DEPARTMENT OF ECOLOGY
State of Washington

Quality Assurance Project Plan

Monitoring of Tire Contaminants in Coho Salmon Watersheds

November 2023

Publication 23-03-113

Publication Information

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Project Plan (QAPP). The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

This QAPP was approved to begin work in July 2023. It was finalized and approved for publication in November 2023, and it will be valid until November 2028.

The final QAPP is available on Ecology's website at https://apps.ecology.wa.gov/publications/SummaryPages/2303113.html.

Suggested Citation
Smith, R. 2023. Quality Assurance Project Plan: Monitoring of Tire Contaminants in Coho Salmon Watersheds. Publication 23-03-113. Washington State Department of Ecology, Olympia. https://apps.ecology.wa.gov/publications/SummaryPages/2303113.html.

Data for this project are available in Ecology's EIM Database. Search Study ID: RHSM0001.

The Activity Tracker Code for this study is 24-005.

Federal Clean Water Act 1996 303(d) Listings Addressed in this Study. See Section 3.3.

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Quality Assurance Project Plan

Monitoring of Tire Contaminants in Coho Salmon Watersheds

by Rhea Smith

August 2023

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TSU: Toxics Studies Unit
WOS: Western Operations Section

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2.0 Abstract

The goal of this study is to evaluate the most appropriate and effective methods for measuring rubber-derived contaminants in water, sediment, and biota and their effects on aquatic life. Research is needed to understand the occurrence and persistence of 6PPD-quinone (6PPD-q) in salmon-bearing streams to help develop urban watershed solutions to protect salmon habitat. Direct and indirect methods are proposed to measure 6PPD-q and its effects on salmon-bearing streams. Direct methods include measuring 6PPD-q in water, sediments, sorbent media, and bioassays. Indirect methods use bioassessments to measure stream health. This project will guide future 6PPD-q studies and coordinate our research with natural resource management partners.

Methods will be chosen to 1) effectively identify road runoff exposure hot spots as vulnerable habitats[1] and 2) collect baseline data before habitat enhancement projects. Projects include actions to improve chemical and physical stream conditions, such as stormwater retrofits, fish barrier removals, floodplain projects, sustainable urban and transportation planning, and riparian conservation.

Over the past decade, innovative technologies have made storm event sampling more feasible and standardized. Standardized assessments of rubber-derived contaminants will allow data integration at multiple scales of natural resource management. Large spatial scale studies will provide information on the occurrence of 6PPD-q, while more focused monitored stream studies will concentrate on 6PPD-q persistence.

Three main approaches are proposed to support the goals of this project:

- **Spatial studies** to correlate 6PPD-q occurrence with watershed characteristics over a broad spatial scale.
- **Toxics in salmon watersheds bioassay studies** to evaluate methods for measuring salmon habitat health and toxics tolerance ranges.
- **Directed studies** to address the many data gaps in how and where to measure 6PPD-q.

[1] Vulnerable species and their habitats refer to those that are negatively impacted by the contaminant and are more likely exposed to polluted runoff.

3.0 Background

3.1 Introduction and problem statement

The discovery that 6PPD and the transformation product 6PPD-q are responsible for coho salmon (*Oncorhynchus kisutch*) mass mortality events (Kendra 1988; Kendra and Wilms 1990; Ostergaard 1992; Scholz 2011; Du et al. 2017; Tian et al. 2021) compelled federal, state, tribal, and many other interested groups to act. Technical, community, and policy working groups were formed to discuss and share updates on the scope and scale of the tire pollutant problem and identify solutions. Additional research has found that native adult and juvenile coho salmon, steelhead/ rainbow trout[1], and non-native brook trout are acutely sensitive to 6PPD-q (McIntyre et al. 2018; Brinkmann et al. 2022; French et al. 2022; Table 1).

Table 1. 6PPD-q species-specific toxicity variability.

Pacific Northwest Fish Species	Life History	Acute Sensitivity Exposure Time (h)	Acute Sensitivity *in vivo* LC50 (µg/L)	Metabolic Sensitivity *in vitro* (24-h) EC50 (µg/L)
Coho salmon *(Oncorhynchus kisutch)*	Anadromous	24	Juvenile: 0.095[1]; 0.08[2] Fry: 0.04[3]	7.9[2]
Rainbow trout[4] *(Oncorhynchus mykiss)*	Freshwater	72	Juvenile: 1.0[5]	68[2]
Brook trout[6] *(Salvelinus fontinalis)*	Freshwater	24	Juvenile: 0.6[5]	—
Brown trout[7] *(Salmo trutto)*	Freshwater	48	Alevin: No mortality at 12[8]	—
Chinook salmon *(Oncorhynchus tshawytscha)*	Anadromous	24	Juvenile: > 25[2] Fry: > 68[3]	No response at 100[2]
Sockeye salmon *(Oncorhynchus nerka)*	Anadromous	—	—	No response at 100[2]

Note. Coho salmon are the most sensitive, as shown by the LC50[9] (Lethal Concentration 50%). All exposures in the table were in freshwater phase juveniles; no saltwater exposures have been published.

[1] Tian et al. 2022

[2] Greer et al. 2023

[3] Lo et al. 2023

[4] Steelhead trout are the anadromous life stage of rainbow trout; the LC^{50} is assumed to be the same, but verification is needed.

[5] Brinkmann et al. 2022

[6] Brook trout are non-native in the Pacific Northwest

[7] Brown trout are non-native in the Pacific Northwest

[8] Foldvik et al. 2022

[9] The LC_{50} is the median lethal concentration determined from acute toxicity testing — the concentration at which 50% of test organisms died across a dilution series (EPA 1995: Pub 9345.0-05I).

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[1] Steelhead is the same species as rainbow trout, but with different life histories. More toxicology research is needed to confirm similar sensitivity among life histories.

3.1.1 Multi-Scalar Science and Management Coordination

The anti-degradant used to enhance tire safety and durability, 6PPD (parent compound) and 6PPD-q (transformation product), can potentially cause coho mortality anywhere there is untreated road runoff discharging into salmon-bearing streams (Figure 1). The frequency and intensity of rainfall in the Pacific Northwest and the number of vehicles and roads crossing salmon-bearing streams pose a difficult challenge for addressing 6PPD contamination of aquatic ecosystems.

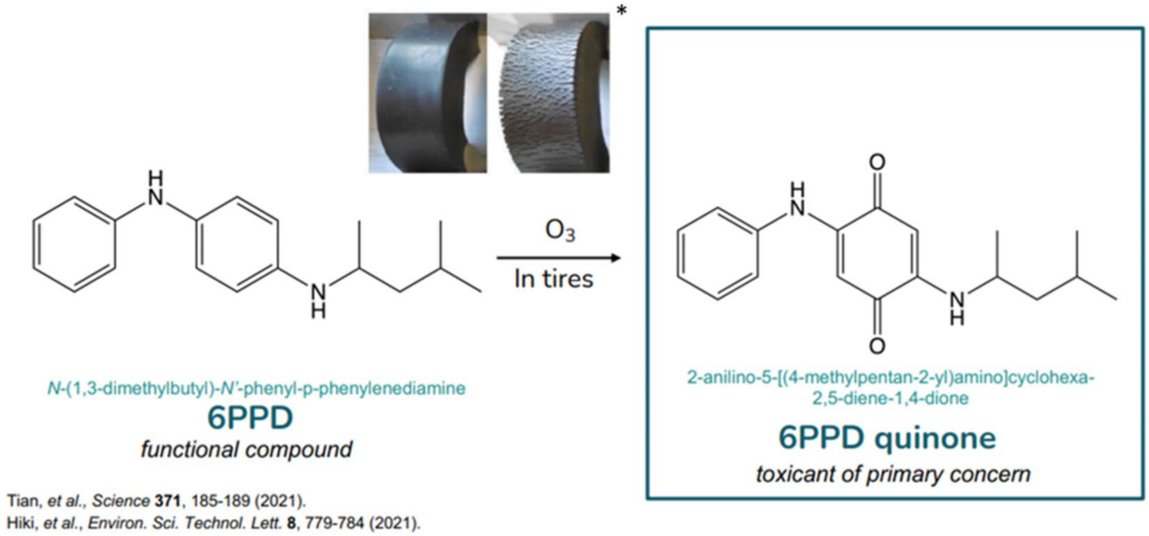

Figure 1. Tire anti-degradant 6PPD reacts with ozone and transforms into 6PPD-q.
6PPD-q is acutely toxic to coho salmon and rainbow, steelhead, and brook trout (Tian et al. 2021; Hiki et al. 2021; Brinkmann et al. 2022; French et al. 2023).
*Rubber with 6PPD (left) and rubber without 6PPD (right) courtesy of US Tire Manufacturers Association.

Reducing toxics in urban watersheds requires a multi-scalar prioritization approach to support effective conservation and restoration planning and actions (Feist et al. 2017; Levin et al. 2020; Ettinger et al. 2021). Open, transparent collaboration is needed between scientists and managers at all levels of community and government to address this widespread and harmful new contaminant. Isolated local monitoring and planning can result in fragmented assessments due to jurisdictional barriers within each salmon recovery watershed. Standardizing polluted road runoff monitoring will allow information to be integrated at multiple scales and inform state and federal management (Bugnot et al. 2019).

We are beginning to understand the effects of this lethal contaminant on aquatic ecosystems. This project will focus on measuring 6PPD-q in salmon habitats at multiple scales. Smaller, short-term directed studies will be designed to understand some of the many data gaps regarding 6PPD-q environmental behavior.

3.1.2 Tire Contaminants, Pacific Salmon, and Climate Change

The timing of major salmon migrations and polluted runoff into streams is somewhat synchronized. Juvenile salmon leave their natal streams during freshets, large and sustained rain, or snow-melt events, often associated with riparian flooding (Downen and Mueller 1999).

Similarly, adult salmon return to natal streams during high tides and freshets when spawning areas are most accessible. These same intense rain events wash tire wear particles and additives into streams if stormwater is undertreated or uncontrolled. Smaller watersheds where flooding is driven by surface water from rain rather than snowmelt are thought to be more susceptible to polluted runoff.

Aging urban stormwater systems were originally designed to control flooding, not pollution. Stormwater is delivered to natural receiving waters through a network of ditches and pipes that follow our roads. Natural filtration processes are reduced or absent in urban areas and no longer protect streams and aquatic life from polluted road runoff (McCarthy et al. 2008; Dhakal et al. 2016; Levin 2020). Outdated stormwater systems and overflows are overwhelmed by large storm events, leading to the direct transport of pollutants to vulnerable aquatic ecosystems. Stormwater retrofit planners are looking for opportunities to restore natural filtration processes using green infrastructure and low-impact development (LID) applications and prepare for more intense climate change-driven storms (Dhakal et al. 2017).

Watersheds with greater impervious surfaces, such as compacted dirt, paved roads, and parking lots, are more susceptible to flooding and transporting aggregated pollutants to salmon habitat. Episodic storm events and flooding that overwhelm current infrastructure cause the greatest risk to salmon from road runoff (Figure 2). Climate change is predicted to increase the frequency and occurrence of large storm events. In addition to large storm events, smaller rain events are likely to transport road pollutants continuously (Peter et al. 2020). However, the occurrence, persistence, and transport of 6PPD-q to salmon-bearing streams remains poorly understood.

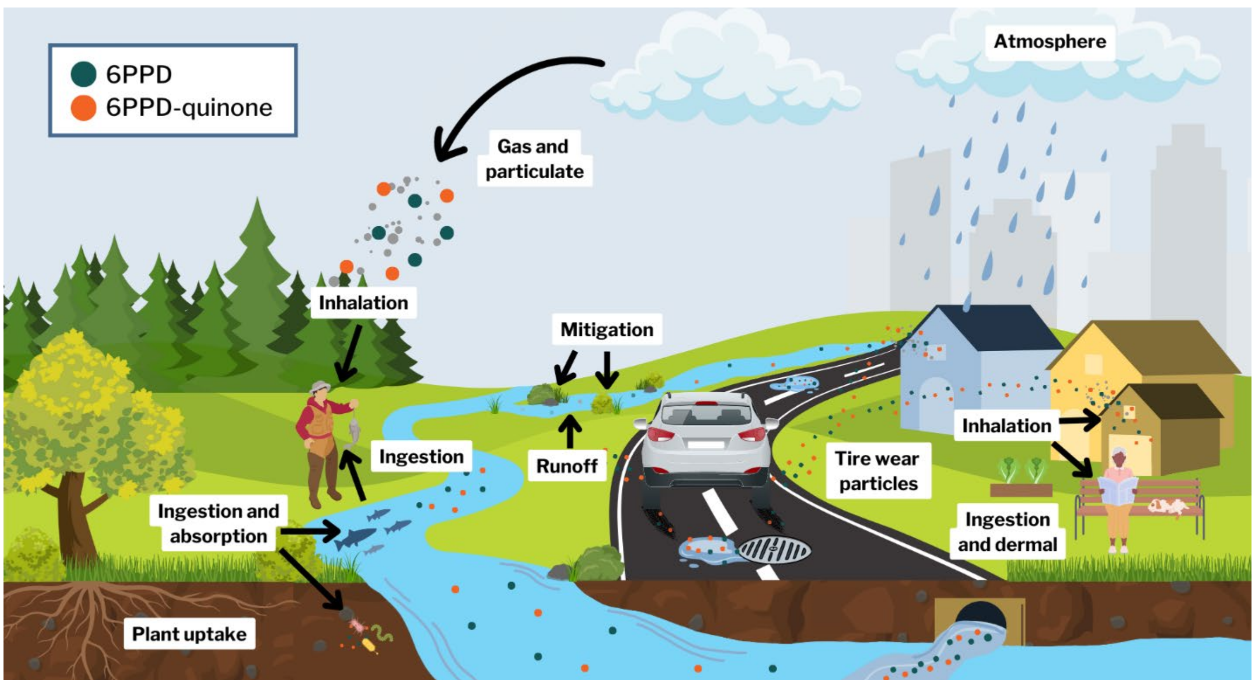

Figure 2. Graphical abstract of tire contaminants in the environment.
Data gaps exist for the occurrence, persistence and transport of 6PPD and 6PPD-q depicted in this graphic. The risk of pre-spawn and juvenile coho mortality is heightened by the convergence of storm-washed road pollutants and salmon migrating during freshets that tend to occur from October to June in Washington State[1].

[1] cliparts.com

The frequency and intensity of storms in the Pacific Northwest are predicted to increase over the next 100 years. Identifying where flooding and king tides overwhelm transportation and stormwater infrastructure will help proactively protect salmon-bearing streams. Measuring and mapping areas where surface runoff overflows and transports toxics to streams will help prioritize sites for mitigation efforts (Figures 3 and 4).

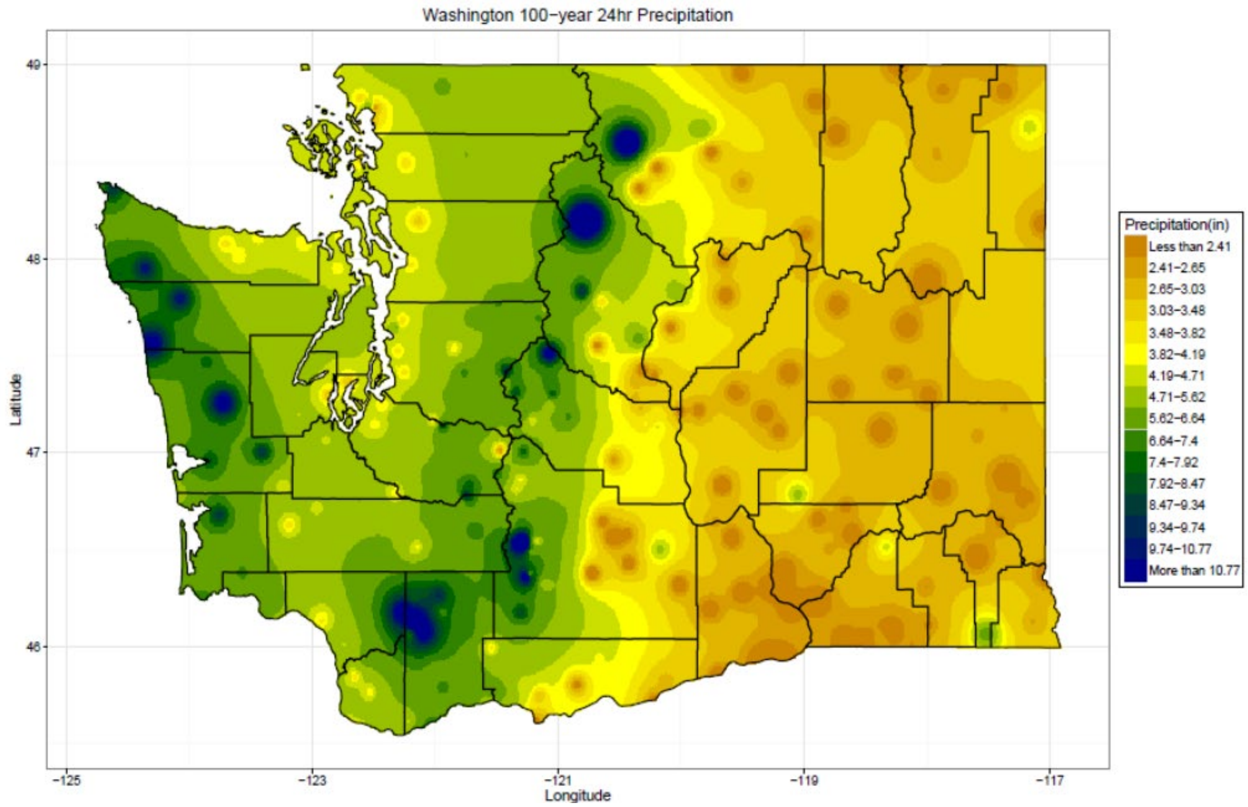

Figure 3. Extreme predicted precipitation for a 24-hour storm with a 100-year return period for the State of Washington.

Greater runoff leads to more non-point pollution loading to streams from roads and parking lots.

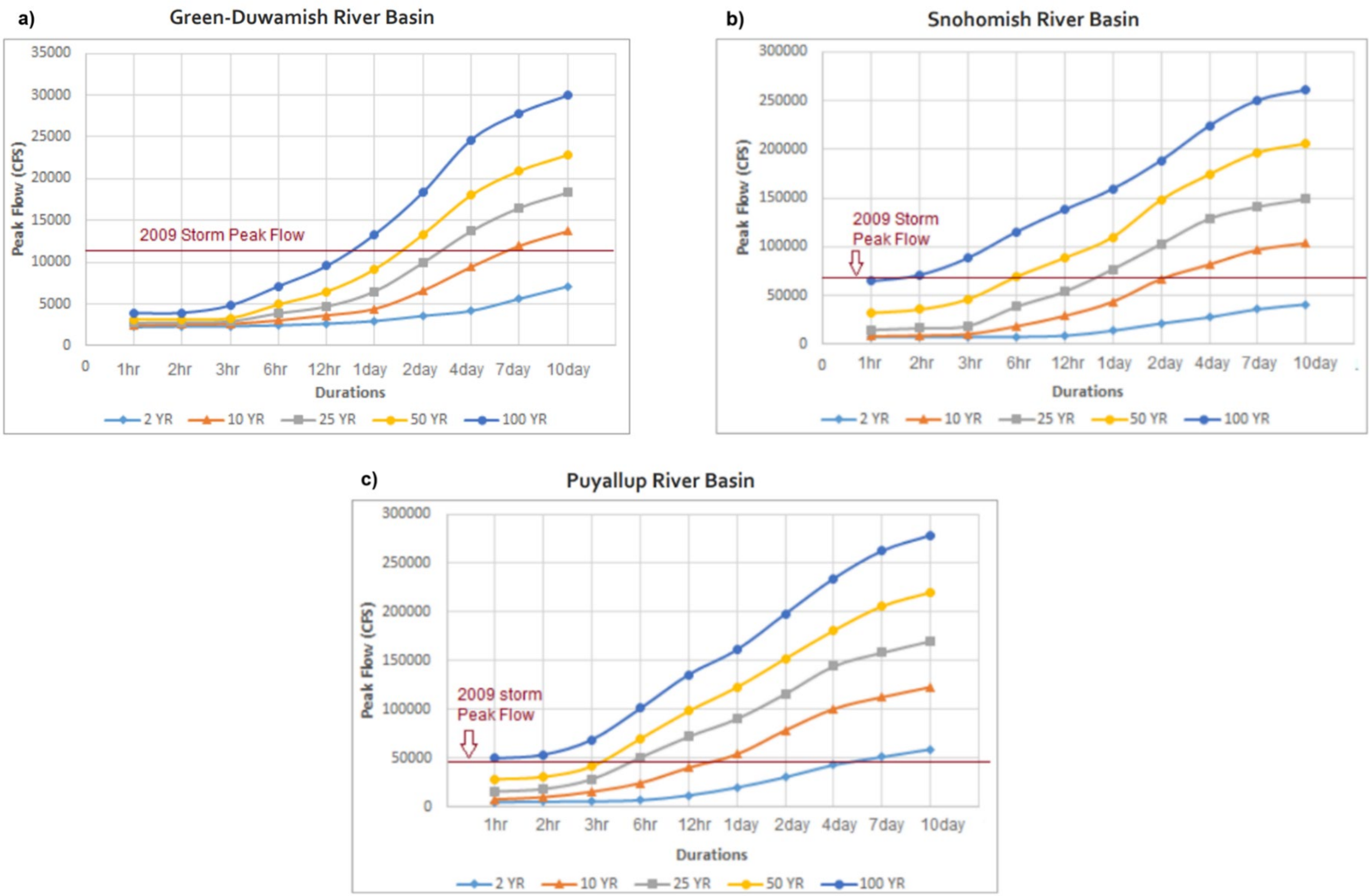

Figure 4. IDF curves for the a) Green, b) Puyallup, and c) Snohomish Rivers .

Intensity-Duration-Frequency (IDF) curves describe the relationship between rainfall intensity, duration, and return period (Yonus and Mortuza 2016). Climate change is predicted to intensify storm event frequency, duration, and corresponding runoff and flooding over the next few decades.

In addition to more intense and frequent storms, impervious surfaces in Washington State urban areas continue to expand. More impervious surface and decreased natural infiltration leads to more flooding and transport of pollutants to salmon-bearing streams (Figure 5).

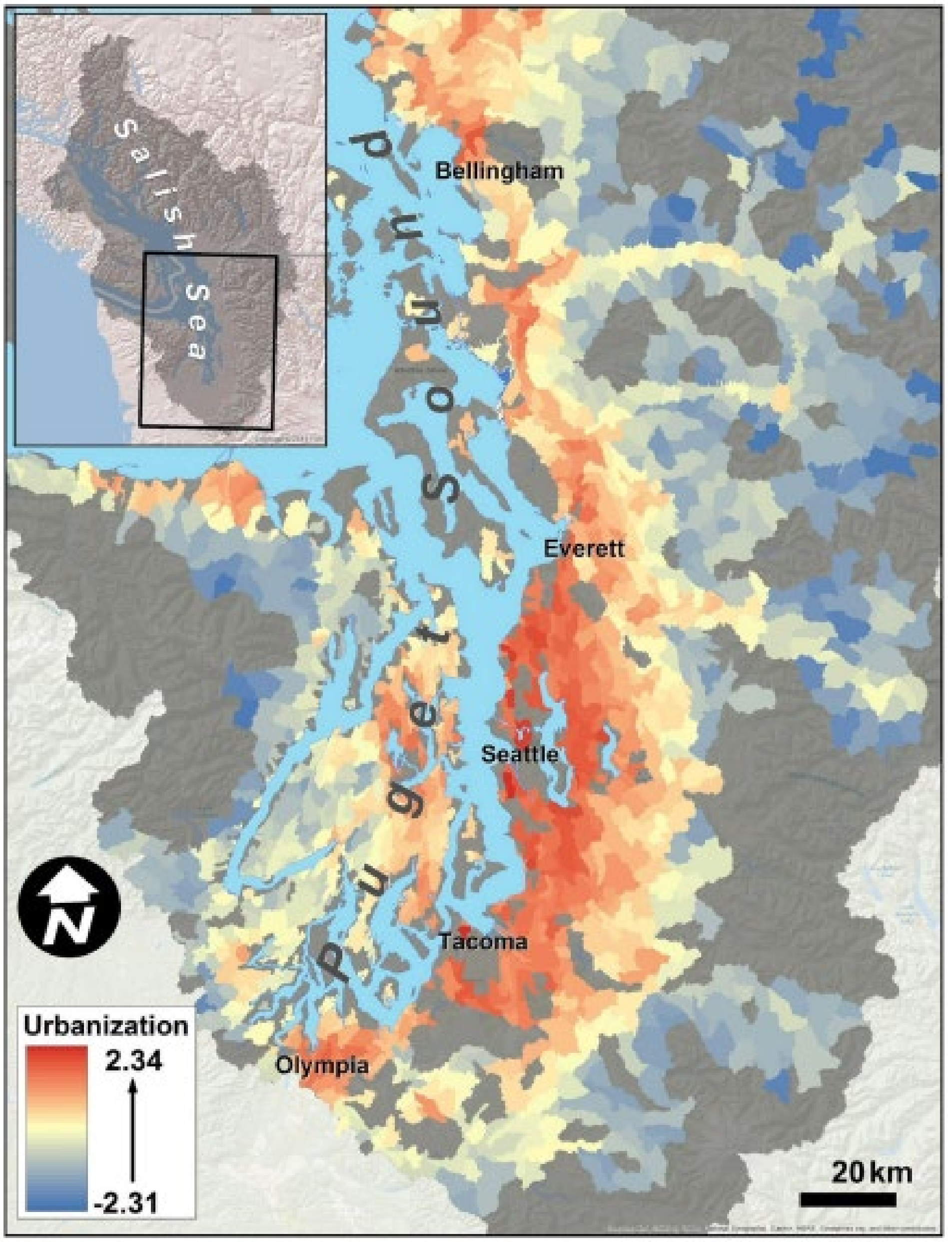

Figure 5. Trends in urbanization that threaten salmon-bearing streams.
Urbanization increases pollutants in streams, including 6PPD-q (Ettinger et al. 2021). The gradients of urbanization represent the combined impacts of 19 land cover and land use attributes on coho pre-spawn mortality risk, estimated using a Bayesian structural equation model (Feist et al. 2017; Ettinger et al. 2021).

3.1.3 Salmon Mortality and 6PPD-q Observations

The extent of the decline in the wild coho salmon population makes direct observations of salmon mortality challenging due to their lower abundance overall (Spromberg and Scholz 2011). The amount of coho salmon caught commercially has decreased over time (Figure 6), making it challenging to find symptomatic and pre-spawn mortality coho salmon. Therefore, pre-spawn and juvenile coho mortality correlations with 6PPD-q may not truly reflect the full extent of the spatial and temporal occurrence and persistence of 6PPD-q exposure and its effects on Pacific salmon.

Toxics from urbanization is only one of many stressors impacting salmon populations at sea and within our watersheds. Climate change, overfishing, predation, disease, parasites, changes to ocean conditions and ecosystems, physical habitat degradation, and physical water quality (DO, temperature, conductivity, and pH) are some additional challenges for salmon recovery.

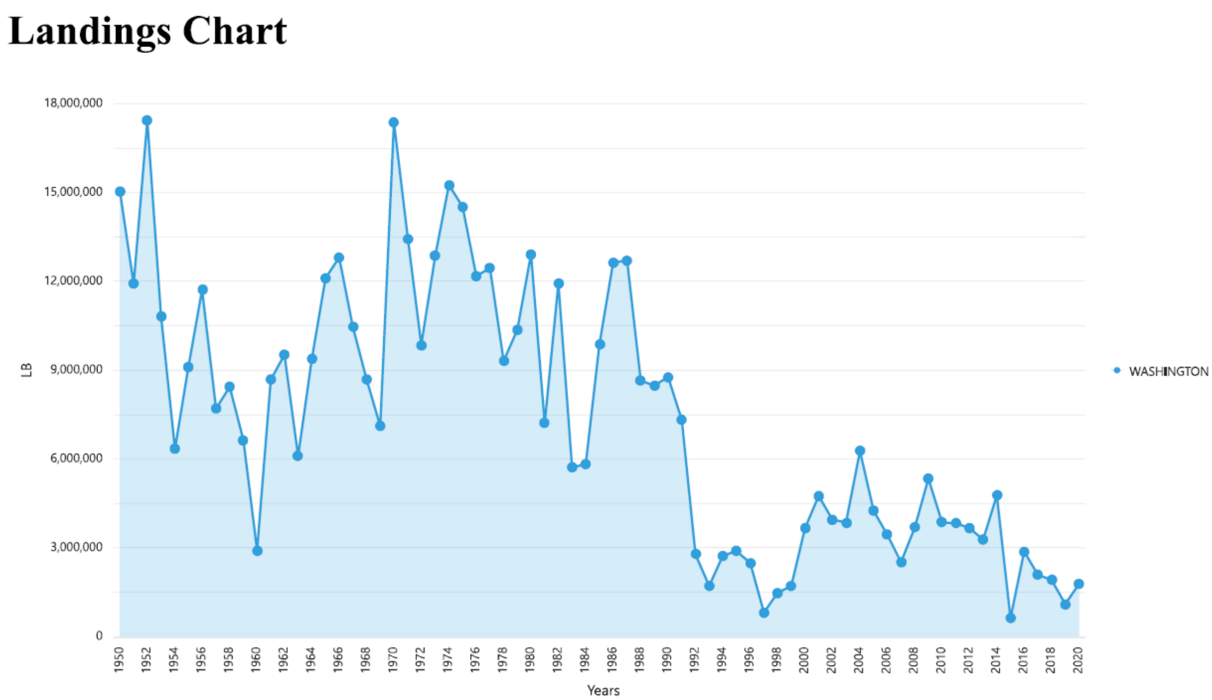

Figure 6. Coho salmon landings in Washington state.
Commercial fishing landings of coho salmon (number of fish caught) have decreased over time (API NOAA).

Most contaminants of emerging concern and many legacy pollutants are difficult to measure reliably. Specially trained technical field and lab staff are often required. The tire contaminant 6PPD and its transformation product 6PPD-q are fleeting and difficult to observe at their maximum concentration (Appendix B, Table B-1), adding to assessment challenges. Preliminary studies suggest that tire contaminants are more easily detected during or following rain events and are rarely detected during dry periods (Johannessen et al. 2021a & 2021b; Nedrich 2022; Tian et al. 2022). In summary, both coho mortality events and 6PPD-q are difficult to detect simultaneously in streams due to salmon population declines and the fleeting nature of storm-transported organic contaminants.

3.1.4 Rubber-derived Contaminants in Salmon Watersheds

Rubber consumer products regularly release contaminants directly to the environment. A tire releases an estimated 16% of its weight over its lifetime, resulting in a major source of microplastics that are found in air, water, land, and organisms (Kole et al. 2017; Sieber et al. 2020; Baensch-Baltruschat et al. 2020; Leads & Weinstein 2019; Werbowski et al. 2021; Wik & Dave 2009). Tire particles are estimated to exceed the emissions of other pollutants, including pharmaceuticals and pesticides (Wagner et al. 2018). A recent study conducted in San Francisco Bay estimated that 85% of plastic particles were tire-derived microplastics from untreated stormwater runoff (Moran et al. 2021). This project will consider method development studies to investigate the transport and fate of rubber-derived contaminants and micro-rubber particles to air, water, biota, and sediments.

In addition to tire wear, motor vehicles are a source of other contaminants deposited to roadways and parking lots Cu from brake wear (Wesley and Whiley 2013), and Cu and Zn from road surface wear (Kennedy et al. 2002) and leaking petroleum products (Gobel et al. 2007). Extensive research has been conducted on Cu and Zn contamination from roadways and parking lots, while there is little research on trace organic contaminants, such as 6PPD and 6PPD-q. Metals will be collected during the toxics in salmon watersheds bioassay studies to explore the correlation between rubber-derived (data-poor) contaminants and legacy (data-rich) pollutants. Past efforts have attempted to use Zn as a tracer for stormwater, but natural background levels made it difficult. There are no known natural sources of 6PPD or 6PPD-q.

3.1.5 Rubber-derived Contaminant Environmental Assessment Strategies

Three monitoring strategies are proposed to address some of the tire contaminant data gaps and provide the necessary information to support informed decision-making. These strategies include spatial studies, toxics in salmon watersheds bioassay studies, and directed studies (Figure 7).

The overall goal of this initial 6PPD-q monitoring project is to address three main data gaps:

- **Spatial studies** — Occurrence of 6PPD-q in salmon-bearing streams (spatial exposure risk).
- **Toxics in salmon watersheds bioassay studies** — Persistence and timing of 6PPD-q (temporal exposure risk).
- **Directed studies** — Methods to further characterize and measure rubber-derived contaminants (method development and ecosystem impacts).

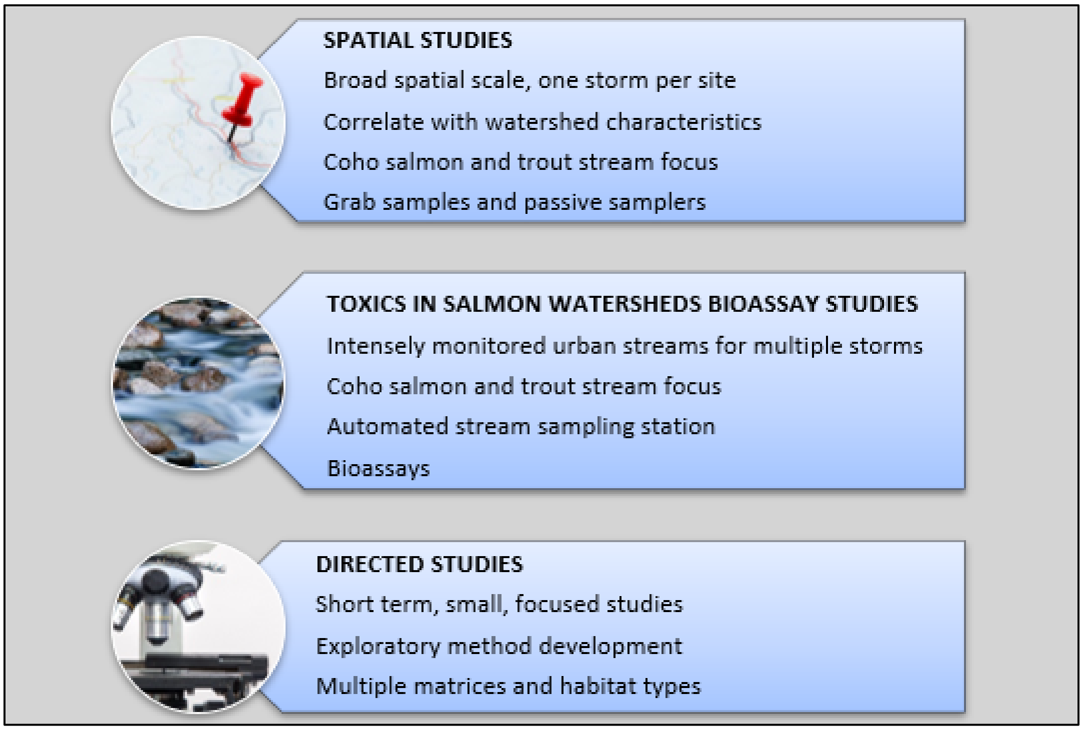

Figure 7. The three-pronged approach to measuring and understanding 6PPD-q in the environment.

Initial 6PPD-q investigations have further confirmed the fleeting nature of 6PPD-q in streams and that the rate of transport and exposure increases with the percentage of impervious surface within a watershed (Appendix B). The contaminant can persist for days in urban areas during or following storm events. More 6PPD-q measurements are needed across land use, watershed, and traffic gradients to correlate loading, transport, and concentrations found in receiving waters. Each project research strategy has multiple geographic scales (Figure 8).

Multi-Scale Environmental Assessment Approach:

1. **Spatial studies (broad-scale)** — To understand the occurrence of 6PPD-q, areas across the following gradients will be measured:

    - High and low urbanization
    - High and low traffic counts
    - High and low precipitation
    - Habitat type

Priority areas include Puget Sound, Lower Columbia (Vancouver), Mid-Columbia, Upper Columbia, Lower Snake River, and along Highway 101, which encircles the Olympic Peninsula and crosses several important fish-bearing streams and rivers. Areas that meet the site selection criteria, such as near urban areas, vulnerable areas near roadways, and areas designated as essential fish habitat for coho salmon, and steelhead/rainbow trout, will be chosen. See Appendix C, Table C-1, for an initial list of stream catchments of interest for opportunistic spatial sampling.

2. **Toxics in salmon watersheds bioassay studies (mid-scale)** — The proof-of-concept study (testing of bioassay methods) will be conducted in the South Sound Area. Storm-transported contaminants are difficult to measure reliably and consistently. Alternative bioassay methods will be evaluated to understand where 6PPD-q affects salmon and trout.
3. **Directed studies (fine-scale)** — A combination of outdoor and indoor analytical experiments to continue method development and understand the persistence and loading of 6PPD-q.

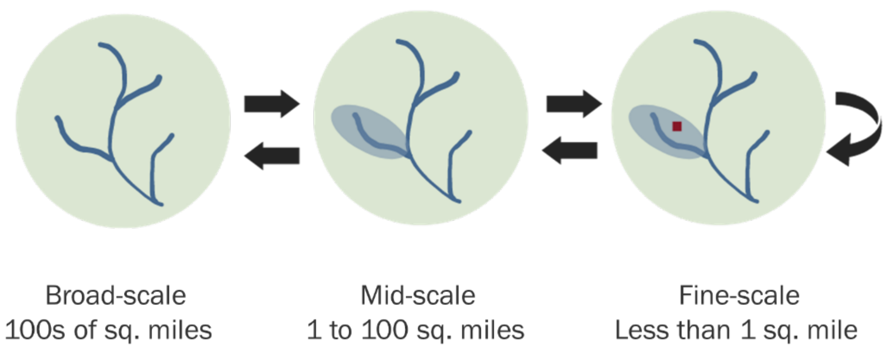

Figure 8. Assessment strategies for this project.
Designed to address multiple scales of exposure risk to road runoff and its effects on salmon. Provides standard methods to support local and regional scale data visualizations and integrations.

3.2 Study area and surroundings

The study area is salmon habitat surrounded by human occupation. Tire contaminants are present anywhere there is a combination of motor vehicles and pavement, such as parking lots, local roads, driveways, bridges, and highways. A 6PPD Spatial Technical Advisory Committee (STAC) was formed in the Spring of 2022 to support the development of the 6PPD in Road Runoff: Assessment and Mitigation Strategies Report[1] (Ecology 2022a). GIS was quickly identified as an effective coordination platform and an initial assessment tool to visualize the potential scope and scale of the problem.

A preliminary mapping effort was conducted where exposure pathways (traffic), vulnerable ecosystems (coho, rainbow, steelhead, and brook trout habitat), land cover, and land use were overlayed to identify suspected 6PPD-q hot spots (Figure 9). The amount and duration of traffic and precipitation needed to produce enough road runoff to transport toxic amounts of 6PPD-q to salmon-bearing streams is currently unknown.

[1]https://app.leg.wa.gov/ReportsToTheLegislature/Home/GetPDF?fileName=ECY%206PPD%20in%20Road%20Runoff%20Report_32dc8c92-b98a-4023-97f2-d6d2ec19b390.pdf

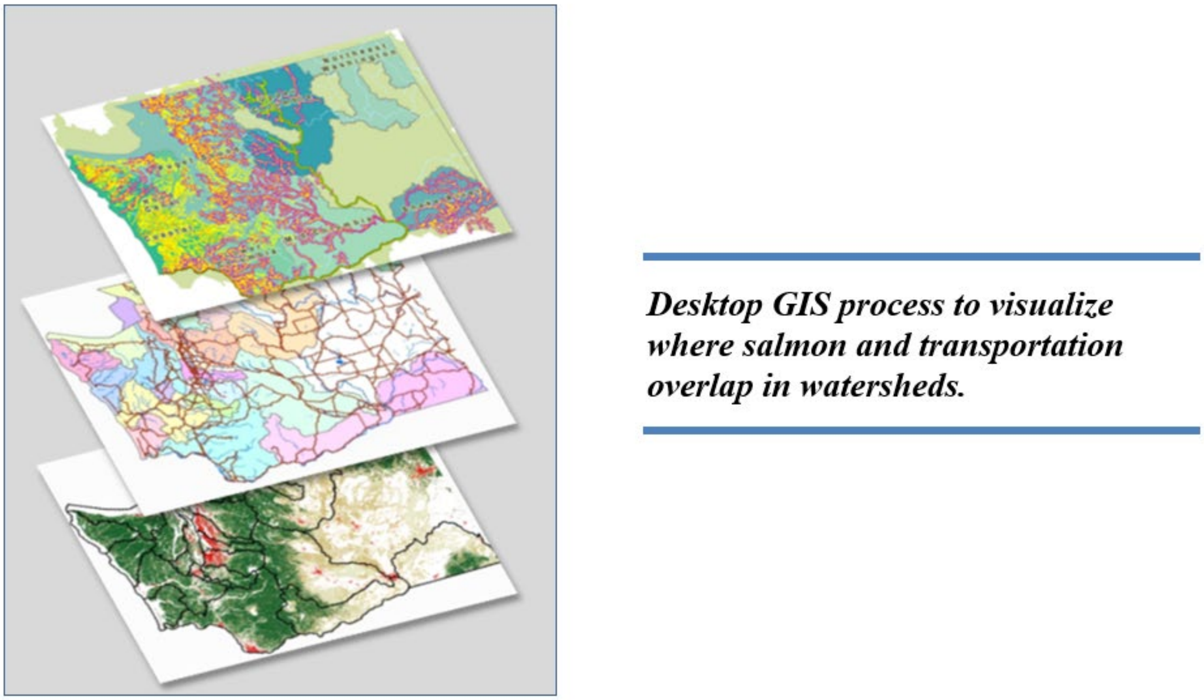

Figure 9. Conceptual GIS process to help focus 6PPD-q hot spot reconnaissance efforts. The top layer is salmon and trout distributions, the second layer is traffic and roads, and the third layer is watershed characteristics, including land cover, land use, and water quantity.

3.2.1 History of study area

Coho salmon have been adversely affected by the "urban stream syndrome," the aquatic habitat degradation of streams affected by urbanization. Road runoff transports toxic-coated sediments and polluted waters to natural lowland streams with low flushing rates. As a result, salmon are harmed by a combination of physical and chemical impairments (Walsh et al. 2005).

Bioassessments can be a powerful measurement for overall stream health. However, it is difficult to indicate a single stressor responsible for the absence of sensitive species (Larson et al. 2019). Coho salmon are harmed by urbanization more than other salmonids because they prefer the middle reaches of small, low-energy streams. Other salmon species prefer the faster waters of the upper reaches of a watershed (Table 2).

Decades of research have established motor vehicles as a major contributor to the urban runoff problem. The number of drivers, vehicles, and associated chemicals has also grown. Today, stormwater comprises an "urban chemical cocktail" of thousands of chemicals with the potential for transformation products and toxicity effects on aquatic life (Du et al. 2017; Peter et al. 2018; Peter et al. 2022). Historically, stormwater is monitored and managed one contaminant at a time. Meanwhile, the number of toxic substances in consumer products has increased over time, and the range of chemical diversity across urban gradients requires a new adaptive management approach. Understanding where untreated stormwater is affecting salmon-bearing streams will help focus solutions.

Despite progressive stormwater management for new development, there remains an aging infrastructure that provides little to no treatment or control of toxic substances (Ecology and

King County 2011). The tire wear particles and the contaminant 6PPD-q may provide an opportunity to screen for surface water hot spots until a safer tire anti-degradant alternative is found. Toxic hot spot mapping is another GIS layer for practitioners to consider when deciding where to focus site-specific assessments. Toxic hot spot mapping is also helpful in determining the most appropriate green or grey infrastructure type, performance requirements, sizing, cost, and feasibility. For instance, green infrastructure costs vary widely depending on land value, space limitations, existing utilities, and watershed characteristics such as slope and soil. Therefore, solutions and costs will vary from one watershed to another.

6PPD-q has been identified as a critical parameter to manage. Care needs to be taken when selecting projects that will meet the goals of providing fishable and swimmable waters. Salmon and human habitat benefits need to be weighed against project types. We need to understand the occurrence and persistence of contaminants from road runoff to compare the costs and benefits of proposed projects.

Table 2. List of Pacific salmonids habitat preferences and a qualitative assessment of water quality vulnerability to urbanization impacts.

Species	Distribution	Relative Sensitivity to WQ impacts	ESA[1] Listed
Coho salmon (Silver) *Oncorhynchus kisutch*	Middle reaches of small streams	High	Lower Columbia
Steelhead (AD) and Rainbow Trout (FW) *Oncorhynchus mykiss*	Uppermost tributaries	High	Puget Sound Lower Columbia Middle Columbia Snake River
Sockeye (Red, Blueback, or Kokanee) *Oncorhynchus nerka*	Lakes	High	Ozette Lake
Chinook (King) *Oncorhynchus tshawytscha*	Mainstem and larger tributaries	Moderate	Upper Columbia Snake River Lower Columbia Puget Sound
Pink *Oncorhynchus gorbuscha*	Big rivers, lower reaches	Moderate	Lower Columbia Hood Canal
Chum (Dog) *Oncorhynchus keta*	Lower reaches of small streams	Moderate	Lower Columbia Hood Canal
Cutthroat *Oncorhynchus clarki*	Headwaters of small streams and estuaries	High	—
Brook Trout *Salvelinus fontinalis*	Upper Watersheds, mountains	Moderate	—
Bull Trout *Salvelinus confluentus*	All Recovery Regions	High	—

[1]ESA: Endangered Species Act at risk and threatened species lists. Report Card on Recovery: Reviews Assess 28 Salmon and Steelhead Species Returning to West Coast Rivers | NOAA Fisheries[1].

[1] https://www.fisheries.noaa.gov/west-coast/endangered-species-conservation/report-card-recovery-reviews-assess-28-salmon-and

Environmental Assessment Strategy 1

Spatial studies — Broad-scale sampling of salmon-bearing habitat across urbanization, transportation, and land use gradients. This is to conduct a “scan” of rubber-derived contaminants to understand the occurrence of 6PPD-q.

- Conduct opportunistic spatial sampling of the salmon watershed on a broad scale to correlate concentrations with watershed characteristics (Table 2).
- A web-based 6PPD-q hot spot map will help with site selection planning and tracking.
- Spatial sampling will be coordinated to evaluate exposure and mass loading indicators and to support modeling efforts and stormwater retrofit planning (Table 3).

Table 3. List of Ecology and WDFW toxic studies initiatives that may present sampling opportunities and the corresponding rationale.

Project/ Program	Rationale
Toxics in Juvenile Chinook TBioS (WDFW) and EAP: Toxic Studies Unit (TSU)	Chinook tend to reside in upper areas of watersheds; however, all salmon species use the same estuarine habitats, including steelhead and coho salmon, which are most sensitive to 6PPD-q. It would be valuable information to add 6PPD-q sampling during the wet season sampling of this program if a storm event has occurred within 72 hours of planned sampling. The TBIOS research program at WDFW has monitored toxics in juvenile Chinook for the past 10 years. TBIOS monitoring program can opportunistically collect samples to support 6PPD-q in tissue method development at MEL and NOAA and collaborate with Ecology's Toxic Studies Unit to couple marine and freshwater sampling efforts. WDFW and participating Tribes plan to opportunistically collect additional species at the fish traps to support further 6PPD-q method development and proof of concept studies. Toxics Studies Unit staff will be available for sampling assistance, sample transport, and analysis as needed.
Mussels TBioS (WDFW)	WDFW has conducted a toxics in mussels study as part of the TBioS program for almost 10 years. Mussels are an ideal indicator species, given their sessile nature and the amount of water they filter per day. WDFW and NOAA have recently conducted a pilot study that confirmed the uptake of 6PPD-q. Coordinating with WDFW helps support this valuable work and would provide data to explore this method further for road runoff impacted watershed comparisons.
PFAS Chemical Action Plan (CAP) Monitoring (HWTR/EAP/TSU)	Stormwater is suspected to be a major source of PFAS; as part of the PFAS CAP, the program lead is conducting stormwater sampling around the Lake Washington area across a land use gradient, providing an opportunity to add 6PPD-q to some of the smaller streams where coho tend to reside.
WSDA Pesticides monitoring	The Washington State Department of Agriculture (WSDA) has been conducting annual monitoring to evaluate pesticides in surface waters since 2003. This sampling may provide opportunities for surface runoff sampling in salmon-bearing streams between March and October. This monitoring effort helps refine exposure estimates and model assumptions routinely used in risk assessments.
PCB Monitoring	The PCB Monitoring program plans to install autosamplers to continuously measure PCBs in larger rivers and streams.
BEACH	The Beach program conducts coliform testing along shorelines associated with areas where people recreate. There might be opportunities to collect 6PPD-q samples and rubber-derived particle samples at these same stations.
Groundwater Monitoring	The fate and transport of 6PPD-q is not well understood. The physiochemical characteristics and the affinity for 6PPD-q to stick to particles rather than stay in dissolved form suggests minimal transport to groundwater. However, there may be interest and opportunities to verify this assumption by coordinating with EAP's groundwater monitoring program.

Project/ Program	Rationale
Freshwater fish contaminant monitoring	The acute lethal impacts on coho salmon have been observed mainly in urban streams and some more rural. There may be opportunities in future sampling events to collect tissue samples for 6PPD-q analysis in urban lakes to understand the full aquatic scope of the road runoff problem. Many lake docks have tires for bumpers, impervious surfaces that drain directly to lakes, and boat trailers backed into urban lakes.
PBT Monitoring	Tires contain many additional chemicals, including PAHs and Zinc. Coupling additional chemicals already being measured with 6PPD-q sampling may help identify road contaminant hot spots. Freshwater fish sampling in urban and rural lakes conducted across the state may provide sampling opportunities for 6PPD-q and compare across urban gradients.
Ambient Freshwater Monitoring	The Ambient Freshwater monitoring unit conducts water quality assessments all year round in rivers and streams that may provide sampling opportunities, but timing and capacity need to be evaluated.
PSEMP Marine Monitoring	Tire wear particles are a major contributor to the microplastics in our aquatic systems. Opportunistic benthic sediment sampling to collect and measure 6PPD-q and tire wear particles in marine sediments will provide useful information on the ecosystem impacts of tires.

Site Selection Criteria — Watersheds that host vulnerable species and a gradient of urbanized and transportation land uses will be evaluated. Many of these watersheds have been listed as Essential Fish Habitat for coho salmon (PSFC[1]; SSHIAP[2]). These watersheds were identified by salmon recovery work groups or desktop GIS evaluations (Appendix C). Spatial study sites will be measured during or following a storm event along an urbanized gradient. The toxics studies unit will continually work with the 6PPD Tribal liaison and planners to identify areas of concern.

Ideally, smaller tributaries (~10 – 20 ft. in width) within the selected watersheds will be prioritized for sampling. Washington State has 72 watersheds at the hydraulic unit code 8 scale (HUC8). Over half of our watersheds support coho salmon, chinook, and steelhead/rainbow trout and are potentially exposed to road runoff. A tire monitoring ArcGIS StoryMap has been produced to help visualize the potential extent of the exposed vulnerable areas. A spatial studies map is under development and will be used to help track potential sources, given the assumed common occurrence of 6PPD and 6PPD-q.

[1] https://www.fisheries.noaa.gov/national/habitat-conservation/essential-fish-habitat
[2] https://nwifc.org/about-us/habitat/sshiap/

Table 4. a) Potential source location sampling type examples and b) proposed indicators of mass loading and exposure to tire contaminants.

a) Source Location Type
Road runoff discharge to surface waters
Turf and crumb rubber field runoff
Playground surface runoff
Parking lot surface runoff
Bridge outfall runoff
Industrial and commercial surface runoff
Community runoff
Groundwater
Air particulates
Tire collection and disposal sites

b) List of Potential Indicators
Traffic gradients (low, medium, and high traffic counts)
Urbanization (low, medium, and high impervious surface; percent cover)
Land use zoning (residential low, medium, high, industrial, commercial)
Salmon distribution (location and number of populations)
Number of outfalls
New and old development (pipe size, year built)
Water quantity characteristics (flashiness and volume)
Water quality characteristics (existing WQ conditions)
PAH, PFAS, Zinc, TSS, conductivity, and SSC
Tire wear particle size

PAH = Polycyclic aromatic hydrocarbons; PFAS = Per- and polyfluoroalkyl substances; TSS = Total suspended solids; SSC = Suspended solids concentration.

Environmental Assessment Strategy 2

Toxics in salmon watersheds bioassay studies — Small streams will be selected for more intensive monitoring. Initial criteria include:

- The presence of an urban gradient within the stream watershed where the upstream reaches can function as a reference site.
- Ideally supports a vulnerable resident trout or coho salmon or steelhead population.
- Has a mix of traffic gradients (local vs. highway).

Site Selection — Proposed study streams where 6PPD-q has been verified during the stream reconnaissance sampling in 2022 that meet the site selection criteria. Additional sites will be evaluated.

- Deschutes watershed — Indian Creek
- Kitsap watershed — Annapolis Creek

Environmental Assessment Strategy 3

Directed studies examples — Site selection will depend on study goals.

- **Saltwater gradient study** — This study will collect water for 6PPD-q analysis along a saltwater gradient transect line. This information will be used to evaluate analytical methods for a saltwater matrix to support future fate and transport studies. A vertical profile will be sampled at each station to understand the tire wear particle and 6PPD-q depth profile if detected.
- **Tire wear particle studies** — Sediments will be collected from verified 6PPD-q hot spots to measure the benthic flux of 6PPD-q before and after suspected source inputs, such as roads and parking lots. Sediment, road, and tire wear particles will be sent to a sub-contractor to support tire wear particle separation and characterization method development.
- **eDNA** — a small study to evaluate the use of eDNA to help verify the presence of vulnerable species may be conducted.
- **Shellfish and fish tissue method development** — coordinate with WDFW and regional fish and wildlife biologists to collect shellfish and fish tissue. This will support analytical method development and help evaluate field methods to best explore the presence, occurrence, and persistence of 6PPD-q in estuaries.
- **Bioassay method development** — develop methods to assess the exposure of 6PPD-q to sensitive species using an in-situ toxicity test.
- **Tire anti-degradant screening** — coordinate with the 6PPD alternative chemical toxicity testing to measure for related PPD contaminants of interest in the environment.
- **6PPD-q transport pathways** — support alternative transport studies beyond surface water, including air and groundwater, as needed.

3.2.2 Summary of previous studies and existing data

A review of 6PPD and 6PPD-q current knowledge and research was synthesized in a 6PPD road runoff legislative report (Ecology 2022a: Publication 22-03-020[1]). An assessment of alternatives to 6PPD is available in a technical memo to the legislature (Ecology 2021: 6PPD Technical Memo[2]). A product chemical profile for 6PPD and 6PPD-q was published in the priority product proposal process (DTSC 2022[3]). Several research programs have developed and continue to maintain general information on the contaminant (listed below).

- Puget Sound Institute[4]
- Washington Stormwater Center[5]
- San Francisco Estuary Institute & Aquatic Science Center[6]
- Washington State Department of Ecology[7]
- National Oceanic and Atmospheric Administration[8]
- Monitoring is essential to Puget Sound[9]

A summary of important take-aways and more recent updates for this project are listed below.

1 https://app.leg.wa.gov/ReportsToTheLegislature/Home/GetPDF?fileName=ECY%206PPD%20in%20Road%20Runoff%20Report_32dc8c92-b98a-4023-97f2-d6d2ec19b390.pdf
2 https://www.ezview.wa.gov/Portals/_1962/Documents/6ppd/6PPD%20Alternatives%20Technical%20Memo.pdf
3 https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf
4 https://www.pugetsoundinstitute.org/2021/08/discovery-of-tire-related-chemical-that-kills-coho-salmon-sparks-widespread-response/
5 https://www.wastormwatercenter.org/research/tiresandsalmon/
6 https://www.sfei.org/news/toxic-tire-contaminant-found-bay-area-stormwater#sthash.rkEZVO3x.dpbs
7 https://ecology.wa.gov/Waste-Toxics/Reducing-toxic-chemicals/Addressing-priority-toxic-chemicals/6PPD
8 https://www.fisheries.noaa.gov/feature-story/roadway-runoff-known-kill-coho-salmon-also-affects-steelhead-chinook-salmon
9 https://ecology.wa.gov/Blog/Posts/November-2018/Monitoring-is-essential-to-Puget-Sound

Current knowledge and assumptions regarding 6PPD and 6PPD-q:

1. Adult and juvenile coho salmon are acutely sensitive to low levels of 6PPD-q, resulting in mortality within hours (0.09 µg/L, Tian et al. 2022; 0.04 µg/L, Lo et al. 2023).
2. Once coho salmon are exposed to 6PPD-q in toxic amounts, they do not recover, making lethal and sublethal field assessments challenging (McIntyre et al. 2018; Chow et al. 2019).
3. 6PPD-q has variable pathways to streams and residence times (Seiwert et al. 2022), making direct coho mortality correlations challenging. One study in Toronto estimated a 4-hr. delay between maximum stream discharge and the peak in 6PPD-q concentration (Johannessen et al. 2022).
4. A small percentage of pre-spawn mortality events are natural, but the multi-year, high mortality rate observed in the Puget Sound area exceeds expected background mortality (Spromberg & Scholz 2011; Scholz et al. 2011; Feist et al. 2011, 2017, Spromberg et al. 2016).
5. Low amounts of traffic can lead to 6PPD-q mass loading or coho mortality along local roadways and public highways (Fiest et al. 2017; Tian et al. 2021, 2022; Peter et al. 2020). Understanding the mass loading of tire wear particles (TWP) and 6PPD-q will help predict areas of greater exposure risk to salmon-bearing streams (Tian et al. 2021, 2022).
6. 6PPD is also toxic, but the modeled and observed short half-life (minutes to hours) makes it difficult to detect analytically, and it is assumed to be less persistent in the environment compared to 6PPD-q, which is estimated to persist for days to weeks (Ecology 2022a; DSTC 2022).
7. Tires shed particles containing 6PPD to the environment that are transported to aquatic environments (Halle et al. 2020, 2021; Wagner et al. 2018, 2022; Kole et al. 2017) that may continue leaching 6PPD and 6PPD-q (Klöckner et al. 2021; Hu et al. 2023).
8. Coho salmon populations in the Pacific Northwest are depleted due to a variety of physical and chemical habitat disturbances during their freshwater life stage (e.g., agricultural, industry, development, and habitat degradation), during their marine life stage (e.g., climate change driven diet shifts and fishing), and from disease, parasites, and invasive species.
9. The majority of remaining coho salmon runs are a combination of hatchery stocked and wild populations. Watersheds that support wild coho salmon runs are a high priority for conservation and restoration actions to support self-sustaining populations and genetic diversity.
10. Surface water is considered a major delivery pathway of 6PPD and related chemicals; however, more research is needed to understand additional pathways (air and ground).
11. Removing 6PPD from tires is the most effective source control measure, but until then, 6PPD-q provides a surrogate for road runoff associated pollution and tire wear particles.
12. Discharging undertreated road runoff has the potential to be harmful to aquatic life.

Table 5 is an updated version of the physiochemical properties recently published.

Table 5. Properties of 6PPD-q.

Property	6PPD-q	Reference
Molecular Formula	$C_{18}H_{22}N_2O_2$	Tian et al. 2021, 2022
Molecular Name	2-((4-Methylpentan-2-yl)amino)-5-(phenylamino)cyclohexa-2,5-diene-1,4-dione	Hu et al. 2023
$\log K_{ow}$ [1]	4.3 ± 0.02	Hu et al. 2023
Sw[2]	38±10 ug/L; readily dissolves in water and is easily transported.	Hu et al. 2023
Bioaccumulation	Chemicals within the range of $\log K_{ow}$ = 3–7 are likely to be taken up by gill tissues, and chemicals with $\log K_{ow}$ values < 4.5 are less likely to bio-concentrate, although other mechanisms may need to be considered; more research is needed.	Hu et al. 2023
Sorption	High sorption losses are observed during sampling and lab analysis.	Hu et al. 2023
MOA	Unknown	Varshney et al. 2022

MOA = Mechanism of action.
[1] Octanol-water partitioning coefficient
[2] Water solubility is the maximum concentration of a chemical that dissolves in a given amount of pure water.

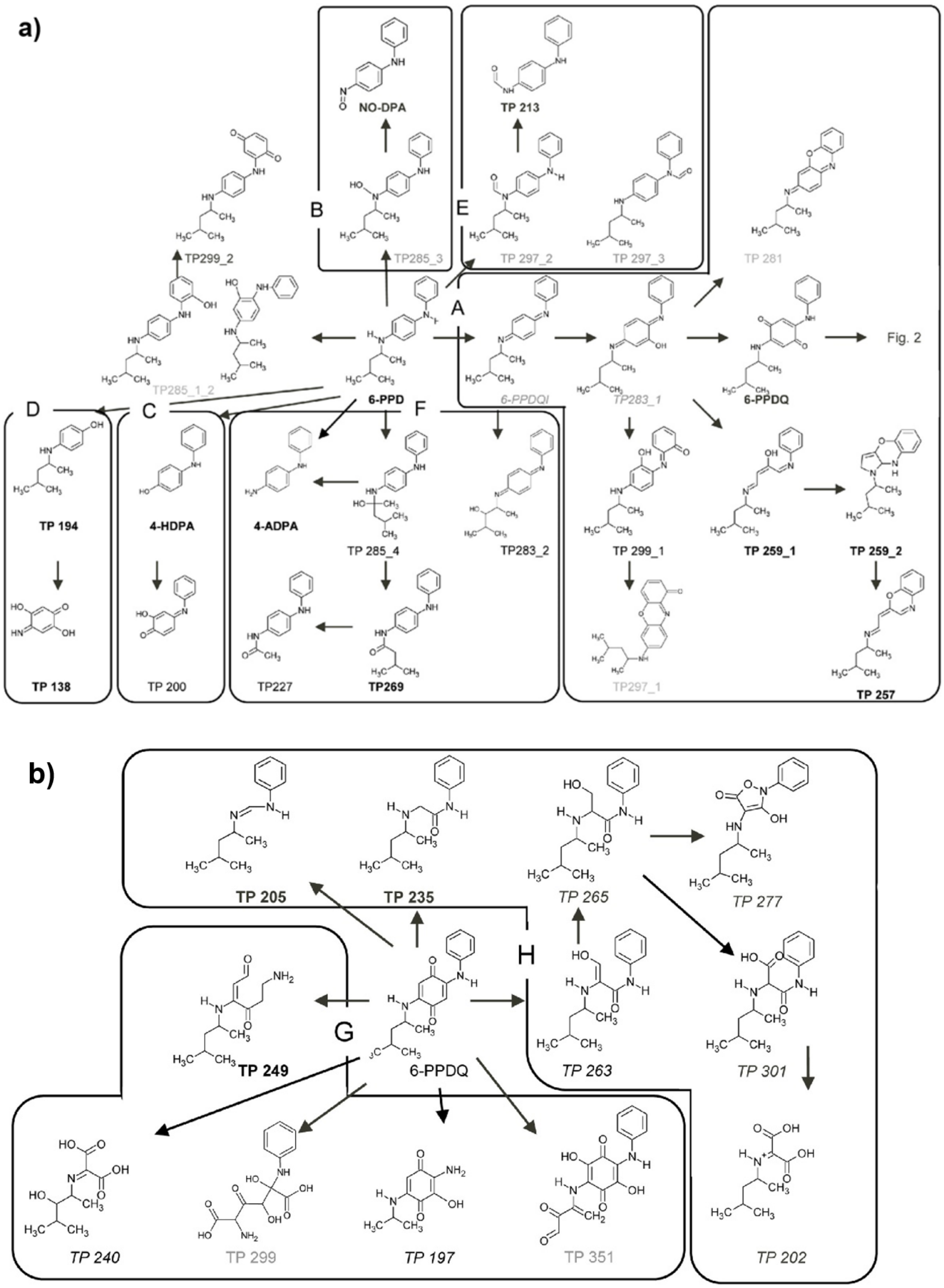

Figure 10. Additional a) 6PPD and b) 6PPD-q transformation products with little to no information (Seiwert et al. 2022).

Automobiles and tires are a well-documented, continual source of known contaminants that are harmful to aquatic life and human health (Legret & Pagotto 1999; Kennedy et al. 2002; Mahler et al. 2004; Scholz et al. 2011; Spromberg et al. 2016; Denier van der Gon et al. 2018; Bookter 2017; Mayer et al. in review).

3.2.3 Evaluated existing water quality and quantity monitoring at Ecology for opportunistic road runoff sampling

The following programs make up the regional and statewide monitoring and assessment programs.

- River and Stream Water Quality Monitoring
- River and Stream Flow Monitoring
- Intensively Monitored Watersheds
- Stream Biological Monitoring
- Watershed Health Monitoring
- Aquatic Plant Monitoring
- BEACH Program
- Marine Water and Sediment Monitoring
- Toxics Studies and Monitoring
- Water Quality Effectiveness Monitoring
- Marine Nearshore Mussels and Fish in the Puget Lowlands Ecoregion (WDFW-TBioS)
- Guidance for Effectiveness Monitoring of Total Maximum Daily Loads in Surface Water

In addition to Ecology's Puget Sound and statewide monitoring programs, other local, State, Federal, and Tribal governments have additional, targeted water quality and quantity monitoring efforts. The scope and scale of each monitoring program evaluate impacts on a variety of receiving water types (streams, rivers, lakes, and estuaries) and the effectiveness of water resource management actions (Table 6).

Table 6. Monitoring types for addressing different questions.

Question	Type of monitoring
What are the current WQ conditions?	Baseline
What is the overall status of water in watersheds?	Status
Are conditions changing over time?	Trend
Are WQ standards and TMDL[1] /NPDES[2] targets being met?	Compliance
Are source control devices being maintained?	Implementation
Are additional source controls needed?	Source Identification
Is the WQ model correct?	Validation
Are changes in WQ linked to implementation of toxic control measures?	Effectiveness

[1] TMDL = Total Maximum Daily Load.
[2] NPDES = National Pollutant Discharge Elimination System.

6PPD-q Spatial Studies Review Summary

A specific evaluation of potential sampling opportunities for tire wear particles and contaminants can be found in Appendix A. The summary of this evaluation identifies the best candidates for opportunistic sampling (Table 7). Most 6PPD-q water sampling must be conducted during storm events, preferably in urban or transportation-impacted salmon-bearing streams.

Storm event sampling is challenging. Therefore, many of our river and stream monitoring programs have adopted bioassessments to measure overall health (King County 2015). A 6PPD-q centric sampling regime is proposed to verify some of the early information regarding the occurrence and persistence in the environment. Bioassessment methods employed by the Watershed Health Monitoring Program will be incorporated to correlate 6PPD-q with the existing Biological Index of Biotic Integrity (B-IBI: Puget Sound Stream Benthos[1]).

[1] https://pugetsoundstreambenthos.org/

Table 7. Review of existing water quality and quantity monitoring programs at Ecology that meet the water body type and timing criteria for road runoff sampling.

Criteria	Type	Effectiveness Focus	Season	Storms	Small Streams	IAA
River and Stream Water Quality Monitoring	Directed studies; Status & Trends	Water Quality (TMDL) & Projects	All year	Yes	Yes	—
River and Stream Flow Monitoring	Status & Trends	Water Quantity	All year	Yes	Yes	Big Rivers — USGS
Watershed Health Monitoring	Status & Trends	Water Quality	Summer	No	No	—
Water Quality Effectiveness Monitoring	Effectiveness Monitoring; Selected TMDL Sites	Water Quality Cleanup Plan Effectiveness Monitoring	All year	Yes	Yes	—
Aquatic Plant Monitoring	Lakes Focused	Technical Assistance	Spring—Summer	No	No	—
BEACH Program	Swimming beaches	Human Health Monitoring	All year	No	Yes	DOH
Marine Water and Sediment Monitoring	Directed studies; Status & Trends	Water Quality & Toxic Reduction Actions	Year Round	Random	Output from urban streams	—
Toxics Studies and Monitoring	Directed studies; Status & Trends	Toxic Reduction Planning & Actions	All year	Yes	Yes	—
Marine Nearshore Mussels & Juvenile Salmon (TBios)	Status & Trends Probabilistic	Stormwater Management & Toxic Reduction Actions	Every other year in Winter	Yes	Yes	WDFW
Shellfish Monitoring	Stratified	Population Trends	Twice a year	Random	Estuaries	WDFW

Note. The highlighted rows indicate the greatest potential to collect 6PPD-q samples effectively at sites and seasons of interest. The rain clouds highlight the monitoring efforts that are conducted during the wet season. Small streams are of greatest interest at this stage because these are often areas of greatest exposure to road runoff and urbanization and often host coho salmon and trout species that are most sensitive to 6PPD-q.
DOH = Department of Health
WDFW = Washington Department of Fish & Wildlife
USGS = US Geological Survey

Table 8 provides an overview of the study types proposed for this initial project. Adaptive monitoring and assessment strategies are needed to adjust to new information regarding the characteristics of tire wear particles and associated contaminants and chemical action planning. The goal of this project is to conduct stream reconnaissance, study design evaluations, and support further method development.

Table 8. Types of exploratory studies needed to evaluate 6PPD-q in the environment.

6PPD-q Questions	Type of Study	This project	Site Selection
Where should we focus initial assessments?	GIS Desktop/Recon	Yes	Traffic counts, salmon distribution, and land use
What is the most efficient and dependable study design to identify areas impacted by road runoff?	Exploratory	Yes	6PPD-q verified site
What are the best analytical methods for collecting and measuring 6PPD-q in water, sediments, and tissues?	Focused	Yes	6PPD-q verified site
How do variable factors influence the mass loading and transport of 6PPD-q to urban streams and watersheds?	Spatial	Yes	Urban and traffic gradients
Where should stormwater control devices be installed?	Source Identification	No	Site-scale assessments
Are existing BMPs controlling the transport of tire wear particles and contaminants to streams?	Effectiveness (Impact)	No	Areas where BMPs have been employed
What landscape factors should be incorporated into a road runoff model?	Calibration	No	Spatial gradient information and correlated data
How well does the model predict the road runoff impacted areas?	Validation	No	Stratified random
Are the source control actions maintained? Are there adaptive management actions needed? Are NPDES management strategies working?	Status & Trend	No	Stratified random

Note. The main focus of this project are highlighted, including method development, study design evaluation, and salmon-bearing stream reconnaissance.
BMP = Best management practice.
NPDES = National Pollutant Discharge Elimination System.

3.2.3 Parameters of interest and potential sources

Tires are currently thought to be the main source of 6PPD and 6PPD-q, although more research is needed to evaluate additional consumer and post-consumer sources of 6PPD (Ecology 2022a, Ecology 2021; DTSC 2022; Zhao et al. 2023). Additional consumer and post-consumer products include tire crumb rubber, roofing materials, sealants, asphalt, rain gear, wipers, shoe soles, and camping gear. Spatial studies are flexible enough to support source identification of additional consumer and post-consumer product sources in the environment.

Additional road runoff contaminants of interest

If 6PPD is replaced with a safer alternative, the transportation pollution problem remains. Additional contaminants associated with motor vehicles have been selected for analysis, including Metals (Cu, Zinc, and Pb) to correlate with tire anti-degradants. These contaminants are known to be toxic to aquatic life, including Pacific salmon (EPA[1]).

Tires, 6PPD, and 6PPD-q are known to have additional chemicals and transformation products that we know very little about (Figure 11). Additional chemicals of concern have been added to our list of target analytes of interest for the Toxics in salmon watersheds pilot studies.

3.2.4 Regulatory criteria or standards

6PPD-q research is in an exploratory stage. There are currently no regulatory quantitative criteria. Yet, a qualitative narrative water quality criterion is being employed during this early stage: no toxics in toxic amounts.

Most water quality standards require that all surface waters be **free** from the following:

- Putrescent or otherwise objectionable bottom deposits.
- Oil, scum, and floating debris in unsightly amounts.
- Nuisance levels of odor, color, and other conditions.
- Undesirable or nuisance aquatic life.
- Substances in amounts toxic to humans or aquatic life.

The Clean Water Act requires natural water bodies to be fishable and swimmable.

The Endangered Species Act protects declining populations of concern and requires an in-depth aquatic habitat impact review process.

[1] https://www.epa.gov/mobile-source-pollution/research-health-effects-exposure-risk-mobile-source-pollution

4.0 Project Description

Given the acute toxicity of 6PPD-q, we need to understand the occurrence, persistence, fate, and transport of 6PPD-q and the distribution of sensitive species (currently includes coho salmon, rainbow, steelhead, and brook trout) in Washington State. Reliable methods for measuring 6PPD-q in salmon habitats are needed to identify areas at the greatest risk of exposing vulnerable species to harmful tire contaminants and provide the greatest benefit to supporting resilient salmon populations.

4.1 Project goals

The goal of this study is to develop effective and consistent methods for measuring 6PPD-q in salmon habitats. Ecology will use the information to help fill data gaps and inform toxic reduction planning.

The goal of this project is to:

- Develop and compare methods for monitoring 6PPD-q in salmon habitats.
- Identify 6PPD-q hot spots to understand the occurrence and persistence of 6PPD-q.
- Collect baseline data before future salmon habitat recovery and water quality enhancement projects.
- Design and conduct directed studies to help fill priority data gaps and support analytical method development.

4.2 Project objectives

The objectives of this project are to:

- Collect water and sediment samples following storm events to evaluate the consistency and accuracy of proposed methods and support further method development.
- Collect tissue samples to support method development at Manchester Environmental Laboratory (MEL) and participating labs.
- Work with MEL staff to evaluate a workflow for 6PPD-q and other related analytes and establish laboratory contracts to support analyses unavailable at MEL.
- Evaluate how the chemical and physical characteristics drive the fate and transport of 6PPD-q in the environment.
- Correlate the presence or absence of 6PPD-q with watershed characteristics.
- Summarize and report findings to inform next steps and help standardize methods to ensure comparability of data across districts and geographic scales.
- Use the desktop maps to help coordinate and direct toxics in salmon watersheds reconnaissance.
- Further develop and maintain an ArcGIS StoryMap of toxics in salmon watersheds.
- Apply internal database QA review procedures and finalize data entry.

- Collaborate and coordinate with analytical partners.

4.3 Information needed and sources

The discovery of 6PPD-q as the cause of urban runoff mortality syndrome, also referred to as pre-spawn coho mortality, prompted Washington State policymakers to request a legislative report from Ecology. The report assignment was to assemble and summarize the available information regarding 6PPD-q transport and impacts on salmon and Ecology's first steps to address the new contaminant. The report, *6PPD in Road Runoff: Assessment and Mitigation Strategies,* includes extensive background information.

Preliminary GIS analysis and a related Tire Contaminant Monitoring StoryMap will be available as a coordination platform to support this project. These mapping efforts were used to make a preliminary list of vulnerable areas and suspected hot spots based on the ecosystem, transportation, and watershed characteristics.

Salmon recovery community coordination and site reconnaissance visits will be required to evaluate areas of concern for high-risk exposure to vulnerable habitats.

4.4 Tasks required

Tasks required to achieve the study objectives:

- Project planning meetings and discussions with local interest groups.
- Reconnaissance of best accessible sampling sites.
- Deployment and retrieval of active and passive water samplers for comparisons.
- Sediment collection using cores and grabs to support sediment method development.
- Installation and trial of a remotely operated autonomous stream sampling station.
- Analysis of samples for 6PPD-q prior to lab accreditation.
- Verification of analytical and data quality.
- Data management
- Data analysis and report production.
- Presentations to toxics and salmon habitat working groups.

4.5 Systematic planning process

This QAPP constitutes a suitable planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 9. Roles and responsibilities of collaborators.

Staff	Title	Responsibilities
Jessica Archer **EAP SCS** **360-407-6698**	Client and EAP SCS Manager	Clarifies and reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Jim Medlen **TSU, EAP** **360-407-6139**	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Rhea Smith/TBD **TSU, EAP** **360-763-2584**	Monitoring Strategist NRS3	Coordinates the science with State, Federal, and Tribal groups. Designs the toxics monitoring program and writes the QAPP. ***Funded until December 2023.***
TBD **TSU, EAP**	Monitoring Program Lead, NRS4	Implements and manages field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM.
TBD **TSU, EAP**	Field Lead NRS2	Coordinates sample collection, helps with study designs and records, and quality controls field information.
Alex Gipe **TSU, EAP** **360-584-4447**	Peer review Co-investigator	Reviews QAPP and provides technical and field assistance.
TSU Team, **EAP**	Project support and co-investigators	Supports opportunistic field sampling efforts. Provides technical support. Co-investigators.
Myrna Mandjikov **MEL, EAP** **360-871-8814**	Analytical 6PPD Method Development Lead (Chem 4)	Reviews draft QAPP, supports and guides 6PPD-q analytical method development in water, sediment, and tissues. ***Funded until December 2023.***
Chad Larson **WHEM, EAP** **360-407-7456**	Stream Ecologist, Technical Advisor	Provides internal review of the QAPP and technical support for stream bioassessments, including eDNA, bug traps, and biofilms.
Brad Hopkins & **Dan Dugger** **FMU, EAP** **360-628-2284**	Hydrologist, Technical Advisor	Provides internal review of the QAPP and technical support for stream automated sampling design.
Molly Gleason **TMDL Modeling, EAP** **360-485-2649**	Hydrogeologist 3	Supports Directed studies to understand the production of 6PPD-q from TWP in stream sediments in the Soos Creek Watershed.
Stacy Polkowske **WOS, EAP** **360-464-0674**	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Dean Momohara **MEL, EAP** **360-871-8801**	Manchester Lab Director	Reviews and approves the final QAPP.
Arati Kaza **360-407-6964**	Ecology QA Officer	Reviews and approves the draft QAPP and the final QAPP.

Staff	Title	Responsibilities
Andrea Carey WDFW TBioS Team (360) 480-3443	Research Collaboration	Opportunistically collects fish and shellfish tissue samples to support MEL method development. Collaborates on study designs. TSU collects samples and supports their projects as needed.
Tanya Williams & Craig Manahan, HWTR 360-688-4993	6PPD Alternative Chemical Team	Provides toxicity research and action planning guidance.
Morgan Baker & Madison Bristol WQP	6PPD in Stormwater Team	Provides stormwater research and policy coordination.
Chelsea Morris WQP 360-764-0890	SAM scientist	Leads the urban streams status and trends monitoring program and provides stormwater research collaboration and guidance.
Abbey Stockwell & Amy Waterman, WQP 360-280-2934	MS4 Permit writers	Provides SMAP coordination and guidance.
Doug Howie WQP 360-870-0983	Senior Stormwater Engineer	Provides technical guidance on existing stormwater features.
Nick Hehemann WSDOT 360-742-7515	Environmental Scientist	Collaborates on road runoff sampling, defining stormwater features between road and stream, and traffic count data collections.
Tatiana Dreisbach WSDOT 360-485-3871	Stormwater retrofit planner	Coordinates on 6PPD-q hotspots to inform retrofit prioritization efforts.
Jeremy Graham City of Olympia 360-753-8097	Stormwater and toxic reduction manager	Coordinates road runoff projects in the City of Olympia.
Michelle Myers Stormwater SIL 360-741-2513	NEP Project Coordinator	Coordinates stormwater and 6PPD-q projects in Thurston County.
Sarah Brunelle The WA Nature Conservancy (TWNC), 206-343-4344	Project Coordinator for Stormwater Heatmap	Coordinates road runoff and 6PPD-q projects in Puget Sound.
Steve Todd Suquamish Tribe	Natural Resource Manager	Coordinates salmon habitat and WQ surveys in the Kitsap area, helps identify areas of concern to sample, and collaborates on bioassay study.
Zach Holt Bremerton	Stormwater Manager	Coordinates road runoff and 6PPD-q projects in Bremerton and Port Orchard, helps identify areas of concern to sample, and collaborates on bioassay study.
Renee Scherdnik Kitsap County 360-731-3553	Stream monitoring lead	Coordinates and helps with stream reconnaissance and opportunistic sampling.
Justin Greer, John Hansen & Rachael Lane USGS	Ecotoxicology Scientists	Coordinates 6PPD-q collection for USGS in Northwest, developed a method for cell line toxicity testing, accepting split 6PPD-q samples for a comparison study to support the bioassay study.

Staff	Title	Responsibilities
Salmon and Shellfish Units WDFW	Shellfish and fish populations	Estimates populations to understand the status and trends of shellfish and fish populations in Washington State. Prioritizes habitats in need of enhanced protection and recovery.
NWIFC	Shellfish and fish populations	Supports the WA tribes by curating the SWIFD spatial database to help identify salmon distribution throughout the State of Washington.
Center for Urban Waters, UWT	Toxics in runoff research	Conducts research to help natural resource managers understand tire contaminants in the environment and their impacts on biota and help find solutions. Discovered 6PPD-q as a transformation product from 6PPD in tires.
Washington Stormwater Center, WSU	Toxicology and runoff research	Conducts toxicology research to help natural resource managers understand tire contaminants in the environment and their impacts on biota and help find solutions. Currently conducting toxicology experiments to find less harmful alternatives to 6PPD in tires.

Note. EAP: Environmental Assessment Program; EIM: Environmental Information Management database; FMU: Freshwater Monitoring Unit; HWTR: Hazardous Waste Toxics Reduction; QAPP: Quality Assurance Project Plan; MEL: Manchester Environmental Lab; MS4: Municipal Separate Stormwater System; NEP: National Estuarine Program; NWIFC: Northwest Indian Fisheries Commission; NRS: Natural Resource Scientist; SAM: Stormwater Action Monitoring; SCS: Statewide Coordination Section; SMAP: Stormwater Management Action Plan; SWIFD: Statewide Integrated Fish Distribution; TBioS: Toxics Biological Observation System TMDL: Total Maximum Daily Load; TSU: Toxics Studies Unit; TWP: Tire Wear Particles; WDFW: Washington Department of Fish & Wildlife; WHEM: Watershed Health and Effectiveness Monitoring; WQ: Water Quality; WQP: Water Quality Program; WOS: Western Operations; WSDOT: Washington State Department of Transportation.

5.2 Special training and certifications

All personnel conducting field activities receive training on using water, sediment, and biota sample collection equipment, sample handling, program quality assurance/quality control (QA/QC), and safety. Everyone must be familiar with this QAPP and field procedures described in our standard operating procedures (SOPs). New technicians are given demonstrations of field procedures before they perform field activities. Senior staff conducts periodic field checks to ensure consistent sampling performance among staff and partner trainees. Results from these checks are discussed with the team, and appropriate updates or changes are implemented if necessary. All personnel conducting rescreening, sorting, and/or identification of samples have a college education in marine and/or environmental sciences and direct experience with sample handling, analysis, QA/QC, and chemical safety.

5.3 Organization chart

6PPD in tires and 6PPD-q transport and impact on sensitive habitats are priority issues in Washington State. We are in the research phase of a new contaminant, and therefore, research and development resources are needed to address the many data gaps. Toxics in aquatic life is a priority, especially in the Pacific Northwest, where Orcas rely on Pacific salmon for their diets and WA Treaty Tribes are concerned for their fishing rights. Currently, the toxics studies unit requires the necessary staff and analytical capacity to effectively address the exponential growth of contaminants of emerging concern. A joint team of technical staff is needed across

Manchester Environmental Laboratory and Ecology's Toxics Monitoring Programs to address common toxics released from our consumer products in the environment.

5.4 Proposed project schedule

This is a programmatic QAPP with a proposed five-year duration that will require periodic QAPP Amendments or Work Plan Memos at the discretion of the EAP Toxics Unit Supervisor and the QA Officer (Tables 10, 11, and 12).

Table 10. Schedule for completing field and laboratory work for opportunistic sampling.

Field and Lab Work	Estimated start	Estimated end	Lead staff
Spatial Studies	Fall 2023	Ongoing	Project lead (NRS4)
Directed studies	Summer 2023	Ongoing	Project lead (NRS4)
Coho Watershed Pilot Study	Winter 2024	Ongoing	Project lead (NRS4)
Laboratory analyses	Fall 2023	Ongoing	MEL/TBD
Contract lab data validation	Spring 2024	Ongoing	MEL/TBD

Table 11. Schedule for data entry.

Task	Due date	Lead staff
EIM data loaded[1]	September 2027	Field lead
EIM QA	October 2027	Project lead
EIM complete	November 2027	TBD

[1]EIM Project ID: RHSM0001

EIM: Environmental Information Management database

Table 12. Schedule for final report.

Task	Due date	Lead staff
Draft to supervisor	Spring 2028	Project Lead
Draft to client/ peer reviewer	Spring 2028	Project Lead
Draft to external reviewers	Summer 2028	Project Lead
Final draft to publications team	Summer 2028	Project Lead
Final report due on web	October 2028	Project Lead

5.5 Budget and funding

As part of the 6PPD Proviso, MTCA funds were awarded to support the spatial analysis and monitoring strategy development to best identify areas where untreated runoff is transported to vulnerable habitats. The equipment needed to support this proof-of-concept monitoring to collect samples using an autonomous sampling station that reduces the need for storm chasing was purchased during the 2021 – 2023 biennium.

The MTCA funds currently support an NRS3, a toxics monitoring strategist (6PPD-q), and a Chemist 4 through 2023; additional MTCA funding has been awarded to support an NRS4 project lead, and a NRS2 project field lead and one 6PPD-q Chemist 3. The 6PPD-q sample analysis budget is supported through the NRS4 and Chemist 4 combined research funding and the MEL analytical pool. Additional research funding needs to support sub-contracts and interagency agreements will be assessed annually.

Table 13. Laboratory budget details (estimated annual).

Parameter	Sample Type	Number of Samples	Cost Per Sample ($)	Lab Subtotal ($)
6PPD-q LC/MSMS[1]	Water	600	—	—
SSC	Water	160	21	3,360
TSS	Water	160	16	2,560
TOC/DOC	Water	160	85	13,600
TWC	Water	20	—	—
6PPD-q - Passives	Water	60	20	1,200
eDNA — Actives	Water	25	195	4,875
6PPD-q	Sediment/Biofilm	72	—	—
TOC	Sediment/Biofilm	152	53	8,056
Metals (6)	Sediment/Biofilm	20	148	2,960
6PPD-q — biota	Tissue	TBD	—	—
Metals (6)	Tissue	10	148	2,960
eDNA (gut contents)	Tissue	25	195	4,875
Total	—	—	—	**44,446**

eDNA = Environmental DNA.
MSMS = Coupled mass spectrometry.
N/A= Not applicable.
SSC = Suspended sediment concentration.
TOC = Total organic carbon.
TSS = Total suspended solids.
TWC = Tire wear contaminants; HRMS: Method development with USGS, no cost or alternative funding.
[1] Analysis and chemist are funded by 6PPD Proviso to support this work.

6.0 Quality Objectives

6.1 Data quality objectives[1]

The main data quality objective (DQO) for this project is to collect sufficient water, sediment, and tissue samples to verify the best methods for measuring 6PPD-q in the environment and correlate its concentrations with watershed characteristics. MEL has developed a method for measuring 6PPD-q in water and is developing methods for sediments and tissues using liquid chromatography with tandem mass spectrometry (LC-MS-MS). An EPA method for 6PPD-q is being developed. MEL will soon be accredited for 6PPD-q analysis and a lab waiver will be required to send samples to any non-accredited labs. Measurement quality objectives described in the subsequent section detail the targets for analytical precision, bias, and sensitivity.

6.2 Measurement quality objectives

The MQOs for this study are detailed in Table 14. The MQOs for the field parameters (pH, dissolved oxygen, temperature, and conductivity) are in Table 15.

[1]DQO can also refer to ***Decision*** Quality Objectives. The need to identify Decision Quality Objectives during the planning phase of a project is less common. For projects that do lead to important decisions, DQOs are often expressed as tolerable limits on the probability or chance (risk) of the collected data leading to an erroneous decision. And for projects that intend to estimate present or future conditions, DQOs are often expressed in terms of acceptable uncertainty (e.g., width of an uncertainty band or interval) associated with a point estimate at a desired level of statistical confidence.

Table 14. Measurement quality objectives.

Parameter	Matrix	Duplicate Samples (% RPD)	Verification Standards (%, LCS, CRM, CCV)	Matrix Spikes (% Recovery)	Matrix Spike-Duplicates (%)	Surrogate Standards (% Recovery)	MDL
6PPD-q	water	±40	50–150 (LCS), ±30 (CCV)	40–160	±40	20–200	0.368 ng/L
SSC	water	±20	80–120	N/A	N/A	N/A	0.5 mg/L
TSS	water	±20	80–120	N/A	N/A	N/A	0.1 mg/L
TOC	water	±20	80–120	75–125	N/A	N/A	0.5 mg/L
DOC	water	±20	80–120	75–125	N/A	N/A	0.5 mg/L
TWC[1]	water	TBD	TBD	TBD	TBD	TBD	TBD
eDNA	water	N/A	N/A	N/A	N/A	N/A	N/A
6PPD-q[2]	solid	±40	50–150 (LCS), ±30 (CCV)	40–160	±40	20–200	TBD/g
TOC	solid	±20	80–120	N/A	N/A	N/A	1%
Zinc (Zn)	solid	±20	85–115	75–125	±20	N/A	2.5 mg/kg dw
Copper (Cu)	solid	±20	85–115	75–125	± 0	N/A	0.05 mg/kg dw
Lead (Pb)	solid	±20	85–115	75–125	±20	N/A	0.05 mg/kg dw
Cadmium (Cd)	solid	±20	85–115	75–125	±20	N/A	0.01 mg/kg dw
Arsenic (As)	solid	±20	85–115	75–125	±20	N/A	0.05 mg/kg dw
Nickel (Ni)	solid	±20	85–115	75–125	±20	N/A	0.05 mg/kg dw

CCV = continuing calibration verification standards.
CRM = certified reference materials.
DOC = Dissolved organic carbon.
eDNA = Environmental DNA.
LCS = laboratory control sample.
N/A = Not applicable.
RPD = relative percent difference.
SSC = Suspended sediment concentration.
TICs = Tentatively Identified Chemicals (non-target).
TOC = Total organic carbon.
TSS = Total suspended solids.
TWC = Tire wear contaminants (e.g., PAH, HMMM, PPDs).
6PPD-q = 6 p-phenylenediamine.
[1] Tire Wear Contaminants measured by HRMS — DPG, HMMM, PAH, Metals, and TP 274.
[2]. Measured in wet weight (ww) for tissues.

6.2.1 Targets for precision, bias, and sensitivity

Table 15. Measurement quality objectives for multi-probe sonde calibration checks.

Parameter	Units	Accept	Qualify	Reject
pH	std. units	≤ +0.2	> +0.2 and ≤ +0.8	> +0.8
Conductivity[1]	µS/cm	≤ +5	> +5 and ≤ +15	> +15
Temperature	°C	≤ +0.2	> +0.2 and ≤ +0.8	> +0.8
Dissolved Oxygen	% saturation	≤ +5	> +5 and ≤ +15	> +15
Dissolved Oxygen	mg/L	≤ +0.3	> +0.3 and ≤ +0.8	> +0.8

[1] Criteria expressed as a percentage of readings; for example, buffer = 100.2 µS/cm and Hydrolab = 98.7 µS/cm; (100.2-98.7)/100.2 = 1.49% variation, which would fall into the acceptable data criteria of less than 5%. Criteria for longer-term deployments will be developed.

6.2.1.1 Precision

Precision measures the variability in the results of replicate measurements due to random error. Precision for two replicate samples is measured as the relative percent difference (RPD) between the two results. If there are more than two replicate samples, precision is measured as the relative standard deviation (RSD). Measurement quality objectives for the precision of laboratory duplicate samples and matrix spike duplicate samples are shown in Table 15. A coordinated laboratory split will be performed to support lab accreditation and method development for 6PPD-q.

6.2.1.2 Bias

Bias is the difference between the measured value and the true value. For this project, bias is measured as an acceptable % recovery. Acceptance limits for laboratory verification standards, matrix spikes, and surrogate standards are shown in Table 15.

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance above the background noise of the analytical system. The laboratory reporting limits (RLs) for the project are described in Section 9.2.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

Section 8.2 lists the standard operating procedures (SOPs) for field sampling. MEL has applied for 6PPD-q accreditation. However, there is currently no lab accredited or a single standard operating procedure (SOP) at this exploratory and discovery stage of this new contaminant of concern. An interstate analytical working group is coordinating efforts at this early stage to make sure there is comparability between labs. A goal of this exploratory research will be to conduct a laboratory splits across multiple labs to verify the comparability between labs. Other methods have existing SOPs and are regularly performed by Ecology.

6.2.2.2 Representativeness

Representativeness is a measure of whether the sample media reflects reality. We will ensure proper representatives by adhering to the approved SOPs and sampling protocols. Samples will be preserved and stored in a way that ensures holding conditions and lab holding times are met. Samples will be collected to represent large storm events and small storm events. Pollutographs of watersheds will be conducted to understand the time it takes the road runoff transported 6PPD-q to reach the receiving waters. This information will be used to adaptively program the autosamplers.

For the urban watershed pilot study, a stream sampling station will be deployed and triggered by standardized precipitation and flow conditions. However, some flexibility of the sampling criteria will be needed at this exploratory stage.

For the spatial studies, passive samplers and autosamplers will be deployed for the same duration between sites for comparability. Storm event information will be collected from local weather stations. Some flexibility in deployment timing for passive samplers may be needed due to sampling logistics.

6.2.2.3 Completeness

Given the exploratory nature of this research to support method development, the challenges with storm event sampling and the completeness of data collection and analysis will need to be flexible. The 6PPD-q monitoring methods will solidify over the study duration as best methods are evaluated.

6.3 Acceptance criteria for quality of existing data

All data used to support the findings of this project will meet project DQOs. Any previous data used will also be evaluated for compliance with current DQOs.

6.4 Model quality objectives

N/A

7.0 Study Design

7.1 Study boundaries

This study is focused on developing methods to detect 6PPD-q and tire wear particles (TWP) in urban watersheds that support vulnerable species, including coho salmon and steelhead/rainbow trout. Much of the method development work will be done in the Mid and South Sound areas at verified 6PPD-q hot spots.

Study design approaches:

- **Spatial studies** to support the watershed spatial assessments and take advantage of ongoing monitoring and available resources. Spatial sampling will be a scan across a large spatial scale (Washington urban areas supporting vulnerable species: Appendix C).
- **Toxics in salmon watersheds bioassay studies** to develop bioassay methods to measure if tire contaminants impact a stream and resident fish. Studies will be conducted on urban streams that were selected and the presence of 6PPD-q verified. Reference sites will be established upstream from suspected hot spots.
- **Directed studies** to support method development and address data gaps. The site selection criteria will depend on the study goal.

7.1.1 Spatial studies.

Grab and composite samples will be collected opportunistically from the sites identified from the desktop GIS efforts and local advisory group areas of concern. Additional sample types will be collected to support tissue and sediment method development efforts as needed. See Appendix C for a list of potential sites.

7.1.2 Toxics in salmon watersheds bioassay studies

Table 16. Selected sites for bioassay studies.

Watershed	NHD Reach Code	County	Land use	TMDL status	TMDL type
Indian Creek	1711001902085	Thurston	Mixed	Recreation	Bacteria
Annapolis Creek	1711001900388	Kitsap	Mixed	Recreation	Bacteria
TBD	—	—	Mixed	—	—

Note. Indian and Annapolis creeks were verified to have 6PPD-q.

Indian Creek

Indian Creek is the location of a past study using many methods proposed for the Toxics in salmon watersheds Bioassay pilot study design. Outfalls were identified as sources of stormwater contamination; however, the causal agent of the impaired bioassay was not fully identified (Era Miller 2013). Having past study information and outfalls identified will help target areas and verify whether 6PPD-q is indeed responsible for past bioassay mortality in Indian Creek. Study sites with a gradient of road runoff types, including local roads, highways, and residential areas

(Figures 11 and 12), were selected. Indian Creek is the proposed first pilot study site to evaluate the bioassay methods for 6PPD-q (Figure 13).

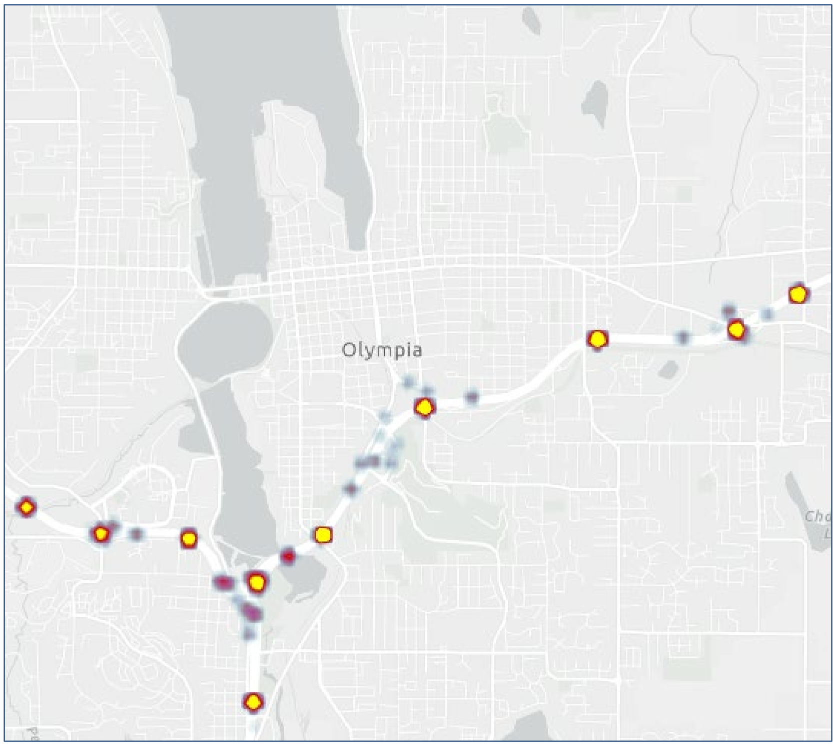

Figure 11. Indian Creek Urban Watershed Pilot Study Site.
Heat map of traffic intensity, yellow equals higher traffic counts.

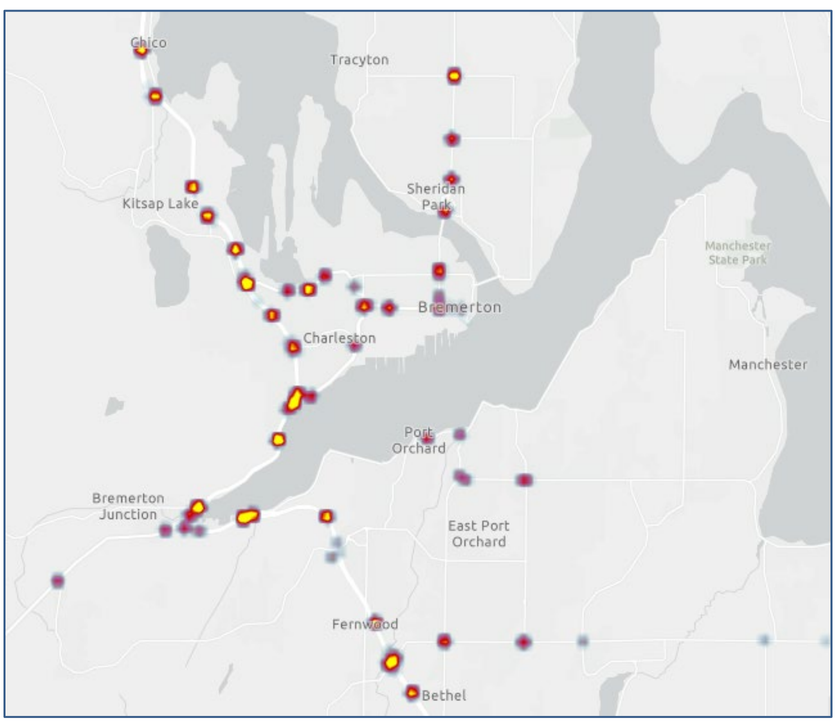

Figure 12. Annapolis Creek Urban Watershed Pilot Study Site.
Heat map of traffic intensity, yellow equals higher traffic counts.

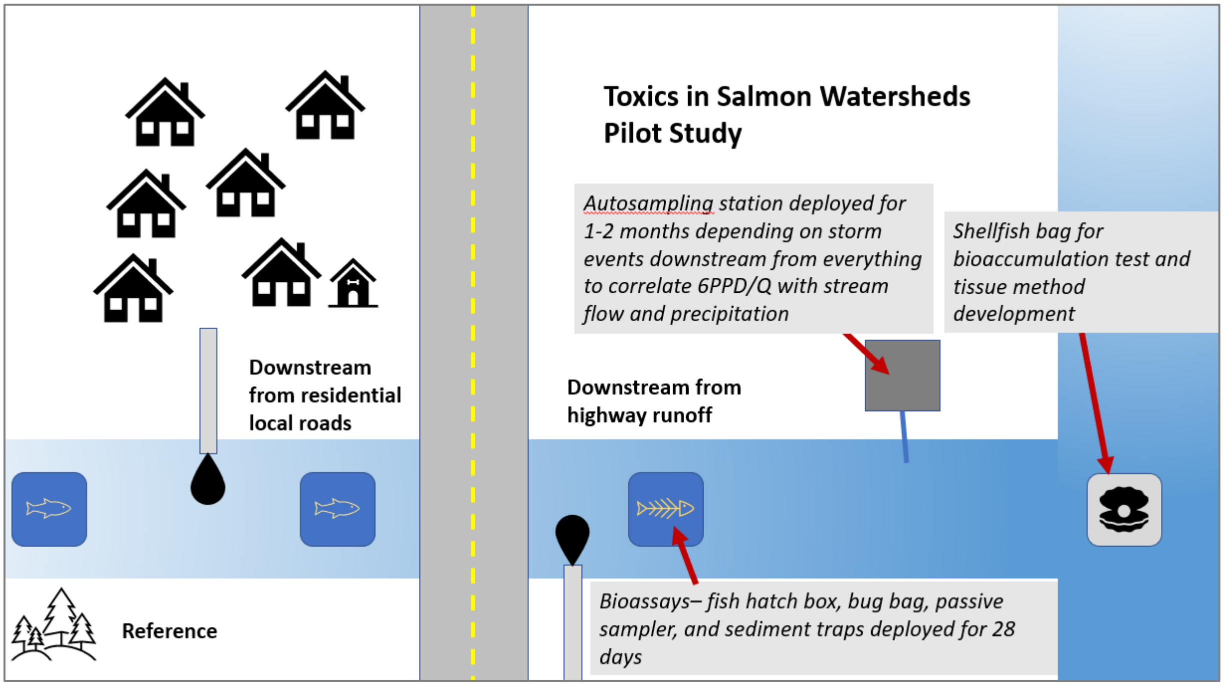

Figure 13. Toxics in salmon watersheds bioassay pilot study design.

7.1.3 Directed studies.

Directed study sites will vary depending on the study and opportunities.

7.2 Field data collection

7.2.1 Sampling locations and frequency

Most of the sampling will be implemented in the wet season during or after storm events. Some dry season samples will be collected to verify the assumption that 6PPD-q is transported by road runoff and is short-lived compared to other more persistent chemicals. The half-life of 6PPD-q is thought to be days to weeks (Ecology 2022a). A delay from the time the stream flow increases and when the pulse of 6PPD-q has been detected in larger rivers during storms events; therefore, the amount of rainfall and duration it takes to transport tire wear particles and 6PPD-q most likely varies from one watershed to another (Johannesen 2022; Figure 14 and 15). Sample timing will begin by targeting variable storm event durations and intensities and may need to be adjusted as more information regarding the transport of 6PPD-q is available (Table 17).

Table 17. Suggested storm event sample timing for 6PPD-q grab and auto-sampling.

Storm Event Characteristics	Definition	Targeted Criteria
Storm event	A measurable storm event	Measurable discharge
Storm event volume	The total volume accumulated over 24 hrs.	> 0.1 inches
Storm event duration	Elapsed time from start to stop of a rain event.	> 1 hour
Sample timing	Sampling collections from start to end of storm	Collect the sample within 72 hours of the storm start
Time controlled sampling	The ideal timing to sample	**Grab sample** (1 time point) — >2 hour after storm start. **Grab samples** (3 time points) — >2, 12, and 24 hours after storm start. **Autosampler** option 1 — composite — start within 1–8 hours after storm start and continue sampling for >24 hours. **Autosampler** option 2 — sequential — start within 0–8 hours after storm start, collect samples every 3 hours. **Autosampler** option 3 — sequential & composite start within 0–8 hours after storm start, collect sequential for the first 12 hours every 2 hours, then switch to collecting composite for 4 hours and then 12 hours; once a pollutograph has been produced, adjust program accordingly (See Figure 15 for example).
Volume controlled sampling	The ideal volume rate change to sample	The more impervious surface, the flashier a stream tends to be. Ideally, evaluate existing flow data, if available, before setting an actuation volume or depth sampling criteria. Ideally, use rainfall (rain bucket) and change in depth (pressure) to trigger a storm event sampling.

Note. These are suggested criteria to help standardize the collection of 6PPD-q during storm events; yet, if the storm event characteristics are recorded, they can be used to correlate the absence and presence of 6PPD-q under different storm event sizes and durations from one watershed to another. The sample timing to start the autosampler will depend on whether it is attached to a rain, depth or flow gauge that triggers the sampler with a set criterion, time programmed or manually started. Initially, getting samples prior to the storm to get a baseline concentration will be helpful. Care should be taken to not accidently stack the samples after a full 12- or 24-hour cycle, depending on how many bottles are used. The composite sampling is a good option when screening for the presence or absence of a new contaminant.

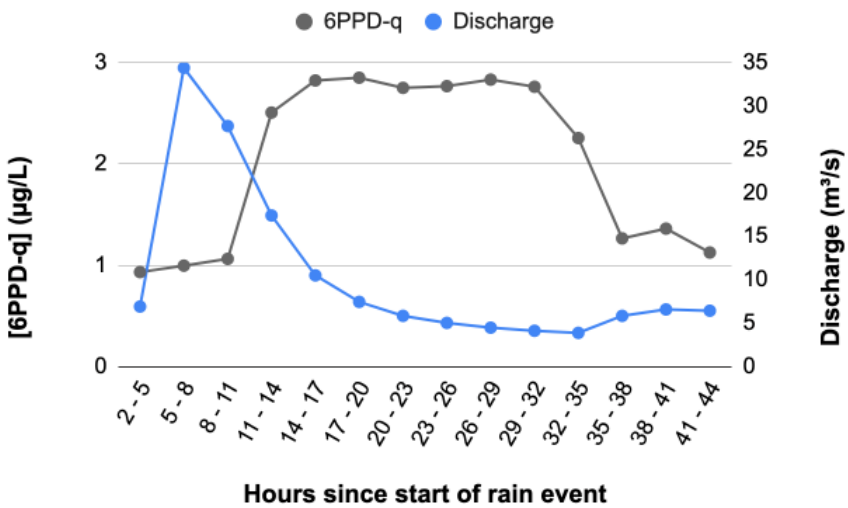

Figure 14. A pollutograph for 6PPD-q in the Don River.
Toronto, CA (left) and a photograph of the Don River (right). The pollutograph shows up to a 10-hour delay post peak flows (Johannessen et al. 2022). Pollutographs vary with watershed characteristics, mass loading, surface runoff conveyance, rainfall intensity and duration, and additional in situ sources (Photo Credit: Mark Watmough[1])

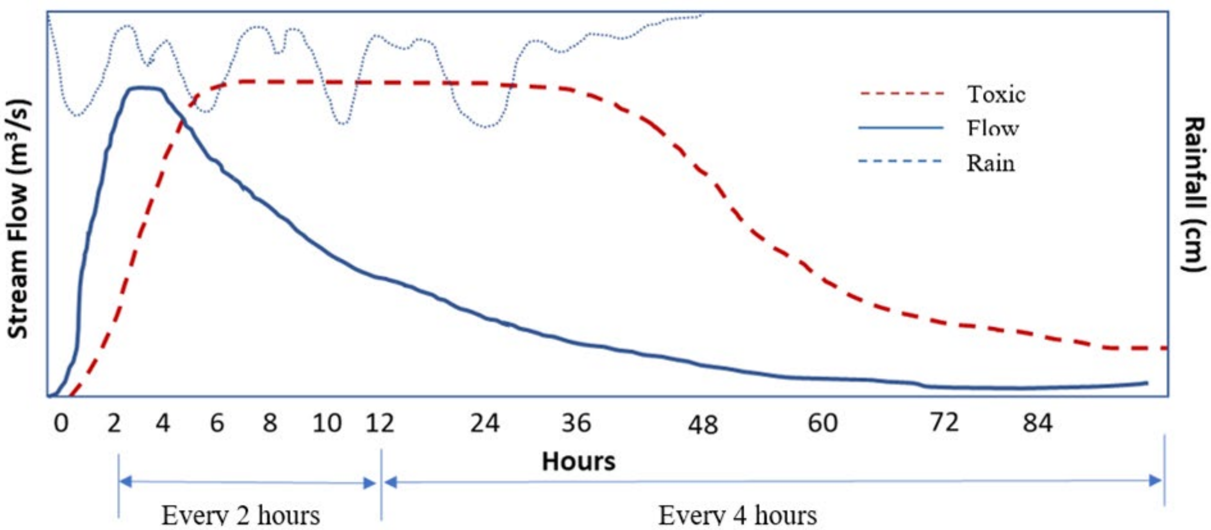

Figure 15. Suggested 6PPD-q specific sampling program for autosampler.
Adjust accordingly for the number of sample bottles. This is a conceptual diagram.

The following information should be recorded during rainfall storm event sampling:

- The date and duration (in hours) of the rainfall event.
- Rainfall total (inches) for that rainfall event.
- Time (in hours or days) since the previous measurable storm event.

[1] https://www.flickr.com/photos/markwatmough/8829469990/, CC BY 2.0, https://commons.wikimedia.org/w/index.php?curid=26369552)

For snowmelt monitoring, record the date of the sampling event.

Sampling opportunities for the spatial assessments will be identified by cross-referencing the qualifying watersheds of essential fish habitats, the vulnerability maps created during the 6PPD Proviso, and existing sampling sites or sites of concern. The streams selected for the toxics in salmon watersheds studies have been screened and verified for the presence of 6PPD-q (Table 18). Focused study locations and measured analytes will vary, but most activities will be conducted in areas where the presence of 6PPD-q has been verified.

Table 18. Locations for proposed sampling by environmental assessment type.

Location	Timing	Spatial studies	Salmon in Urban Watersheds	Directed studies
Indian Creek	Spring 2024	—	X	—
Annapolis Creek	Fall 2024	—	X	—
TBD	Spring 2025	—	X	—
Impacted Areas Statewide	Year 1–5	X	—	—
Reference Areas Statewide	Year 1–5	X	—	—
TBioS (WDFW) Method development	Year 1–2	—	X	X
TBioS (WDFW) Spatial coordination	Year 2–5	X	X	X
WDFW (Shellfish and fish units)	Year 2	—	—	X
Estuaries	Year 2–5	—	X	X
Streams	Year 1–5	X	X	X
Rivers	Year 1–5	X	—	—
Lakes and ponds	Year 3–5	X	—	X
Marine	Year 2	—	—	X

Sampling frequency will depend on storm events, available field staff and resources, and analytical capacity. This programmatic QAPP will need occasional amendments as new information emerges, including the need to adjust sampling frequency and final site selections following reconnaissance and coordination efforts.

7.2.3 Field parameters and laboratory analytes to be measured.

Table 19. Analytes to be measured for each sampling strategy.

Analyte	Sample matrix	Spatial studies	Salmon in Urban Watersheds	Directed studies
6PPD-q	water	X	X	X
6PPD-q	sediment	—	—	X
6PPD-q	tissue	—	—	X
SSC	water	X	X	X
TSS	water	—	—	X[1]
TOC	water	X	X	X
TOC	sediments	—	—	X
DOC	water	X	X	X
eDNA	water	—	—	X
eDNA	periphyton	—	X	X
eDNA	diet	—	—	X
TWC	water	X	X	X
Total Metals (6)	water	—	X	—
Total Metals (6)	sediments	—	X	—
Total Metals (6)	tissue	—	X	—
Total Metals (6)	periphyton	—	X	—

DOC = Dissolved organic carbon.
eDNA = Environmental DNA.
SSC = Suspended solids concentration.
TOC = Total organic carbon.
TSS = Total suspended solids.
TWC = Tire wear contaminant.
[1] TSS is being measured to correspond with water quality criteria. However, not all studies or sites will require both SSC and TSS.

Table 20. Sample collection timing for each environmental assessment strategy and estimated 6PPD-q sample numbers per season.

Environmental Assessment Strategy	Fall	Winter	Spring	Summer
Spatial Studies	150 = 8 batches	60 = 3 batches	150 = 8 batches	40 = 2 batches
Toxics in salmon watersheds	—	126	126	—
Directed studies	TBD	TBD	TBD	TBD

Note. Numbers include field QA samples but not lab QA samples. Directed studies sample numbers will vary.

Table 21. Anticipated start and end timing for each environmental assessment strategy.

Environmental Assessment Strategy	Expected Start Time	Expected End Time
Spatial studies	Fall 2023	Fall 2026
Toxics in salmon watersheds	Spring 2024	Spring 2028
Directed studies	Winter 2023	Fall 2027

7.3 Modeling and analysis design

6PPD-q concentrations across varying watershed characteristics will support ongoing spatial risk assessments.

7.4 Assumptions underlying design

Assumptions associated with the study design are that 6PPD-q in water, sediments, and tissues can be accurately measured. Given the exploratory nature of studying a newly discovered chemical, some flexibility for sites and timing of sampling is needed. The few monitoring studies implemented thus far have supported the assumption that 6PPD-q is transported during storm events. However, we know little about the mass loading from traffic and the amount of precipitation needed to transport the contaminant to natural waterways. The underlying design aims to verify these assumptions by sampling across different watershed characteristics and media.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

Storm event sampling is challenging. Relying on innovative stream sampling stations coupled with passive samplers and bioassays will address many of these challenges. Making sure that the equipment is properly set up by qualified field leads trained in telemetry and instrument programming and that the assets are locked securely will limit the time that field staff need to be at these urban sites where theft and vandalism are a concern. This project proposes a list of small, short-term projects to help address the many 6PPD-q in the environment data gaps. Field work for developing new methods requires adaptation to unexpected conditions and may only provide part of the information desired; however, any information is useful at this exploratory stage. Time for coordination with local communities to help locate the ideal sites to place the sampling station will help set this project up for success. The site selection for opportunistic sampling and short-directed studies will be coordinated with the Puget Sound National Estuarine Program[1] Strategic Initiatives project leads to maximize research coordination.

7.5.2 Practical constraints

The practical constraints for this project are having adequate personnel and equipment to support sampling efforts. The 6PPD-q monitoring lead must balance field sampling with their other responsibilities, including research coordination and communication, site accessibility, and upholding safety and quality standards.

7.5.3 Schedule limitations

Contingency laboratory funding has been built into the budget to support the exploratory nature of the project. If method development and lab capacity building to support new monitoring activities take longer than anticipated, an extension may be required. Additional schedule limitations may occur during external data validation and the production of the QAPP and report. Sharing of field resources, personnel, and weather conditions may shift timing.

[1] https://www.epa.gov/puget-sound

8.0 Field Procedures

8.1 Invasive species evaluation

Field personnel for this project must be familiar with and follow the procedures described in SOP EAP070 (Parsons 2023), Minimizing the Spread of Invasive Species. One of the intended study watersheds is a known New Zealand mudsnail-impacted stream. Furthermore, urban streams and stormwater ponds are known hot spots for invasive species. If the intended site to be sampled is known or suspected of harboring invasive species, the decontamination protocol will be followed.

8.2 Measurement and sampling procedures

Water, sediment, tissue, and bioassessment samples will be collected and performed during these studies. Most sampling methods for this study have been employed in source identification studies for toxics (Johnson et al. 2013; Hobbs 2018). Only preliminary sampling and analysis efforts have employed these approaches for 6PPD-q.

8.2.1 Surface Water Sampling

Evaluating sampling methods for tire contaminants is a high-priority data gap. Sampling methods have been chosen based on the chemical characteristics of 6PPD-q, preliminary research by Ecology and partners, and the professional judgment of the Toxics Studies Unit senior scientists. Sampling methods vary among the three environmental assessment strategies (Table 21).

Table 22. Sampling methods intended for each of the three assessment strategies.

Study Design Type	Objective	Methods	Media
Spatial Studies	Measure occurrence	Discreet grab samples Passive samplers Composite sampling	Water
Salmon in Urban Stream Bioassays	Measure exposure risk and persistence	Autonomous interval sampling Passive samplers In situ deployments	Water Sediment Bioassessments Bioassay
Directed Studies	Method Development	A variety of sampling methods and matrices [1]	Water Sediment Biota Air

[1] Directed studies will be reviewed by the unit supervisor and quality assurance officer to determine if a more detailed work plan is needed.

8.2.1.1 Grab Samples (Spatial Studies)

Grab samples will be taken to measure the total and dissolved organic carbon (TOC/DOC), and suspended sediment concentrations (SSC) at each site during the polar organic chemical integrative sampler (POCIS) deployments. 6PPD-q is estimated to readily sorb to organics and particulates. Grab samples will be collected using Ecology standard operating procedures (Ward 2017; Joy 2021). Additional field parameters will be measured in situ during water sampling using a multiprobe sonde (Swanson 2007). The parameters to be measured will include temperature, pH, dissolved oxygen, and conductivity. 6PPD-q samples will be collected in 250 mL glass amber bottles to avoid photodegradation of the tire contaminants. Minimal headspace should be left to prevent 6PPD and 6PPD-q oxygenation reactions.

8.2.1.2 Active Samplers

Previous studies confirmed the effectiveness of autosamplers for collecting timed samples during and following a storm event (Figure 16). Most programmed autosampler collections for a previous stream reconnaissance study have been composite sampling to minimize the number of samples and maximize the chance of catching such a fleeting chemical (Table B-1).

Figure 16. Autosampling unit.

- **Composite sampling** — A preliminary program for the autosampler collections aimed at compositing 200 mL every 2 hours for 72 hours. Composite sampling is good for the initial screening of 6PPD-q presence but not for understanding the transport and residence timing. The composite (10 L) sampling allows room for ice to be packed around the container. It also provides a longer window of time to catch the presence of the contaminant compared to discreet grab samples.
- **Sequential sampling** — Sequential sampling provides more detailed information about the transport pathway (conveyance) and the persistence of the contaminant. For sequential

sampling, collecting at shorter intervals for the first 12 – 24 hours and then shifting to longer intervals is recommended (see section 7.2.1 for more detail on timing).

- **Sample preservation** — The ambient temperatures in the Pacific Northwest during the fall to spring seasons rarely require a refrigerated unit. Preliminary lab method testing demonstrates 6PPD-q concentrations being stable for over a 28-day hold time at a range of temperatures, including ambient. For this study, most of the sampling will occur during the wet and cold seasons. Therefore, we are not using a refrigerated autosampler for this project. However, an insulated sampling container will be used to maintain temperatures. Dry, warm weather sampling will employ passive samplers or grab samples, however, if an autosampler is used, the samples will be kept on ice and a temperature logger will record ambient conditions.
- **Sample materials** — 6PPD-q readily attaches to many plastics and other rubber products (Hu et al. 2023). Therefore, glass bottles and PTFE tubing are recommended to minimize the loss of 6PPD-q during sampling. Priming the tubing with ambient stormwater is recommended prior to starting the program. Additional information on sample timing and actuation can be found in Table 17. Transferring the sample from the clear glass autosampler bottle to an amber 250 mL sample bottle is recommended to avoid photodegradation. The cap liner should ideally be lined with PTFE or similar inert plastic material. PE composite containers may be used for temporary sample storage.
- **Sample volume** — A minimum of 10 mL of sample is needed and a maximum of 250 mL for analysis at MEL. The minimum is what is needed for the LC-MS-MS instrument, and the maximum is the capacity of the extraction/filtration columns. The 6PPD-q analytical community has recommended whole bottle extractions because of how readily the chemical binds to surfaces. A smaller amber glass bottle allows the extraction team to invert the bottle into the extraction column until drained and rinsed with solvent. Another unknown is how homogenous the compound remains in a larger vessel. If transferring from the autosample bottle to an amber glass bottle, swirl the sample first and transfer. When performing lab splits, a sample splitter is recommended.
- **Sample automation —** Ideally, active samplers should be autonomous and programmed to trigger at certain rain and flow criteria using an actuator. This study will use a rain bucket and depth or flow sensor to detect storm-driven discharge events (Figure 18). Weather forecasts and delayed starts will be employed when actuation is not an option.

  Automated, telemetry-capable samplers actuated by a combination of precipitation and stream depth or flow criteria will help standardize the data and minimize logistically challenging storm chasing that can lead to field staff working off hours in unsafe conditions. The ability to standardize and quickly adjust sampling remotely will increase the quality of the project. As new information emerges, the flow and storm event timing criteria will likely need to be adjusted (Figures 17 and 18). The change in depth sensor will need to be calibrated with an in-stream flow meter.

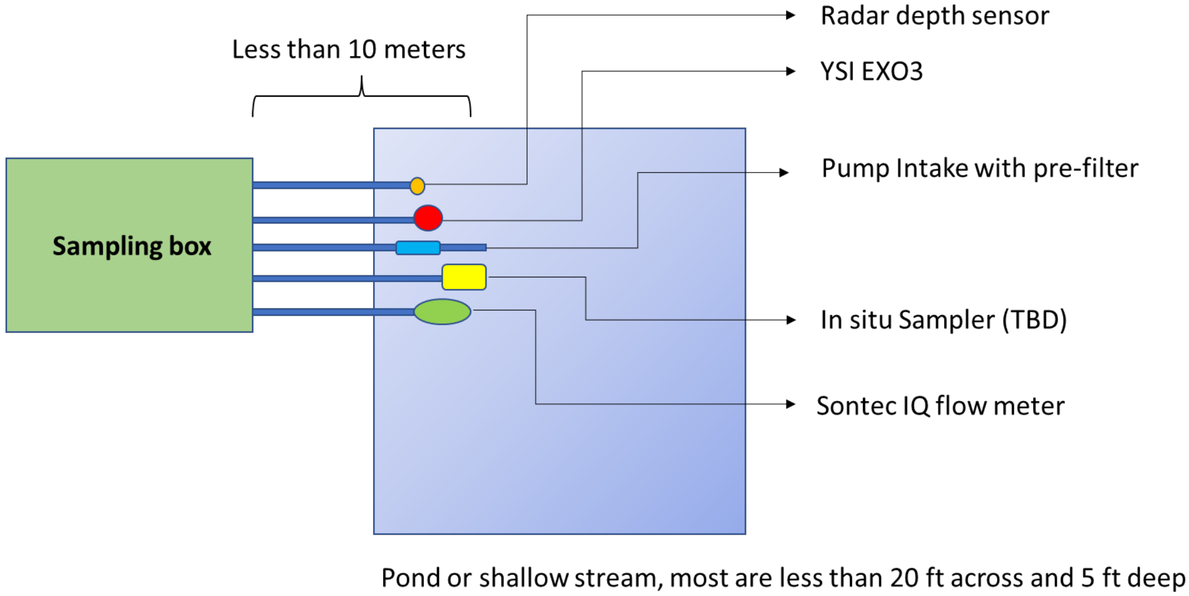

Figure 17. The autonomous stream sampling station design.
The pump intake with pre-filter is optional and part of a directed study.

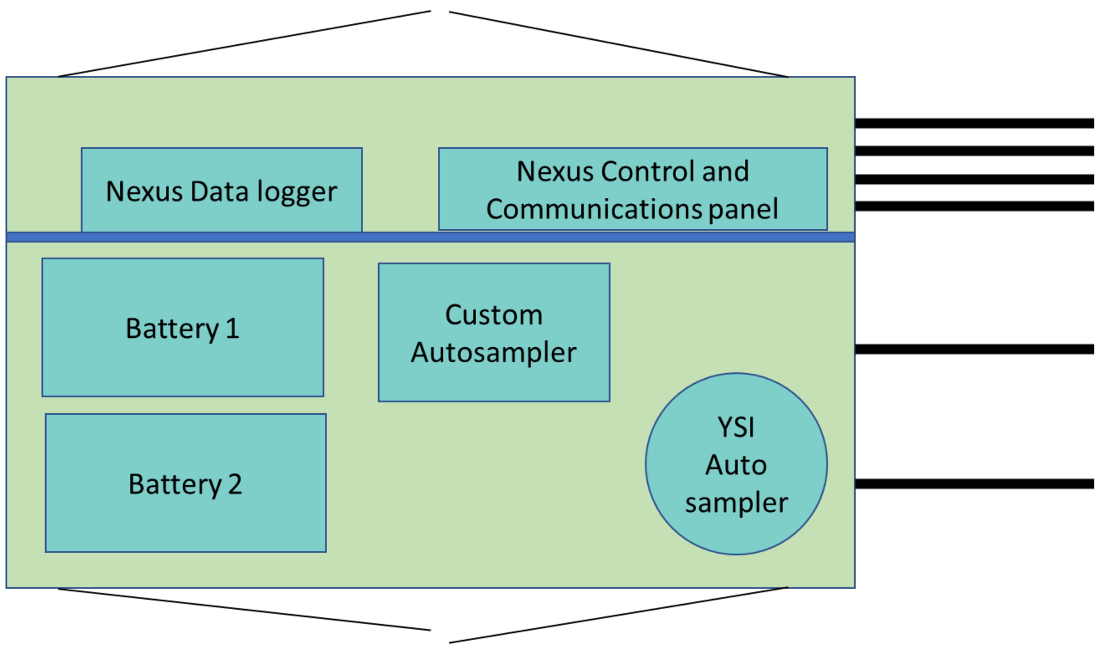

Figure 18. Schematic of the typical stream sampling station that is triggered at programmed storm event criteria.
This is an example and subject to change during station integration.

8.2.1.3 In situ active sampling

A second method for auto-sampling surface and sub-surface water is using in situ pumps and filters (Wong 2019). Continuous Low Level Aquatic Monitoring (C.L.A.M.) sampler is one example of an active sampler that can be deployed directly into a stream and continuously sample for 1 – 2 days (Figure 19). An initial test of these devices was performed in spring 2023. Preliminary data support the need for ongoing testing and use of in situ active sampling devices. The limiting factor with deployment times is the clogging of the filter in receiving waters with high particulates. However, the current design of the C.L.A.M. has a totalizer that counts the amount of water pumped through the filter. Solid Phase Extraction (SPE) — Hydrophilic-Lipophilic Balanced (HLB) media effectively binds to polar analytes. Media can be spiked with a performance reference compound isotope to measure the recovery and loss during deployment and storage. Glass fiber filters are available as a pre-filter to capture particles and potentially provide a particulate and dissolved fractioning of 6PPD-q. MEL has built the capacity to extract 6PPD-q from GFF and HLB SPE filters.

Figure 19. An example of an active sampling device that collects water in situ.
Device in a waterproof case (left) and a closeup of the device (right).

8.2.1.4 Horizontal and Vertical Transect Water Sampling in Bays and Estuaries

Vertical and horizontal profiles will be collected at the mouth of select rivers and estuaries to characterize the baseline 6PPD-q and tire wear particle concentrations. Tire wear particles that are thought to continue leaching in the environment float at a micro-scale and likely sink at macroscales. 6PPD-q has an affinity towards particulates and carbon. Conducting depth profiles will help support or challenge the modeled physiochemical characteristics in the environment and provide information regarding the fate and transport of tire wear chemicals and 6PPD-q. MMU standard methods for Niskin bottle sampling will be followed (Dutch 2018).

8.2.2 Passive Samplers

Passive sampling provides a useful assessment of time-integrated environmental risks and mobility of organic compounds — potentially saving considerable resources per site in unnecessary investigation, remediation, and management costs.

8.2.2.1 POCIS

Passive samplers will be deployed for multiple days to weeks to catch storm events at select locations to estimate 6PPD-q over equal time to provide cross watershed comparisons. POCIS contain HLB media housed between two permeable membranes. The polar nature of 6PPD-q is predicted to filter through the membrane drawn by the polarity of the HLB media and slowly sorb to the SPE media during deployment (Alvarez 2010; Figure 20). A pilot study conducted in the spring of 2023 confirmed the ability to measure 6PPD-q. Tidbit sensors will be deployed with the passive samplers to estimate average ambient water and air temperatures (Dugger and Newell 2021; Nelson and Dugger 2022).

Figure 20. POCIS passive sampling device (USGS and EST).

8.2.2.2 SP3

The SP3™ sampler provides data to estimate contaminant bioavailability to environmental receptors that is more representative than conventional grab samples, as it quantifies contaminants only in the dissolved form. The SP3™ sampler quantifies hydrophobic organic compounds in pore water (sediment and soil), surface water, and stormwater. A device study was conducted in February 2023, supporting the ongoing evaluation of this method (Figure 21).

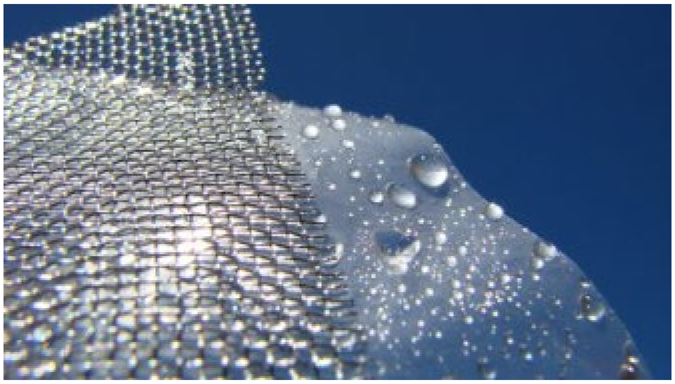

Figure 21. SPMDE (Semipermeable membrane) sampling device (SPMDE) (photo by SiREM).

8.2.3 Stream Bioassessments

8.2.3.1 Periphyton

Periphyton is a complex community of microbes, algae, and bacteria living on hard substrates such as rock, shells, and logs in aquatic environments (Figure 22). Periphyton community diversity and abundance are key indicators of stream health, like benthic macroinvertebrate assessments (Larson 2022).

Periphyton will be collected from inert substrates before the hatch boxes are deployed. Replicate substrates will be sampled to incorporate the heterogeneous communities. The sampled substrates will be at similar water depths and near larger pebbles or riffles.

Foil templates of the substrates will be made by wrapping the areas where the periphyton sample was removed. These templates are later used to calculate the surface area of periphyton collection. An alternative method that involves deploying small settling plates to standardize the biofilm area and age may be employed as well.

Standard protocols for sampling attached algae will be followed to collect biofilm samples (Stevenson and Bahls 1999; Larson and Collyard 2019; Hobbs et al. 2019). Periphyton will be scraped from the settlement surface and collected in a stainless bowl for weighing in the field to confirm that sufficient biomass is retrieved (~10 g ww). Samples will be homogenized and subsampled into 1) a clean amber glass jar for 6PPD-q analysis, 2) a cryotube for eDNA community analysis, and 3) a 500 mL Nalgene sample bottle and preserved and shipped for identification and enumeration.

Figure 22. Biofilm being scraped from a rock.

8.2.3.2 Macroinvertebrates

Invertebrates are more sensitive to many pollutants than fish. For this reason, benthic macroinvertebrate assessments are now standard tools for determining stream health. The displacement of pollutant-sensitive species by pollutant-tolerant species indicates pollution runoff.

Benthic macroinvertebrates will be collected before bioassays and samplers are installed to avoid disturbance from the placement of these devices. The watershed health monitoring protocol will be followed to collect samples (Larson et al. 2019).

The limiting factor in collections of invertebrate tissues for the analysis of contaminants is the mass required (~ 10g wet weight). Therefore, sampling of invertebrate biomass in small streams will need to be assessed as the project progresses. Alternative macroinvertebrate sampling methods will be used in estuaries and larger rivers (Hobbs 2019). All necessary collection permits will be obtained.

8.2.3.3 Presence of vulnerable species and salmon prey assessments eDNA

eDNA provides a measure of prey diversity for salmon and provides a powerful indicator of stream health (Table 22). Water eDNA will be collected to verify the presence of vulnerable fish species. Biofilm eDNA will be collected to evaluate stream health and compare it with more traditional algal and microbial indicator species methods. The watershed health monitoring program is currently exploring the use of eDNA. Modified methods will be used to collect water and biofilm samples.

Table 23. Major prey items for Pacific salmon based on life stages and habitat types.

Species	Juvenile — Freshwater	Juvenile — Estuarine	Juvenile — Marine	Sub-adult to Adult — Marine
Coho salmon	Insects (Diptera, Ephemeroptera)	insects, epibenthic crustaceans, planktonic crustaceans, polychaetes, fish	fish, planktonic crustaceans	fish, planktonic crustaceans
Chinook salmon	Insects (Diptera, Ephemeroptera)	insects (Diptera, Psocoptera), epibenthic crustaceans (copepods), planktonic crustaceans (decapod larvae, euphausiids. gammarid amphipods, copepods), annelid worms (polychaetes)	fish, planktonic crustaceans, insects	fish, planktonic crustaceans

Note. Measuring the prey in 6PPD-q hotspots will shed light on the bioaccumulative capacity of the contaminant (Aitken 1998; PFMC 2022).

8.2.3.4 Salmon in Urban Streams Bioassay Studies

Bug Bags

If macroinvertebrate sampling is not possible, then "Bug bags" may be deployed instead of ambient collections. Bug bags are an in situ bioassay method to evaluate the toxicity of a stream above and below suspected road runoff outfalls and tire contaminant hot spots (Era-Miller 2010, 2013; Marshall and Era-Miller 2012).

The bug bags will be deployed for approximately 40 days at the downstream and upstream sites (Davies and Tsomides 2002). Bug bags are made using 2-inch gravel stuffed inside square pieces of mesh fencing held together at the edges with zip ties. Each bag has the same dimensions of 12 x 18 inches. Three bug bags will be distributed in downstream transects at each site, encompassing at least 2 riffles. Distances between the bug bags at each site will range from 10 to 35 feet.

For retrieval, the bug bags will be gently scooped up from the substrate in a D-Frame kicknet and then transferred into a tub. The mesh bags are cut open, allowing rocks, debris, and bugs to fall into the rinse tub. Tub contents are then sieved and placed into sample bottles. Samples will be shipped for analysis.

Hatch Boxes

Fish hatch boxes are a type of bioassay evaluated in past TSU studies. Hatch boxes are prepared with rainbow trout, brook trout, or coho salmon eggs and hatched out. Health and mortality are assessed post-egg hatching to correlate with the presence of toxics (Environment Canada 1998; Era-Miller 2014; Chalmers 2014). This method requires a WDFW permit and the procurement of trout eggs from a licensed and approved supplier or a local hatchery. Fish are not released. However, as an extra precaution, triploid fish will be used for this proof-of-concept study.

TSU staff will obtain trout eyed-embryos for the in situ toxicity testing from Trout Lodge in Sumner, Washington. Washed stream gravel (1 to 2-inch diameter) will supplement the native stream gravel in filling and covering the cages containing hatch boxes and trout embryos (Figure 23).

Thirty eyed-embryos will be placed in each Whitlock-Vibert hatch box at the stream site. Hatch boxes are closed and placed within steel wire cages (approximately 7 by 14 inches). Gravel is placed inside the cages to hold the hatch boxes in place. Three or four cages, each containing one hatchbox, will then be deployed side-by-side at each stream station for a total of 90 – 120 eyed-embryos per sampling location.

The method for instream placement of cages and hatch boxes is intended to create conditions in the hatch boxes that mimic natural salmonid spawning conditions (eggs are exposed to flowing water in gravels while being protected from high-flow events and predators). Field staff will select stream locations that have suitable gravel and a steady unidirectional flow outside of the main current (thalweg).

See Figure 14 for a diagram of the cage placement arrangement. There will be three cages at each site in the stream and one control cage in the lab. The sampling site will be excavated by digging an area deep enough so the tops of the cages will be at about the same elevation as the streambed. The cages will then be covered with a small mound of gravel after being placed side-by-side in the excavated area at each station.

Figure 23. Fish hatchbox used to measure the health of a stream for target fish species.

Shellfish bioassay

Shellfish bags will be deployed in the brackish mouth of select streams as an exploratory study to support 6PPD-q method development in tissues (Figure 24). WDFW TBioS[1] program has preliminary data that supports the accumulation of 6PPD-q in mussel tissue. The Toxic Studies program will opportunistically support and coordinate this ongoing method development work.

[1] https://wdfw.wa.gov/species-habitats/science/marine-toxics/species-monitored#mussels

Mussels are a commonly used biomonitoring species because of their wide geographical distribution, large populations, sessile nature, and high filtering rates. Additionally, they cannot metabolize most of the organic contaminants they absorb, so they reflect the profile of bioavailable pollution in their local environments. They accumulate contaminants in their soft tissues via multiple pathways, including ingestion/filtering of contaminated food, sediments, and water, thus integrating exposure from both the water column and benthic sources in the nearshore. As they retain contaminants for approximately two to four months, their contaminant loads reflect recent exposure.

Figure 24. Example of a mesh bag for housing shellfish bioassays.

8.2.4 Sediment Sampling

Sediments will be sampled at select sites to support 6PPD-q in sediments method development. Finer particles suggest a slower, less energetic conveyance and could indicate a settlement point for suspended solids and bound pollutants. Sediment collection will follow Blakley (2008) and rely on composite samples from a PONAR sampler for ponds and lakes and sediment traps for streams and rivers. Benthic cores and incubations will be employed opportunistically. 6PPD-q is modeled to readily bind to organic materials; therefore, sediments will be collected for total organic carbon analysis. Sediment traps deployed in streams will help capture some particles suspended and re-deposited during storm events (Wong and Mathieu 2020).

The Puget Sound Ecosystem Monitoring Program (PSEMP) Marine Monitoring Unit of EAP conducts an annual sediment collection study throughout Puget Sound harbors. There may be opportunities to collect sediments for 6PPD-q. All sampling methods and quality assurance for the MMU are detailed in the approved Quality Assurance Monitoring Plan (QAMP) (Dutch et al. 2018: Hartman 2018).

Benthic flux experiments will be designed as a focused study to understand the benthic community ecosystem-scale effects of tire contaminants. For example, microcosms of contaminated versus uncontaminated sediments will be used to understand further biodegradation and flux of 6PPDq from microbial processes and the impact on benthic communities.

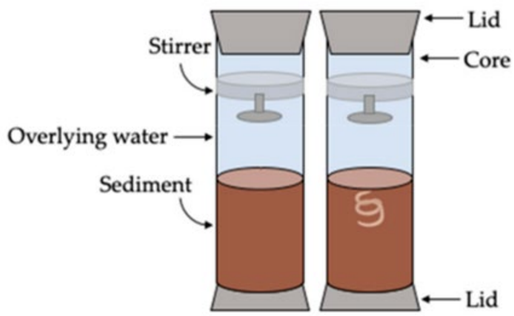

Figure 25. Example of sediment core incubations to measure 6PPD-q flux from sediments.

8.2.5 Placement Strategies

The sampling and deployment methods will vary depending on the type of sampling site. The bioassay pilot studies will be focused on urban runoff to receiving waters. However, directed and spatial studies to support further method development will venture into bigger rivers, estuaries, and the marine environment. In deeper rivers and estuaries, the in-situ sampling devices will be moored on a line. For smaller streams, the devices will be anchored to the stream bank. Anchoring will require steel cables to secure the equipment from high flows or theft. Most sites for this project will be shore accessible. However, spatial sampling and directed studies may require boats to support sample collections (Hobbs 2019).

8.3 Containers, preservation methods, holding times

MEL has developed a Standard Operating Procedure (SOP) for 6PPD-q in water and applied for accreditation. EPA is working on a SOP to help standardize methods across labs. The methods for 6PPD-q in sediments and tissues are in development. The methods provided in Table 24 are based on preliminary investigations and are subject to change during this early method development phase for measuring a newly discovered contaminant.

Table 24. Sample containers, preservation, and holding times.

Lab	Parameter	Matrix	Container or Media	Preservative (°C)	Holding Time (days)
MEL	6PPD-q	water[1]	Certified — 250 mL small mouth amber glass w/ Teflon lid	Cool to 4	28
MEL	6PPD-q	sediments	Certified — 8 oz amber glass wide mouth jar w/ Teflon lid, need ~ 100 g	Cool to 4	28[2]
MEL	6PPD-q	tissue	Certified — 4 oz amber glass wide mouth jar w/ Teflon lid, need ~ 50 g	Cool to 4	28
MEL	6PPD-q	Filter[3] type	HLB or GF — Foil	Cool to 4	28
MEL	6PPD-q	POCIS[4]	HLB — Foil and stainless steel can, pre-extraction	Cool to 6	28
EST; MEL	6PPD-q	extractant	Heat-sealed glass ampules.	Cool to 4	40
Eurofins/ SiREMS	6PPD-q	SP3	Membrane — Foil	Cool to 4	28
MEL	TOC/ DOC	water	125 mL pre-acidified poly bottle — field filtered for dissolved	1:1 HCl to pH ≤ 2 Cool to 6	28
MEL	SSC	water	1L HDPE container	Cool to 6	120
MEL	TSS	water	1L HDPE container	Cool to 6	7
WDFW	eDNA	water, biofilms, sediments, tissue	2L HDPE container (water) or cryotube (solids)	-20 Dry ice	28
USGS	TWC[5]	water	Certified - 250 mL small mouth amber glass w/ Teflon lid	Cool to 4	28
MEL	Total metals	water	500 mL HDPE bottle	Field filter for dissolved HNO3 to pH <2 by the lab within 14 days of collection	6 months after preservation
MEL	Total metals	sediments	Certified — 4 oz amber glass wide mouth jar w/ Teflon lid	Refrigerate at 6°C; can store frozen at -18°C	6 months; 2 years frozen
MEL	Total metals	tissue	Certified — 4 oz amber glass wide mouth jar w/ Teflon lid	Transport at 6°C; can store frozen at -18°C	6 months; 2 years frozen

DOC = Dissolved organic carbon; HDPE = High-density polyethylene; HLB = Hydrophilic-lipophilic balanced; MEL = Manchester Environmental Laboratory; POCIS = Polar organic chemical integrative sampler; SSC = Suspended solids concentration; TSS = Total suspended solids; TWC = Tire wear contaminant; USGS = US Geological Survey; WDFW = Washington Department of Fish & Wildlife.

[1] Minimize head space; collection to extraction hold time at 4C is 28 days (ideally, as soon as possible). Extraction to analysis hold time is 40 days. EPA is working on preservative testing, but no preservative is currently available for 6PPD/Q. Studies are underway to investigate preservative temperatures and holding times.

[2] A tentative 1-year hold time if frozen, although studies are needed to verify.

[3] HLB SPE filters for active samplers are recommended. However, ongoing studies may require alternative filter types.

[4] POCIS membrane should not be frozen; dry ice and extreme temperatures can compromise the membrane before media extraction. Because the 6PPD/Q is bound to the media, the hold time is assumed to be longer. More lab tests are planned to verify.

[5] Select field splits would be sent out for HRMS analysis to correlate with other tire contaminants of concern, e.g., HRMMM, DPG, PAHs, and benzothiazole.

8.4 Equipment decontamination

Decontamination of Sampling Equipment for Use in Collecting Toxic Chemical Samples will be followed between sampling events (Friese 2020).

8.5 Sample ID

MEL and the contract lab will assign Laboratory sample IDs.

8.6 Chain of custody

Chain of custody will be maintained for all samples throughout the project.

8.7 Field log requirements

A field log will be maintained in a bound, waterproof notebook. Corrections will be made with single-line strikethroughs, initials, and dates. The following information will be recorded for each sampling event:

- Name and location of project.
- Field personnel.
- Sequence of events.
- Any changes or deviations from the QAPP.
- Environmental conditions.
- Date, time, location, ID, and sample description.
- Field instrument calibration procedures.
- Field measurement results.
- Identity of QC samples collected.
- Unusual circumstances that might affect the interpretation of results.

8.8 Other activities

No additional activities require description.

9.0 Laboratory Procedures

9.1 Lab procedures tables

9.1.2 Spatial studies sampling plan

Table 25. Measurement methods for Spatial studies.

Analyte	Matrix	Sample Number[1]	Expected Range of Results	MDL	Sample Prep Method	Analytical (Instrumental) Method	Analytical Lab
6PPD-q	water	400	10–500 ng/L	0.368 ng/L	Extractions	LC-MS-MS	MEL
6PPD-q	water splits	40	0.01–500 ng/L	0.368 ng/L	Extractions	LC-MS-MS	TBD
SSC	water	120	0.5–50 mg/L	0.5	N/A	ASTM D3977 B	MEL
TSS	water	120	100–350 mg/L	0.1	N/A	SM2540D	MEL
TOC	water	120	1–20 mg/L	1	N/A	SM 5310B	MEL
DOC	water	120	0.5–20 mg/L	0.5	N/A	SM 5310B	MEL
TWC	water	TBD	—	—	—	HRMS	TBD

Note. Annual estimate for spatial study for an estimate of 24 days of sampling. Collections will be coordinated with local groups.
DOC = Dissolved organic carbon.
MDL = Minimum dectection limit.
MEL = Manchester environmental laboratory.
N/A = Not applicable.
SSC = Suspended solids concentration.
TOC = Total organic carbon.
TSS = Total suspended solids.
TWC = Tire wear contaminant.
[1] Each QA batch consists of 20 samples, with one designated chemist and instrument MEL can analyze up to five batches, or 100 samples/week at full capacity. A more realistic estimate at interim lab capacity is 40 samples per week. Field teams can collect a batch of samples per day/event (3 reps x 5 sites = 15 samples, 2 MS/MSD, 1 FB, 1 MB/ event, a total of 19 samples).

Table 26. Estimated number of samples per day (storm event) for spatial studies sampling.

Analyte	Sample type	Sample number
6PPD-q	Surface water (3/site × 5 sites)[1]	15
6PPD-q	Matrix Spike and Duplicate	2
6PPD-q	Field blank	1
6PPD-q	Manufacture blank (ride-along bottle blank)	1
TOC	Receiving water (1/site × 5 sites) + duplicate	6
DOC	Receiving water (1/site × 5 sites) + duplicate	6
SSC	Receiving water (1/site × 5 sites) + duplicate	6
TSS[2]	Receiving water (1/site × 5 sites) + duplicate	6
TWC	Receiving water (1/site × 5 sites) + duplicate	6

DOC = Dissolved organic carbon.
SSC = Suspended solids concentration.
TOC = Total organic carbon.
TSS = Total suspended solids.
TWC = Tire wear contaminant.
[1] Number of samples/site may be decreased to two depending on initial sampling results.
[2] TSS will be an optional analysis, depending on the selected sites.

9.1.2 Toxics in salmon watersheds Bioassay Study Sampling plan

Table 27. Measurement methods for Toxics in salmon watersheds bioassay study.

Analyte	Sample Matrix	MDL	Sample Prep Method	Analytical (Instrumental) Method
6PPD-q	water sediments periphyton	0.368 ng/L (water) TBD (sediment) TBD (tissue)	Extractions	LC-MS-MS
SSC	water	0.5	—	ASTM D3977 B
TSS	water	0.1	—	SM2540D
TOC	water	1	—	SM 5310B
TOC	sediments	0.1%	PSEP TOC	PSEP TOC
DOC	water	0.5	—	SM 5310B
TWC	water	—	—	HRMS
eDNA	water sediments periphyton diet	—	WDFW SOP	Molecular
Zinc (Zn)	solid	2.5 mg/Kg dw[1]	SW 3050B	SW 6020B
Copper (Cu)	solid	0.05 mg/Kg dw	SW 3050B	SW 6020B
Lead (Pb)	solid	0.05 mg/Kg dw	SW 3050B	SW 6020B
Arsenic (As)	solid	0.05 mg/Kg dw	SW 3050B	SW 6020B
Cadmium (Cd)	solid	0.01 mg/Kg dw	SW 3050B	SW 6020B
Nickel (Ni)	solid	0.05 mg/Kg dw	SW 3050B	SW 6020B

Note. Samples per storm estimate for one stream, the goal is to measure >3 storms/ year in select streams). Solid refers to sediments, periphyton, or tissue.
DOC = Dissolved organic carbon.
MDL = Minimum dectection limit.
SSC = Suspended solids concentration.
TOC = Total organic carbon.
TSS = Total suspended solids.
TWC = Tire wear contaminant.
[1] Measured in wet weight (ww) for tissues.

Table 28. Annual estimate of samples collected per stream for the salmon in urban streams bioassay pilot project.

Analyte	Sample matrix	Samples (number/ storm event)	Number of storms/ year	Number of samples/ stream/ year
6PPD-q	water	48	4	192
SSC	water	8	3	24
TSS[1]	water	8	3	24
TOC	water	8	3	24
DOC	water	8	3	24
eDNA	water	4	3	12
TWC	water	4	3	12
6PPD-q	sediment	12	3	36
TOC	sediment	8	3	24
Metals (6)	sediment	4	3	12
6PPD-q	periphyton	8	3	24
eDNA	periphyton	4	3	12
Metals (6)	periphyton	4	3	12
ID & enumeration	periphyton	4	3	12
Metals (6)	tissue	4	3	12
6PPD-q	tissue	4	3	12

Note. Actual storms sampled per year may vary depending on weather.
DOC = Dissolved organic carbon.
eDNA = Environmental DNA.
SSC = Suspended solids concentration.
TOC = Total organic carbon.
TSS = Total suspended solids.
TWC = Tire wear contaminant.
[1] TSS is an optional analyte and will depend on the site and study.

Table 29. Measurement methods for Directed studies[1].

Analyte	Sample Matrix	Expected Range of Results	MDL	Sample Prep Method	Analytical (Instrumental) Method
6PPD-q	water, sediment, tissue	0.01–500 ng/L; µg/kg for sediment	0.368 ng/L (water) TBD (sediment), TBD (tissue)	Extractions	LC-MS-MS
SSC	water	0.5–50 mg/L	0.5	N/A	ASTM D3977 B
TSS[2]	water	<1500 mg/L	1.0 mg/L	N/A	SM2540D
TOC	water	1–20 mg/L	1	N/A	SM 5310B
DOC	water	0.5–20 mg/L	0.5	N/A	SM 5310B
TOC	sediments	1%–15%	0.1%	PSEP TOC	PSEP TOC
TWC	water sediments	N/A	N/A	N/A	HRMS

DOC = Dissolved organic carbon.
MDL = Minimum dectection limit.
N/A = Not applicable.
SSC = Suspended solids concentration.
TOC = Total organic carbon.
TSS = Total suspended solids.
TWC = Tire wear contaminant.
[1] Sample numbers for directed studies will be estimated and reviewed in work plan memos or IAA QAPPS and at the discretion of the QA officer and TSU supervisor. In general, sample numbers will likely not exceed 30 samples.
[2] TSS is an optional analyte and will depend on the site and study.

9.2 Sample preparation method(s)

In situ active samplers pump water through solid phase extraction (SPE) filters. The filters must be prepped by flushing with a solvent before deployment, preferably at MEL (Wong 2019; Hobbs 2019). In addition, a performance reference compound (PRC) can be added to each filter to measure the loss of 6PPD-q over the duration of the study.

The passive samplers use HLB media as well. The contract lab will prep the HLB media with a PRC in the POCIS prior to shipment.

9.3 Special method requirements

MEL and TSU are working together to develop methods for 6PPD-q in sediments and tissues and comparing the effectiveness of different sampling devices. Many supplies and procedures have been procured and developed during the device comparison study implemented in the winter of 2023 to extract C.L.A.M. HLB and GF filters. Depending on the preliminary results of the device comparison study, additional supplies and methods may need to be developed at MEL to extract the SP3 and POCIS passive samplers before analysis. In addition, the exploratory nature of this programmatic QAPP may require some flexibility and adaptive management as we analyze Ecology's first-ever 6PPD-q sampling results.

9.4 Laboratories accredited for methods

MEL has applied for lab accreditation. The 6PPD-q monitoring lead will request a laboratory waiver for the implementation of this project unless a lab is accredited prior to the approval to start work. Lab waivers will be needed for eDNA work at WDFW and the TWC analysis at USGS.

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

Table 30 presents the QC samples that will be measured in the field, analyzed in the lab, or otherwise evaluated.

Table 30. Quality control samples, types, and frequency.

Parameter	Field Blanks	Field Replicates	Field Method Spikes	Lab Check Standards	Lab Method Blanks	Analytical Duplicates	Lab Matrix Spikes
6PPD-q	1/event[1]	2/event	TBD[2]	1/batch	1/batch	1/batch	1/sample
SSC	—	10% of samples	—	1/batch	1/batch	—	—
TSS	—	10% of samples	—	1/batch	1/batch	1/batch	—
TOC/DOC	—	10% of samples	—	1/batch	1/batch	1/batch	1/batch
eDNA	1/event	1/event	—	1/batch	1/batch	1/batch	—
TWC	TBD	—	—	—	—	—	—

DOC = Dissolved organic carbon.
N/A = Not applicable.
SSC = Suspended solids concentration.
TOC = Total organic carbon.
TSS = Total suspended solids.
TWC = Tire wear contaminant.
[1] Event refers to a new site, matrix, time interval, or device type; 2 samples are the minimum, and 3 samples are preferred depending on the study type until more sampling has been conducted to compare the variability and precision of each sampling method.
[2] The field spike methods are being evaluated; if they are added to the SOP, then 2 samples per event will be collected.

10.2 Corrective action processes

The laboratory analysts will document whether project data meets method QC criteria. Any departures from normal analytical methods will be documented by the laboratory and described in the laboratory data package and in the project's final report. If any samples do not meet QC criteria, the project manager will determine whether data should be reanalyzed, rejected, or used with appropriate qualification. Field instruments will be checked and calibrated prior to the fieldwork. The post-field check of the instrument should be within the MQOs defined in Table 8. The appropriate qualification or rejection threshold is detailed in the MQOs.

11.0 Data Management Procedures

11.1 Data recording and reporting requirements

This project's Environmental Information System (EIM) Study ID is RHSM0001.

Field data will be recorded in a bound, waterproof notebook on Rite in the Rain paper. Corrections will be made with single-line strikethroughs, initials, and dates. Data will be transferred to Microsoft Excel templates for creating data tables and entry into EIM. Data will be entered into EIM by the project data steward. Once entered into EIM, the project manager will verify the sample locations and project description. An R script will verify each entry with the original laboratory data EDD and data tables. Watershed and land use characterizations for each site and the GPS coordinates to support spatial assessments of 6PPD-q hot spots will be recorded.

11.2 Laboratory data package requirements

The laboratory data package will be generated or overseen by MEL. MEL will provide a project data package that will include a narrative discussing any problems encountered in the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. Quality control results will be evaluated by MEL (discussed below in Section 13.0 Data Verification). A level 4 data package will be required from the non-MEL contracted labs, and MEL will be contracted to validate the data package further if required.

The following data qualifiers will be used:

- "J" — The analyte was positively identified. The associated numerical result is an estimate.
- "UJ" — The analyte was not detected at or above the estimated reporting limit.
- "NJ" — The analysis indicates the presence of an analyte that has been "tentatively identified," and the associated numerical value represents its approximate concentration.

The qualifiers will be used following the method reporting limits such that:

- For non-detect values, the estimated detection limit (EDL) is recorded in the "Result Reported Value" column and a "UJ" in the "Result Data Qualifier" column.
- No results are reported below the EDL.
- Only results reported that have a value at least FIVE times the signal-to-noise ratio and meet ion abundance ratios required by the method.
- Detected values that are below the quantitation limits (QL) are reported and qualified as estimates ("J").
- Results that do not meet ion abundance ratio criteria are reported with "NJ." If an Estimated Maximum Possible Concentration (EMPC) value is calculated and reported, the calculation is explained in the narrative, and an example calculation used for this value is provided.

11.3 Electronic transfer requirements

All laboratory data will be accessed and downloaded from MEL's Laboratory Information Management System (LIMS) into Excel spreadsheets. The contract lab will provide an electronic data deliverable (EDD) that meets the format defined by MEL.

11.4 EIM data upload procedures

All completed project data will be entered into Ecology's Environmental Information Management (EIM) database for availability to the public and interested parties, except for the surface water data generated using passive and in situ active samples. Concentrations of 6PPD-q generated using passive samplers are considered estimates by Ecology and are not entered into EIM. Data entered into EIM follow a formal data review process where data are reviewed by the project manager, the person entering the data, and an independent reviewer.

EIM can be accessed on Ecology's Internet homepage at www.ecology.wa.gov. The project will be searchable under Study ID RHSM0001.

11.5 Model information management

N/A

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

No defined audit exists for the fieldwork in this project. The Ecology Environmental Laboratory Accreditation Program evaluates a laboratory's quality system, staff, facilities and equipment, test methods, records, and reports. It also establishes that the laboratory can provide accurate, defensible data. All assessments are available from Ecology upon request, including MEL's internal performance and audits.

Non-MEL contracted labs will provide a level 4 data package, and MEL will be contracted to validate further if required.

12.2 Responsible personnel

The project manager will be responsible for all reporting.

12.3 Frequency and distribution of reports

Interim reports will be written at the end of each focused study. One final report will synthesize the spatial data and the urban watershed pilot study and recommend further actions. The report will review each of the method development strategies and milestones to help guide future work and chemical action planning.

12.4 Responsibility for reports

The TWC monitoring strategist project lead will author the report.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

The field assistant will review field notes once they are entered into Excel spreadsheets. The project manager will provide oversight.

13.2 Laboratory data verification

As previously described, MEL will oversee the review and verification of all laboratory data packages analyzed or managed by MEL. All data managed and generated by MEL contracted labs must be included in the final data package, including but not limited to:

- A text narrative.
- Analytical result reports.
- Analytical sequence (run) logs.
- Chromatograms.
- Spectra for all standards.
- Environmental samples.
- Batch QC samples.
- Preparation of benchsheets.

All necessary QA/QC documentation must be provided, including results from matrix spikes, replicates, and blanks.

Non-MEL contracted labs will provide a level 4 data package, and MEL will be contracted to validate further if required.

13.3 Validation requirements, if necessary

A level 2B data validation will be requested for this project but will include the conversion of contract laboratory flags to MEL-amended qualifiers. The MEL QA Coordinator will conduct data validation. A level 4 data package will be required from contract labs should a level 4 data validation be necessary.

13.4 Model quality assessment

N/A

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

The project manager will determine if the project data are useable by assessing whether the data have met the MQOs outlined in Tables 14 and 15. Based on this assessment, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

14.2 Treatment of non-detects

Data sums will be qualified with the following:

- "J" if that is the only qualifier used.
- "NJ" if that is the only qualifier used.
- "J" if there is a mix of "J" and "NJ" qualifiers.

When all values for individual analytes in the group are reported as non-detects, and the reporting limits are different, the highest value present is assigned as the "total" value. The sum "total" will be qualified with:

- "U" if that is the only qualifier used.
- "UJ" if that is the only qualifier used.
- "U" if there is a mix of both "U" and "UJ."

14.3 Data analysis and presentation methods

Efforts will be made to constrain the local variability of the sample media (through replication) and use this as a confidence interval when comparing sample concentrations. This will determine whether there are true differences between upstream and downstream of suspected hotspots. The assortment of sampling methods being compared requires statistical tests to summarize the performance of each method. The concentration will be correlated with watershed characteristics and temporal and climatic variables. Replication, precision, and accuracy will be measured using similar methods in Hobbs (2018). Data packages, including Excel, R, and ArcPro GIS, will be employed to visualize and compare the data.

14.4 Sampling design evaluation

The sampling design of this project will undergo evaluation between sampling events. The effectiveness of the sample media, the spatial resolution of the samples, and our ability to access the necessary sample sites will undergo revision, if necessary, post-reconnaissance.

14.5 Documentation of assessment

The final report will present this study's findings, interpretations, and recommendations.

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16.0 Appendices

16.1 Appendix A. An evaluation of toxic and aquatic monitoring efforts to identify sampling opportunities.

- River and Stream Water Quality Monitoring[1]
- River and Stream Flow Monitoring[2]
- Intensively Monitored Watersheds[3]
- Stream Biological Monitoring[4]
- Watershed Health Monitoring[5]
- Aquatic Plant Monitoring[6]
- BEACH Program[7]
- Marine Water and Sediment Monitoring[8]
- Toxics Studies and Monitoring[9]
- Water Quality Effectiveness Monitoring[10]
- Marine Nearshore Mussels and Fish in the Puget Lowlands Ecoregion (WDFW-TBioS)[11]
- Guidance for Effectiveness Monitoring of Total Maximum Daily Loads in Surface Water[12]

These programs make up the regional and statewide monitoring and assessment programs used to help Ecology and EPA meet the prerequisites of the federal Clean Water Act. The management plan to control nonpoint sources of pollution describes these programs and explains how they fit into Washington State's overall monitoring strategy (Rau 2015). In addition to Ecology's Puget Sound and statewide monitoring programs, other local, State, Federal, and Tribal governments have additional, targeted water quality and quantity monitoring efforts. Leveraging local monitoring efforts or programs is integral to the success and efficiency of a broad-scale toxics monitoring study.

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[1] https://ecology.wa.gov/Research-Data/Monitoring-assessment/River-stream-monitoring/Water-quality-monitoring
[2] https://ecology.wa.gov/Research-Data/Monitoring-assessment/River-stream-monitoring/Flow-monitoring
[3] https://ecology.wa.gov/Research-Data/Monitoring-assessment/River-stream-monitoring/Intensively-monitored-watersheds
[4] https://ecology.wa.gov/Research-Data/Monitoring-assessment/River-stream-monitoring/Habitat-monitoring/Stream-biological-monitoring
[5] https://ecology.wa.gov/Research-Data/Monitoring-assessment/River-stream-monitoring/Habitat-monitoring/Watershed-health
[6] https://ecology.wa.gov/Regulations-Permits/Guidance-technical-assistance/Aquatic-weed-control-technical-assistance
[7] https://ecology.wa.gov/Water-Shorelines/Water-quality/Saltwater/BEACH-program
[8] https://ecology.wa.gov/Research-Data/Monitoring-assessment/Puget-Sound-and-marine-monitoring
[9] https://ecology.wa.gov/Waste-Toxics/Reducing-toxic-chemicals/Toxics-studies
[10] https://ecology.wa.gov/Research-Data/Monitoring-assessment/Water-quality-improvement-effectiveness-monitoring
[11] https://wdfw.wa.gov/publications/02316
[12] https://apps.ecology.wa.gov/publications/documents/1303024.pdf

Watershed Health Monitoring

Watershed health monitoring utilizes biological indicators of disturbance for status and trends, asking the question. “What is the overall health of this stream or river?”. Site-specific biological monitoring of invertebrates and biofilms provides trends in watershed management effectiveness. Watershed health monitoring requires long-term, consistent measurements of the biological communities and the many potential attributes impacting the condition of the water body. The benthic index of biotic integrity (B-IBI) is a quantitative method for comparing streams and provides a powerful tool for measuring the effectiveness of water quality enhancement (Larson et al. 2019; Figure A-2). Some urban sites are associated with this program, and the Puget Sound watershed is sampled every seven years. **Most of the sampling occurs in the summer during the dry periods and is not designed to measure or capture storm event-driven transport of CECs. However, the application of bioassessment methods used by WHM in conjunction with 6PPD-q analysis in urban watersheds during the wet season would be valuable.**

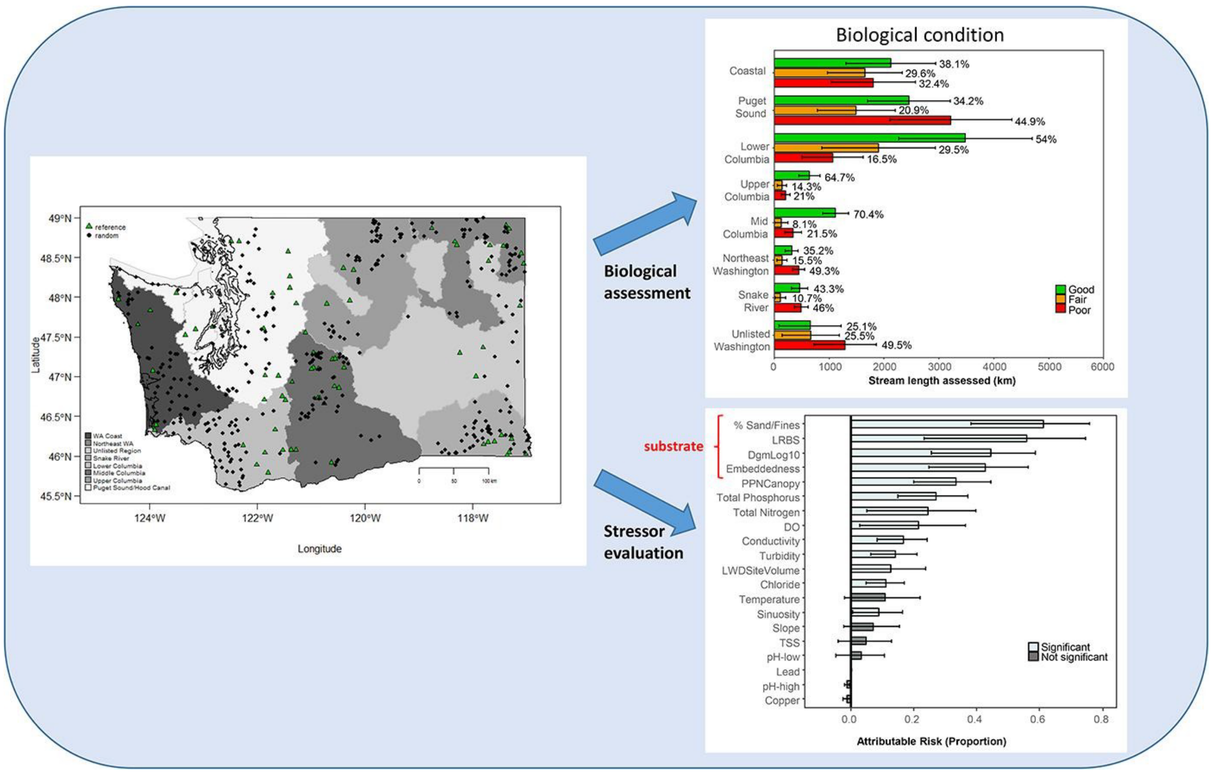

Figure A-2. Sampling sites and corresponding results from the watershed health monitoring program bioassessments (Larson et al. 2019).

Monitoring Freshwater Rivers and Streams

A long-term river and stream monitoring team collects long-term data[1] to track trends in stream health and contribute to watershed studies and water quality improvement plans. In partnership with streamflow scientists, water quality scientists also maintain a network of continuous monitoring stations to collect 24-hour data[2] for dissolved oxygen, temperature, pH, and conductivity in many rivers and streams statewide (Figures A-3 and A-4).

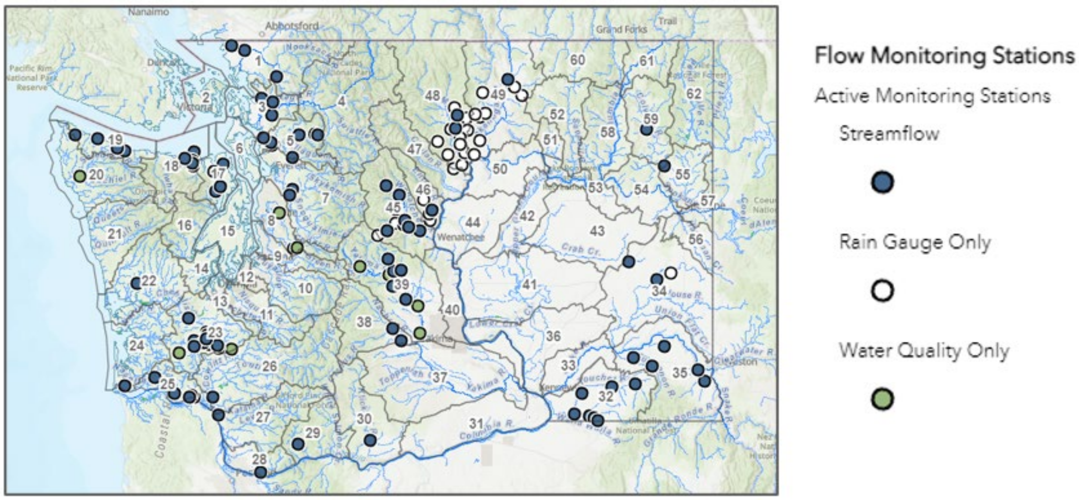

Figure A-3. Active flow monitoring stations maintained by Ecology.

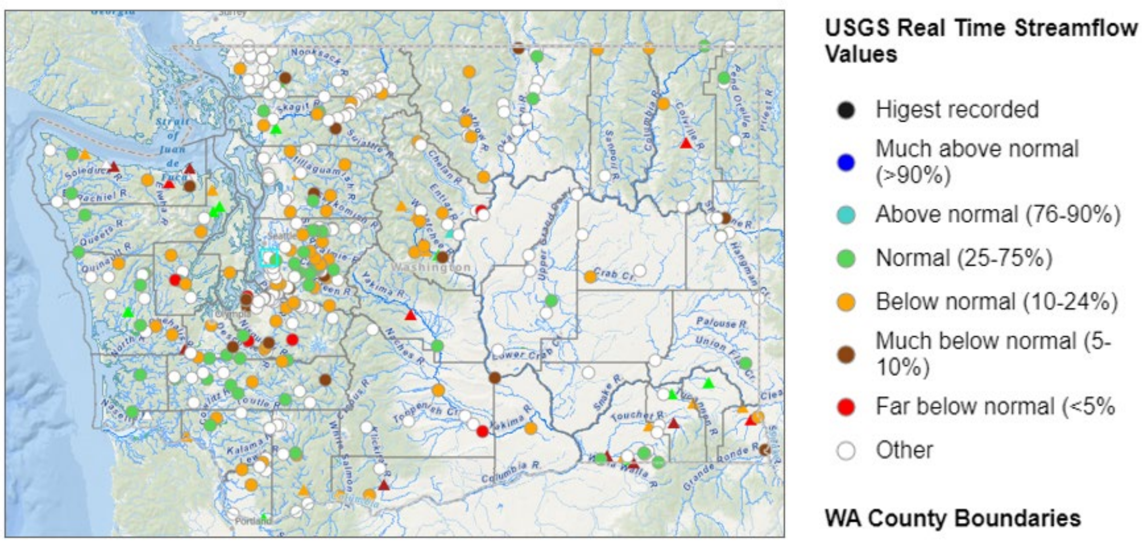

Figure A-4. Stream flow conditions in Washington State, USGS, and Ecology sites.

Stream ecologists use rope and weighted containers to collect single surface-grab samples from highway bridges or, depending on accessibility, from the stream bank. Temperature is measured

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[1] https://apps.ecology.wa.gov/eim/search/SMP/RiverStreamSearch.aspx?StudyMonitoringProgramUserId=RiverStream&StudyMonitoringProgramUserIdSearchType=Equals&MPLocationStatus=Active

[2] https://apps.ecology.wa.gov/continuousflowandwq/

in-stream using a long-line thermistor or electronic tracking device. Water samples are measured in the field or are processed for shipment to the Manchester Environmental Laboratory. Samples are collected year-round from specific sites encompassing larger rivers and streams throughout the State. **Cross-referencing watersheds of interest for 6PPD-q sampling and where there are existing data and collections could help focus opportunistic sampling efforts.**

The freshwater rivers and streams program conducts monthly sampling at 12 different sites for a year to support the water quality assessments. The latest water quality assessment reported that 15% of our water bodies have been assessed over the years. There are 41,988 unique water quality listings on Washington water, a 41% increase from the last assessment (Ecology 2022b[1]). There are 22,721 listings for toxics in Washington State; 15,168 are in the insufficient data category (Table A-1; Figure A-5). **Cross-referencing stream and river conditions with 6PPD-q concentrations could help identify areas affected by road runoff.**

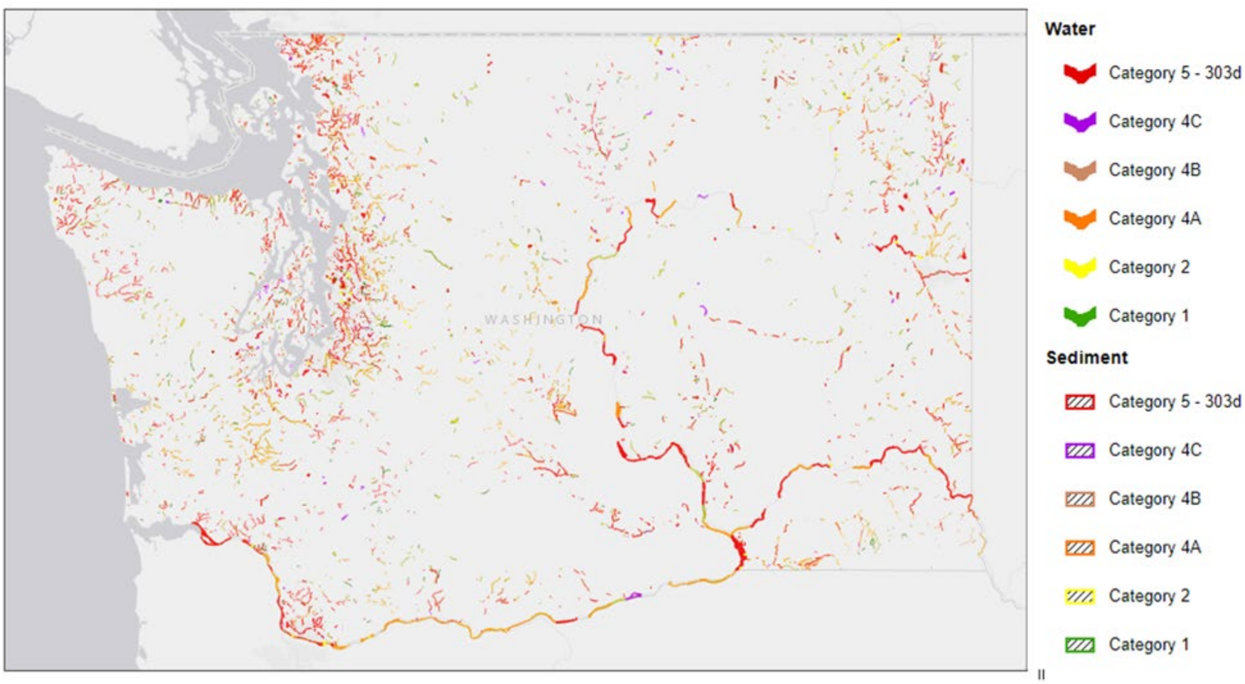

Figure A-5. Water quality assessments conducted by Ecology and readily available data from several other local, state, and federal agencies, tribes, and environmental groups (Table A-1).

[1] https://apps.ecology.wa.gov/publications/documents/2210017.pdf

Table A-1. Water quality assessment listing summary for Washington State (2018).

Assessment Category for Toxics	Listed Waterbodies
Category 1 (meets standards)	4,669
Category 2 (waters of concern)	1,733
Category 3 (insufficient data)	15,168
Category 4 (has a TMDL or CAP)	182
Category 5 (impaired and on the 303d list)	969
Total Listings	22,721

Effectiveness Monitoring for Water Quality TMDL Plans

Effectiveness monitoring helps us gauge how well our projects are working to reduce pollution in state waters. It is important to evaluate whether we have successfully achieved the goals of a water quality improvement plan to meet state and federal clean water standards (Figure A-6).

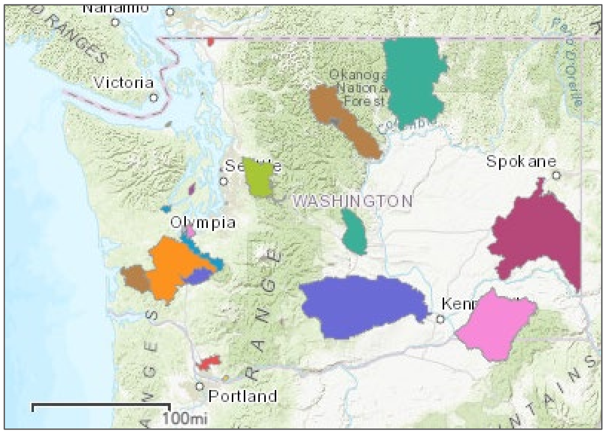

Figure A-6. Watershed scale past and current effectiveness monitoring studies.

Monitoring data guides cleanup plans, particularly those that identify pollution-loading limits known as TMDLs (Total Maximum Daily Loads). We can modify cleanup approaches as needed, upgrade or change water body listings, or seek more effective methods to reduce pollution in the long term.

It is also one of the several required components when (1) we develop Total Maximum Daily Loads (TMDLs) or other watershed-based pollution control plans, or (2) state and federal funds are used to implement nonpoint-source pollution control strategies.

Monitoring for Toxic Chemicals

The toxics studies program collects environmental samples to assess whether toxic chemicals in soil, tissue, and water are increasing, decreasing, or staying the same in Washington. Long-term studies and focused short-term studies are catered to each contaminant, suspected source, and sensitive habitat. Many long-term studies focus on substances that accumulate and are passed through the food chain, referred to as persistent, bio-accumulative, and Toxic substances (PBTs). Directed studies encompass contaminants research for water quality improvement plans, stormwater studies, Chemical Action Plans, and other specific toxics projects in support of agency-wide initiatives.

16.2 Appendix B. Summary of the occurrence of 6PPD-q in the environment.

Table B-1. Summary of sampling events for 6PPD-q.

Location and Timing	Sample Method	Timing	Sample Type	Land Use	Detected	Non-Detected	6PPD-q (µg/L)	Coho LC-50 0.04–0.09 (µg/L)
Seattle, WA, US[1]	Grab	During Storm	Road surface	Urban highway	6	1	<0.05–1.27	Above
Seattle, WA, US[1]	Grab	Between Storm	Creek	Urbanized residential watersheds (Miller Cr., Longfellow Cr., Thornton Cr.)	0	15	—	Below
Los Angeles, CA, US[1]	Grab	During Storm	Road surface	Urban highway	2	0	0.49–0.74	Above
San Francisco Bay Area, CA, US[1]	Time Composite Samples	During Storm	Creek	Urban and Reference sites	4	6	0.12–0.42	Above
Michigan, US[2]	Grab	Post Storm 35 hrs.	Creek	Various	2	17	0.012–0.037	Below
Michigan, US[2]	Grab	Storm	Road surface & puddles	Various	5	0	0.054–0.66	Above
Central California, US[3] Dry Season	Grab	Dry Season	River	—	0	10	—	—
Central California, US[3] Wet Season	Grab	Wet Season	River	—	2	8	0.002–0.014	Below
Toronto, Canada[4]	Composite (42 hours)	Storm	River	Urban, downstream of high-traffic corridor (Don River)	—	—	0.3–2.3	Above
Saskatoon, Canada[5]	Composite	Storm	Outfall	Urban (residential / light industrial)	—	—	0.086–1.40	Above
Saskatoon, Canada[5]	Composite (8–12 snow piles)	Snow	Snow-melt	Urban (residential / light industrial)	—	—	0.015–0.756	Above
Nanaimo, BC, Canada6	Grab	Storm	Creek	Unknown	2	0	0.096–0.112	Above

Location and Timing	Sample Method	Timing	Sample Type	Land Use	Detected	Non-Detected	6PPD-q (µg/L)	Coho LC-50 0.04–0.09 (µg/L)
Nanaimo, BC, Canada[6]	Grab	Storm	Storm-water	Unknown	4	—	0.048–5.58	Above
Hong Kong[7]	Grab	Storm	Road surface	Dense traffic, urban area	9	0	0.021–0.243	Above
Brisbane, Australia[8]	Grab	Post storm 18 days dry	Creek	Sub-urban (low density residential (open space)	9	0	0.0004–0.08	Below

[1] Tian et al. 2022
[2] Nedrich 2022
[3] Patterson, 2022 Eurofin presentation to EPA group
[4] Johannessen et al. 2021, 2022
[5] Challis et al. 2021
[6] Monaghan et al. 2021
[7] Cao et al. 2022
[8] Rauert et al. 2022

16.3 Appendix C. A list of watersheds designated as essential fish habitat and at risk of 6PPD-q exposure.

(Pacific Salmon Fisheries Commission (PSFC), State Wide Integrated Fish Distribution (SWIFD) GIS 2022 and Ecology 2022a: Publication 22-03-020).

This is not a complete list of all the vulnerable streams in Washington State. The 6PPD map has a more complete list of vulnerable areas at a smaller NHDplus stream catchment scale.

Table C-1. Watersheds designated as essential fish habitat[1].

Watershed Code	Watershed Name	General Watershed Land use	Reference available	WA Area	Chinook	Coho	Winter Steelhead	Summer Steelhead
17020005	Chief Joseph	Rural	Yes	Eastern	X	X	—	X
17020011	Wenatchee	Mid-urban	Yes	Eastern	X	X	—	X
17020008	Methow	Rural	Yes	Eastern	X	X	—	X
17020012	Moses Coulee	Rural	Yes	Eastern	X	X	—	X
17030001	Upper Yakima	Rural	Yes	Eastern	X	X	—	X
17030003	Lower Yakima	Mid-urban to Rural (Ag)	Yes	Eastern	X	X	—	X
17030002	Naches	Low-urban to Rural Highway	Yes	Eastern	X	X	—	X
17060103	Lower Snake: Asotin	Mid-urban to Industrial	Yes	Eastern	X	X	—	X
17070101	Middle Columbia: Lake Wallula	Rural Low-urban (Walla Walla River)	Yes	Eastern	X	X	—	X
17060106	Lower Grande Ronde	Low-urban and Rural	Yes	Eastern	X	X	—	X
17060107	Lower Snake-Tucannon	Highway (12) Reference	Yes	Eastern	X	X	—	X
17070105	Middle Columbia: Hood	Low-urban and Rural	Yes	Western	X	X	X	X
17070106	Klickitat	Rural	Yes	Western	X	X	X	X
17080001	Lower Columbia: Sandy	Mid-urban Industrial Rural	Yes	Western	X	X	X	X
17080002	Lewis	Low-urban Highway	Yes	Western	X	X	X	X
17080004	Upper Cowlitz	Rural	Recon	Western	X	X	X	X
17080005	Cowlitz	Mid-urban Rural Highway	Recon	Western	X	X	X	X
17080006	Lower Columbia	High-urban Industrial Rural Highways	Recon	Western	X	X	X	X
17100101	Hoh-Quillayute	Highway Reference	Yes	Western	X	X	X	X
17100102	Queets-Quinault	Highway Reference	Yes	Western	X	X	X	X
17100103	Upper Chehalis	Low to Mid-urban Rural Industrial Highway	Recon	Western	X	X	X	—
17100104	Lower Chehalis	Low to Mid-urban Rural Industrial Highway	Recon	Western	X	X	X	—
17100105	Grays Harbor	Low-urban Highway	Yes	Western	X	X	X	—
17100106	Willapa	Low-urban Highway	Recon	Western	X	X	X	—

Watershed Code	Watershed Name	General Watershed Land use	Reference available	WA Area	Chinook	Coho	Winter Steelhead	Summer Steelhead
17110001	Fraser	High-urban Highway	Recon	Western	X	X	X	—
17110002	Strait Of Georgia	ALL	No	Western	X	X	—	—
17110003	San Juan Islands	Low-urban Rural Local Roads Only	Recon	Western	—	X	—	—
17110004	Nooksack	Mid-urban Rural Industrial Highway	Yes	Western	X	X	X	X
17110005	Upper Skagit	Low-urban Rural Industrial Highway	Yes	Western	X	X	X	X
17110006	Sauk	Highway Reference	Yes	Western	X	X	X	X
17110007	Lower Skagit	Mid-urban Rural Industrial Highway	Recon	Western	X	X	X	X
17110008	Stillaguamish	Mid-urban Rural Highway	Yes	Western	X	X	X	X
17110009	Skykomish	High to Low-urban Industrial Rural Hwy	Yes	Western	X	X	X	X
17110010	Snoqualmie	Mid-urban Industrial Rural	Recon	Western	X	X	X	X
17110011	Snohomish	High to Low-urban Industrial Rural Hwy	Recon	Western	X	X	X	X
17110012	Lake Washington	High-urban Industrial Highways	Recon	Western	X	X	X	X
17110013	Duwamish	High-urban Industrial Highways	Recon	Western	X	X	X	X
17110014	Puyallup	High-urban Industrial Highways	Yes	Western	X	X	X	—
17110015	Nisqually	Mid-urban Industrial Rural Highways	Yes	Western	X	X	X	—
17110016	Deschutes	Mid-urban Industrial Rural Highways	Yes	Western	X	X	X	—
17110017	Skokomish	Low-urban Rural Highway	Yes	Western	X	X	X	X
17110018	Hood Canal	Low-urban Rural Highway	Recon	Western	X	X	X	X
17110019	Puget Sound Suquamish	High-urban Industrial Highways	Recon	Western	X	X	—	—
17110020	Dungeness: Elwha	Rural Highway Reference Site	Yes	Western	X	X	X	—
17110021	Crescent: Hoko	Rural Recreation Highway	Recon	Western	X	X	X	X

[1]This list does not include all vulnerable watersheds in Washington State .

16.5 Appendix D. Glossaries, acronyms, and abbreviations

Glossary of General Terms

Ambient: Background or away from point sources of contamination. Surrounding environmental condition.

Anthropogenic: Human-caused.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

Effluent: An outflowing of water from a natural body of water or from a human-made structure. For example, the treated outflow from a wastewater treatment plant.

Municipal separate storm sewer systems (MS4): A conveyance or system of conveyances (including roads with drainage systems, municipal streets, catch basins, curbs, gutters, ditches, manmade channels, or storm drains): (1) owned or operated by a state, city, town, borough, county, parish, district, association, or other public body having jurisdiction over disposal of wastes, stormwater, or other wastes and (2) designed or used for collecting or conveying stormwater; (3) which is not a combined sewer; and (4) which is not part of a Publicly Owned Treatment Works (POTW) as defined in the Code of Federal Regulations at 40 CFR 122.2.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking, and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

Near-stream disturbance zone (NSDZ): The active channel area without riparian vegetation that includes features such as gravel bars.

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities, including but not limited to atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Point source: Source of pollution that discharges at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites where more than 5 acres of land have been cleared.

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Reach: A specific portion or segment of a stream.

Riparian: Relating to the banks along a natural course of water.

Salmonid: Fish that belong to the family *Salmonidae*. Species of salmon, trout, or char.

Sediment: Soil and organic matter that is covered with water (for example, river or lake bottom).

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Streamflow: Discharge of water in a surface stream (river or creek).

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and water courses within the jurisdiction of Washington State.

Thalweg: The deepest and fastest moving portion of a stream.

Total suspended solids (TSS): Portion of solids retained by a filter.

Turbidity: A measure of water clarity. High levels of turbidity can have a negative impact on aquatic life.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

303(d) list: Section 303(d) of the federal Clean Water Act, requiring Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water — such as for drinking, recreation, aquatic habitat, and industrial use — are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

Acronyms and Abbreviations

BMP	Best management practice
DO	Dissolved oxygen
DOC	Dissolved organic carbon
e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
FC	(see Glossary above)
GIS	Geographic Information System software
GPS	Global Positioning System
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NPDES	(See Glossary above)
PBT	Persistent, bioaccumulative, and toxic substance
PCB	Polychlorinated biphenyls
QA	Quality assurance
QC	Quality control
RM	River mile
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
SRM	Standard reference materials
TIR	Thermal infrared radiation
TMDL	(see Glossary above)
TOC	Total organic carbon
TSS	(see Glossary above)
USGS	United States Geological Survey
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife
WQA	Water Quality Assessment
WRIA	Water Resource Inventory Area
WSTMP	Washington State Toxics Monitoring Program
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
Cfs	cubic feet per second
Cfu	colony forming units
Cms	cubic meters per second, a unit of flow
Dw	dry weight
Ft	feet
G	gram, a unit of mass
Kcfs	1000 cubic feet per second
Kg	kilograms, a unit of mass equal to 1,000 grams
kg/d	kilograms per day
km	kilometer, a unit of length equal to 1,000 meters
l/s	liters per second (0.03531 cubic foot per second)
m	meter
mm	millimeter
mg	milligram
mgd	million gallons per day
mg/d	milligrams per day
mg/kg	milligrams per kilogram (parts per million)
mg/L	milligrams per liter (parts per million)
mg/L/hr	milligrams per liter per hour
mL	milliliter
mmol	millimole or one-thousandth of a mole
mole	an International System of Units (IS) unit of matter
ng/g	nanograms per gram (parts per billion)
ng/kg	nanograms per kilogram (parts per trillion)
ng/L	nanograms per liter (parts per trillion)
NTU	nephelometric turbidity units
pg/g	picograms per gram (parts per trillion)
pg/L	picograms per liter (parts per quadrillion)
psu	practical salinity units
s.u.	standard units
µg/g	micrograms per gram (parts per million)
µg/kg	micrograms per kilogram (parts per billion)
µg/L	micrograms per liter (parts per billion)
µm	micrometer
µM	micromolar (a chemistry unit)
µmhos/cm	micromhos per centimeter
µS/cm	microsiemens per centimeter, a unit of conductivity
ww	wet weight

Quality Assurance Glossary

Accreditation: A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)…that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin 2010)

Accuracy: The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms *precision* and *bias* be used to convey the information associated with the term *accuracy* (USGS 1998).

Analyte: An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella (Kammin 2010).

Bias: The difference between the sample mean and the true value. Bias usually describes a systematic difference reproducible over time and is characteristic of both the measurement system and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI) (Kammin 2010; Ecology 2004).

Blank: A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process (USGS 1998).

Calibration: The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured (Ecology 2004).

Check standard: A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards but should be referred to by their actual designator, e.g., CRM, LCS (Kammin 2010; Ecology 2004).

Comparability: The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator (USEPA 1997).

Completeness: The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator (USEPA, 1997).

Continuing Calibration Verification Standard (CCV): A quality control (QC) sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run (Kammin 2010).

Control chart: A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system (Kammin 2010; Ecology 2004).

Control limits: Statistical warning and action limits calculated based on control charts. Warning limits are generally set at +/- 2 standard deviations from the mean, action limits at +/- 3 standard deviations from the mean (Kammin 2010).

Data integrity: A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading (Kammin 2010).

Data quality indicators (DQI): Commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity (USEPA 2006).

Data quality objectives (DQO): Qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions (USEPA 2006).

Data set: A grouping of samples organized by date, time, analyte, etc. (Kammin 2010).

Data validation: An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability, and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

- No qualifier — data are usable for intended purposes.
- J (or a J variant) — data are estimated, may be usable, may be biased high or low.
- REJ — data are rejected, cannot be used for intended purposes.
  (Kammin 2010; Ecology 2004).

Data verification: Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set (Ecology 2004).

Detection limit (limit of detection)**:** The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero (Ecology 2004).

Duplicate samples: Two samples taken from and representative of the same population and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis (USEPA 1997).

Field blank: A blank used to obtain information on contamination introduced during sample collection, storage, and transport (Ecology 2004).

Initial Calibration Verification Standard (ICV): A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples (Kammin 2010).

Laboratory Control Sample (LCS): A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples (USEPA 1997).

Matrix spike: A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects (Ecology 2004).

Measurement Quality Objectives (MQOs)**:** Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness (USEPA 2006).

Measurement result: A value obtained by performing the procedure described in a method (Ecology 2004).

Method: A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed (EPA 1997).

Method blank: A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples (Ecology 2004; Kammin 2010).

Method Detection Limit (MDL): This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of an analyte that, in each matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero (Federal Register, October 26, 1984).

Percent Relative Standard Deviation (%RSD): A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\mathbf{\%RSD = (100 \times s)/x}$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010).

Parameter: A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all parameters (Kammin 2010; Ecology 2004).

Population: The hypothetical set of all possible observations of the type being investigated (Ecology 2004).

Precision: The extent of random variability among replicate measurements of the same property; a data quality indicator (USGS 1998).

Quality assurance (QA): A set of activities designed to establish and document the reliability and usability of measurement data (Kammin 2010).

Quality Assurance Project Plan (QAPP): A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives (Kammin 2010; Ecology 2004).

Quality control (QC): The routine application of measurement and statistical procedures to assess the accuracy of measurement data (Ecology 2004).

Relative Percent Difference (RPD): RPD is commonly used to evaluate precision. The following formula is used:

$$[\mathrm{Abs}(a-b)/((a + b)/2)] \times 100$$

where "Abs()" is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Ecology 2004).

Replicate samples: Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled (USGS 1998).

Representativeness: The degree to which a sample reflects the population from which it is taken; a data quality indicator (USGS 1998).

Sample (field): A portion of a population (environmental entity) that is measured and assumed to represent the entire population (USGS 1998).

Sample (statistical): A finite part or subset of a statistical population (USEPA 1997).

Sensitivity: In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit (Ecology 2004).

Spiked blank: A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method (USEPA 1997).

Spiked sample: A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency (USEPA 1997).

Split sample: A discrete sample subdivided into portions, usually duplicates (Kammin 2010).

Standard Operating Procedure (SOP): A document which describes in detail a reproducible and repeatable organized activity (Kammin 2010).

Surrogate: For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis (Kammin 2010).

Systematic planning: A stepwise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning (USEPA 2006).

References for QA Glossary

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