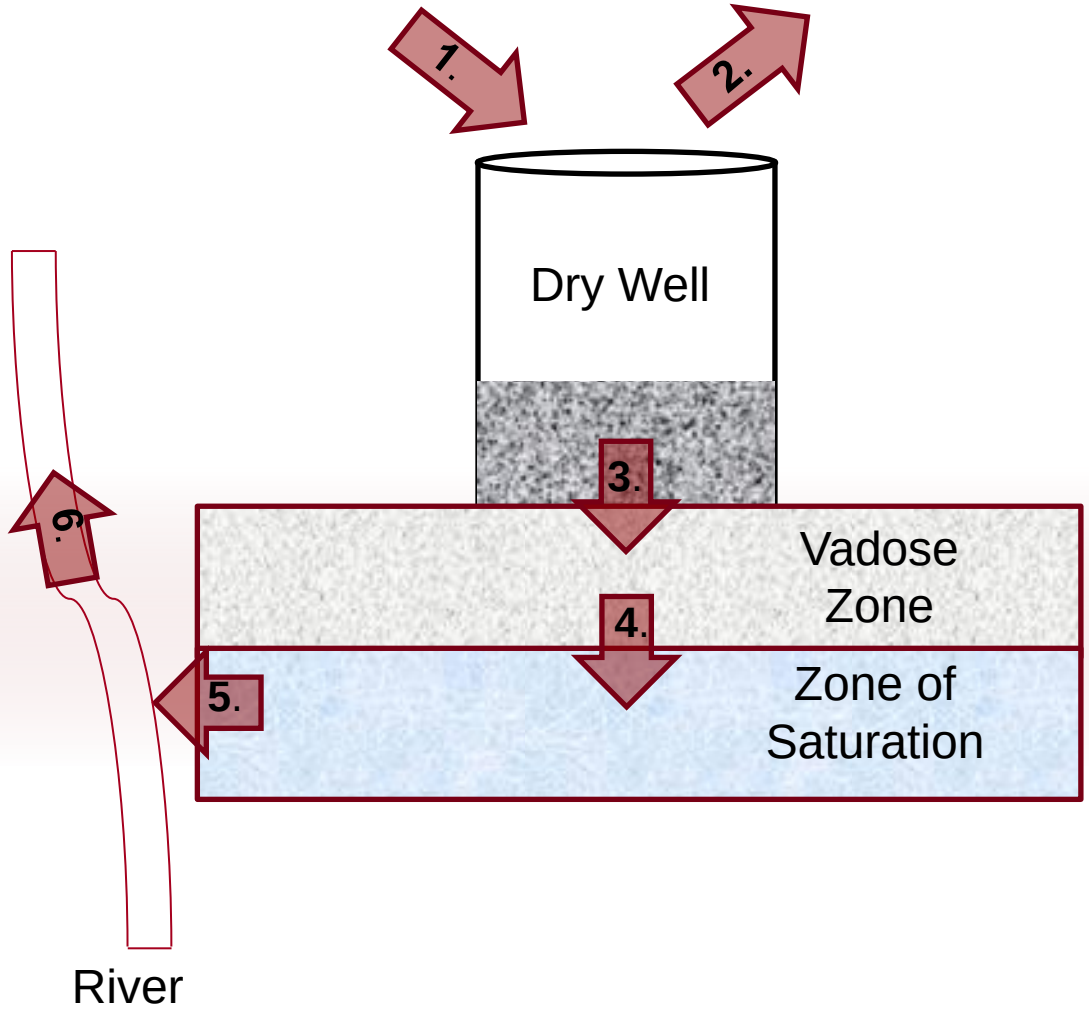
- Mass balance assessments have all been conducted during low flow, dry weather conditions
- Unknown loads that might exist under other conditions
  - Direct discharge of stormwater
    - Storm event monitoring has been conducted at many outfalls – not really an unknown
  - Delivery of infiltrated stormwater loads via groundwater
  - High-flow mobilization of PCB sources

Delivery of Infiltrated Stormwater PCBs via Groundwater

- The large majority of stormwater in the Spokane watershed is not discharged directly to the River
  - Infiltrated to groundwater through dry wells or vegetative infiltration areas
- In most systems, infiltration effectively removes PCBs from transport to surface water via binding to organic matter in soils
  - Spokane soils have low organic carbon content

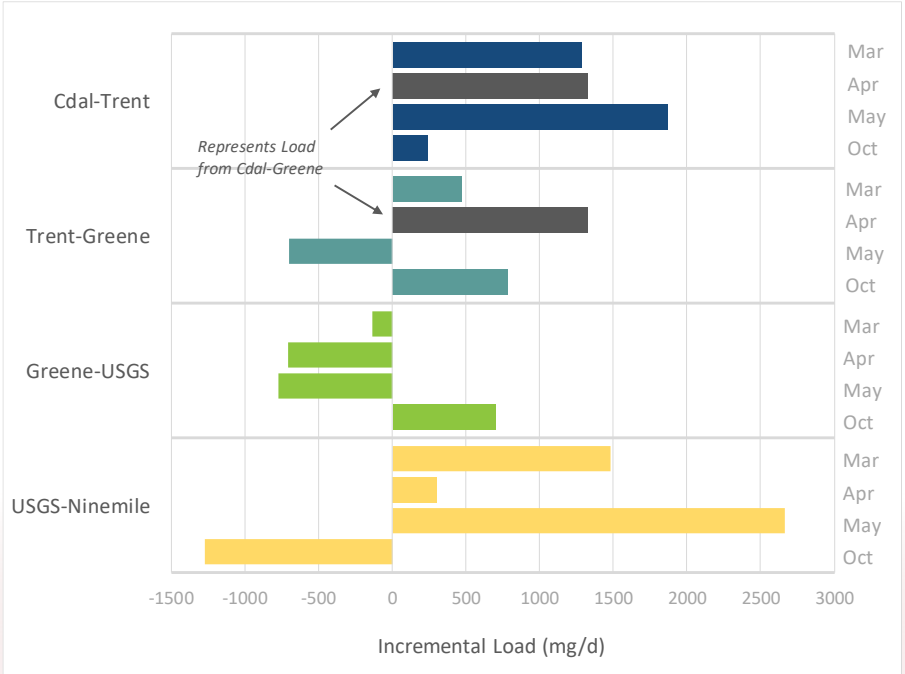
Conceptual Model of PCB delivery from Dry Wells to River

- Components
  1. Stormwater PCB load to well
  2. Well contents Vactored out
  3. PCB delivery to vadose zone
  4. PCB delivery to zone of saturation
  5. PCB delivery to river
  6. PCB transport downstream



High-Flow Mobilization of PCB Sources

- Assessment of Ecology 2003-2004 SPMD and SRRTTF 2016 monthly data showed more load in the river than could be explained by known loads during higher river flow conditions
  - implies potential presence of a flow-dependent source
  - data not designed for mass balance due to limited number of samples, unsteady flow



- Historical evidence of shoreline soil PCB contamination
  - "The soil sample for the 1993-94 PCB investigation was collected along the river shoreline …. Results showed elevated concentrations of PCB-1248 (4,700 ppb) and -1260 (3,900 ppb). *All or part of the area sampled looked to be under water during high flow"*

What We Know and Don't Know

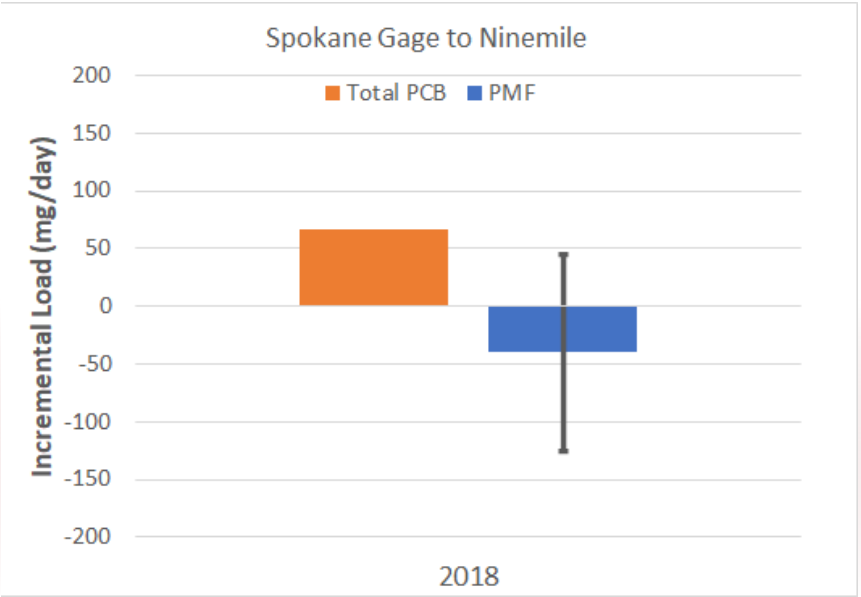
- Key "knowns"
  - Groundwater PCB load enters near Kaiser facility
- What we suspect
  - Presence of groundwater source directly upstream/upgradient of Kaiser
- What we don't know
  - Whether an unknown dry weather source exists downstream of the USGS gage
  - Groundwater/other interactions between Plantes Ferry and USGS gage
  - Groundwater loading of infiltrated stormwater
  - Presence of unknown loads during high flow periods

Candidate Studies: Groundwater PCB Load at Mirabeau

- Additional biofilm monitoring with higher spatial resolution
  - Would better define extent of impact, but not magnitude of load
- Additional water column sampling at Mirabeau
  - Grab samples or SPMD
- Others?

Candidate Studies: Dry Weather Source Downstream of USGS Gage

- Synoptic survey covering USGS gage to Nine Mile
  - Designed to supplement single 2018 mass balance assessment
  - Currently budgeted in 2021-2023 work plan
  - Perhaps not as urgent given results of PMF study
- Others?

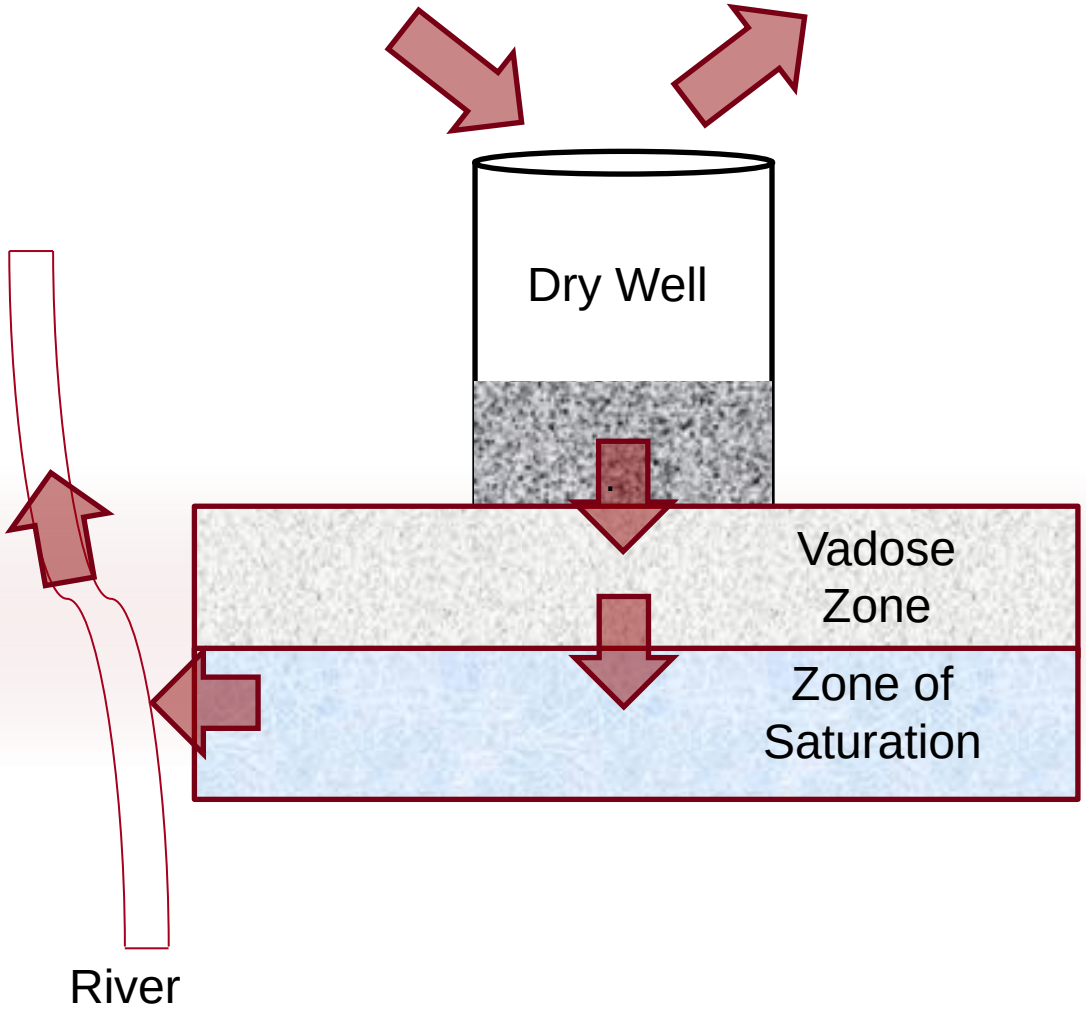


Candidate Studies: Groundwater/Other Interactions between Plante's Ferry and USGS Gage

- Further our understanding of groundwater hydrology
- Synoptic survey with greater spatial resolution
  - Combine with synoptic survey downstream of USGS gage
- Others?

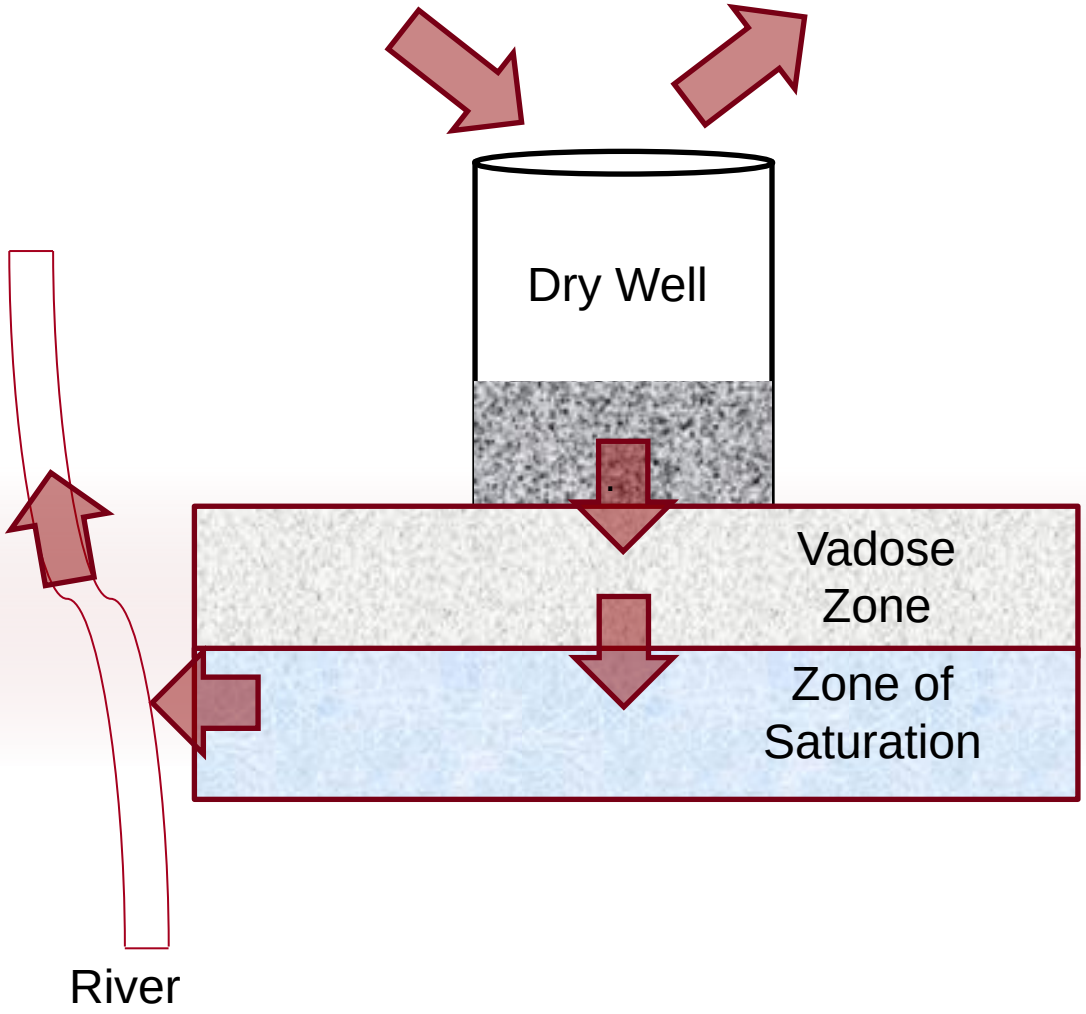
Candidate Studies: Groundwater Loading of Infiltrated Stormwater

- Key Unknowns
  - Do soils in the vadose zone effectively trap PCBs?
  - Where does the infiltrate from dry wells enter the river?
  - What is the timing of delivery?



Potential Things That Could Be Studied

- Net PCB loading to dry wells
  - Mass in minus mass out
- Tracer study
- Sample groundwater
- Review how long it takes dry wells to drain
  - Provides some information on timing of load
- Review capacity of soils in the vadose zone to trap PCBs (i.e., organic carbon content)
  - Monitor PCBs in soil profile to determine whether they are PCB-saturated



Candidate Studies: High-Flow Mobilization of PCB Sources

- Conduct mass balance similar as what was done for low flow
  - Preliminarily scoped at TTWG level
  - Trent to Greene Street reach with an upstream reference station at Barker
  - Not included in 2021-2023 work plan

- Others?