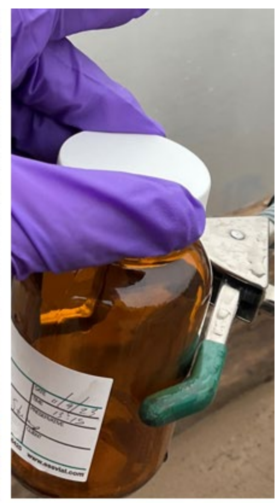
Standard Operating Procedure
EAP093, Version 1.0

Sampling 6PPD-Quinone in Receiving Waters





November 2024

Publication 24-03-205

Purpose of this Document

The Washington State Department of Ecology develops Standard Operating Procedures (SOPs) to document agency practices related to sampling, field and laboratory analysis, and other aspects of the agency's technical operations.

Publication Information

This SOP is available on the Department of Ecology's website at https://apps.ecology.wa.gov/publications/SummaryPages/2403205.html.

Ecology's Activity Tracker Code for this SOP is 24-013.

***Recommended citation*:**
Smith, R.D. 2024. Standard Operating Procedure EAP093, Version 1.0: Sampling 6PPD-Quinone in receiving waters. Publication 24-03-205. Washington State Department of Ecology, Olympia. https://apps.ecology.wa.gov/publications/SummaryPages/2403205.html.

Contact Information

Publications Coordinator
Environmental Assessment Program
Washington State Department of Ecology
P.O. Box 47600
Olympia, WA 98504-7600
Phone: 564-669-3028

Washington State Department of Ecology – https://ecology.wa.gov

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Shoreline 206-594-0000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Union Gap 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

Original Author – Rhea Smith
Date – 9/10/2024

Original Reviewers –
Carley Greyell – King County
Jeff Burkley – King County
Jenee Colton – King County
Dylan Ahearn – Herrera
Brad Archbold – WSDOT
Will Hobbs – Ecology
Siana Wong – Ecology
Mark Jankowski - EPA
Rochelle Labiosa – EPA

Acknowledgements: Thanks to Rachael Lane and Ed Kolodziej labs for container studies

Date – 09/10/2024

QA Approval – Arati Kaza, Ecology Quality Assurance Officer
Certification Date – 09/30/2024

Signatures Available Upon Request

SOP Revision History

1.0 Purpose and Scope

1.1 The purpose of this document is to support standardized occurrence sampling to inform toxics modeling and management strategies.

1.2 This document provides a Standard Operating Procedure (SOP) for the collection of 6PPD-Quinone (6PPD-q) in receiving waters.

1.3 The objective of receiving water sampling is to identify waterways where priority contaminants are a limiting factor for habitat improvement to support aquatic life. Ecology participates in statewide technical coordination work groups to co-locate habitat and pollutant assessments.

1.4 This SOP focuses on measuring outdoor 6PPD-q sourced from (e.g., whole tires, tire wear particles and tire re-use products [e.g. crumb rubber]). Methods for manual, discrete sampling (grab) and autosampling (active) are covered.

1.5 This SOP includes procedures for collecting samples from lotic and lentic waterbodies. Considerations for sampling while wading in water and from boats and bridges are included.

1.6 Following collection, samples must be analyzed at a WA-accredited laboratory using EPA Draft Method 1634. Additional laboratories may be used at the discretion of the Quality Assurance (QA) officer and requires an approved lab waiver. To date, the EPA Draft method is intended for exploratory research and freshwater and stormwater medias. Other medias will require a lab waiver. There is currently no method approved for regulatory sampling under the Clean Water Act.

2.0 Applicability

2.1 This SOP supports 1) research and monitoring to understand the occurrence of 6PPD-q in receiving waters and 2) suspected source identification involving upstream and downstream sampling. It is not intended to satisfy Clean Water Act regulatory sampling requirements. Yet, most of the 6PPD-q considerations discussed are relevant considerations for stormwater discharge monitoring. Additional considerations are provided in Appendix A.

Please see existing stormwater sampling resources:

- Collecting Grab Samples from Stormwater Discharges
- Automatic Sampling for Stormwater Monitoring
- Collection of Stormwater Solids Using In-Line Traps
- Calculating Pollutant Loads for Stormwater Discharges
- Emerging stormwater treatment technologies (TAPE)
- Stormwater Sampling Manual

3.0 Definitions

3.1 6PPD = an organic chemical added to tires and other rubber products to prevent weathering.

3.2 6PPD-q = 6PPD-quinone is an oxidation product of 6PPD.

3.3 Active sample = a sample collected by an autosampler (actively pumps water).

3.4 Autosampler = a sampler that can be programmed to pump water for interval or composite sampling. Many autosamplers can use changes in water quality parameters (e.g. turbidity) or water quantity (e.g. flow and depth) of receiving waters or precipitation to trigger sampling. Some autosamplers can be triggered remotely by the user using cellular or satellite telemetry.

3.5 Composite sample = a sample in which discrete sub-samples collected spatially or temporally, or both, are combined into one container.

3.6 Decontamination = the cleaning of sampling equipment to avoid cross contamination.

3.7 Discrete sample = sample representing one location and point in time.

3.8 Flow-weighted = samples are collected at user-defined continuous incremental volume of discharge (e.g. 20,000 L).

3.9 Flow-weighted composite sampling = user-defined continuous increments are combined into one or more containers.

3.10 Flow-weighted interval sampling = user-defined continuous increments are collected into separate containers.

3.11 Grab sample = a manually collected discrete sample that represents a snapshot in time.

3.12 Influent = the water flowing in.

3.13 Invasive species training = required training to avoid cross contamination of invasive species often from impacted to more pristine waterways.

3.14 Lentic = water bodies such as lakes, ponds, oceans, and bays.

3.15 Lotic = flowing water such as streams, rivers, and canals.

3.16 LAR = Laboratory Analysis Request form.

3.17 Manual start = User manually starts autosampler.

3.18 MEL = Manchester Environmental Laboratory.

3.19 NPDES = National Pollutant Discharge Elimination System. Permit program that addresses water pollution by regulating point sources that discharge pollutants to waters of the United States. Created in 1972 by the Clean Water Act, the NPDES permit program is authorized to state governments by EPA to perform many permitting, administrative, and enforcement aspects of the program.

3.20 Effluent = the water flowing out.

3.21 Peak discharge = when the waterbody (e.g. stream or river) reaches its highest level.

3.22 PPE = Personal protective equipment.

3.23 Receiving water = The water being discharged to.

3.24 Rising limb = The rapid increase of flow from rainfall causing surface runoff and then later throughflow.

3.25 Thalweg = The line defining the points along the length of a stream bed with the greatest volume of moving water, most often the deepest part of the stream.

3.26 Time delayed start = User-defined clock-delayed autosampling start.

3.27 Time-weighted sampling = samples are collected at user-defined time intervals (e.g. 1 hour) and do not represent a constant volume of flow with respect to time.

3.28 Time-weighted composite sampling = user-defined continuous time increments are combined into one or more containers.

3.29 Time-weighted interval sampling = user-defined continuous time increments are discharged into separate containers.

3.30 Triggered sampling = user-defined settings to detect the start of a storm and corresponding sampling.

4.0 Personnel Qualifications/Responsibilities

4.1 Personnel should have training in field safety, environmental collection of toxics, and invasive species management. All Environmental Assessment Program (EAP) field staff must comply with the requirements of the EAP Safety Manual (Ecology 2024).

4.2 All field staff must be familiar with the associated water quality parameters and procedures described in this SOP.

4.3 The field lead directing the sample collection must be knowledgeable in all aspects of the project's Quality Assurance Project Plan (QAPP) to ensure that credible and useable data are collected. All field staff should be briefed by the field lead or project manager on the sampling goals and objectives prior to arriving to the site. Familiarity with organic chemistry and analysis is recommended; And the SOP for 6PPD-q in water analysis (Ecology [MEL][1], 2024; EPA 2023[2]). Familiarity with tire anti-degradant toxicity, source, fate and transport is recommended (Mayer et al. 2024; ITRC 2024).

4.4 EAP staff must be familiar with Ecology's Quality Assurance Manual (Ecology 2019).

4.5 EAP field staff must comply with EAP's Procedure to Minimize the Spread of Aquatic Organisms (Ecology; [3]).

4.6 EAP field staff must complete the Heat stress prevention training.

4.7 EAP science staff must follow MEL Lab User Manual (Ecology: MEL 2016).

5.0 Equipment, Reagents, and Supplies

5.1 **Storage supplies:** regular ice, blue ice, and cooler. There are currently no preservatives for 6PPD-q.

---

[1] Standard Operating Procedure MEL 730136, Version 2.0, Extraction and Analysis of 6PPD-Quinone by EPA 1634 (wa.gov) - https://apps.ecology.wa.gov/publications/SummaryPages/2403203.html

[2] Draft Method 1634 Determination of 6PPD-Quinone in Aqueous Matrices Using Liquid Chromatography with Tandem Mass Spectrometry (LC/MS/MS) (epa.gov) - https://www.epa.gov/system/files/documents/2024-01/draft-method-1634-for-web-posting-1-23-24_508.pdf

[3] Minimize the Spread of Invasive Species - https://apps.ecology.wa.gov/publications/othersupplements/1803201other.pdf

5.2 **Chain of Custody (COC) room:** The research facility must have a designated and secure area to receive, store, stage samples for timely transport.

5.3 Sampling supply list:

- Containers.
- Powder-free nitrile gloves.
- Labels and sample tags with sample numbers pre-assigned by lab.
- Data sheets and clip board or field notebook.
- Pen and pencils.
- Laboratory Analysis Request (LAR) or COC form to record date and time of collection for each pre-assigned sample number.
- Site access tools – equipment to clear brush, manhole hook and sledgehammer, flashlights and work lights, gate keys or permission document if required.
- Subsampling equipment – churn splitter.

5.4 **Container considerations:**

5.4.1 Intermediate sampling containers and devices are not recommended for 6PPD-q sampling to avoid loss from adhesion. However, if special collection equipment is required, follow the container recommendations below.

5.4.2 The contract lab will supply the appropriate sampling bottles. A 250 mL amber glass bottle is supplied for water sampling. Only use bottles that are provided or approved by the participating lab.

5.4.3 Glass and metal are preferred for sampling equipment due to the tendency of 6PPD-q to easily adhere to plastic and rubber surfaces (Hu et al. 2023; Ecology (MEL) 2022; EPA 2023; Lane et al. 2024).

5.4.4 Clear glass bottles are not recommended due to the risk of photodegradation.

5.4.5 Polytetrafluoroethylene (PTFE), High Density Polyethylene (HDPE), Fluorinated ethylene propylene (FEP) or stainless steel can be used for temporary storage when using intermediate containers, when glass isn't an option, but may not be appropriate for low concentration environments. Hu et al. 2023 found moderate sorption tendencies for glass, stainless steel and plastics (PTFE, FEP, PE, and PP), but moderate sorption for trace amounts of 6PPD-q could drive the concentration below the detection or reporting limits. Lane et al. 2024 reported that sorption to plastics occurs rapidly; sorption was 27-48% for HDPE after 29 hours of contact time. Temporary storage refers to the time it takes to collect with an intermediate container and transfer into an amber glass bottle, transfers should be conducted as quickly as possible. And glass is preferred.

5.4.6 Other bottle volumes can be used but coordinate with the lab. 250 mL is recommended to allow for whole bottle extractions (no transferring or splitting required).

5.4.7 Amber glass bottles come in a sealed box that is certified trace clean with a PTFE lid. If the box is open from a previous sampling event, check for damaged bottles or loose lids.

5.5 **Grab sampling supplies:**

- Extension pole with sampling container attachment.
- Bridge or boat sampling equipment.

5.6 **Active sampling supplies:**

- Autosampler with appropriate distribution arm and intermediate containers (glass containers preferred). HDPE bottles are fine for higher concentrations but may not be appropriate for the lower concentrations measured in receiving waters.
- Battery and power cable – battery type will depend on length of deployment.
- Solar panels and power controller for longer deployments or when using refrigerated autosamplers.
- PTFE lined tubing – length of tubing will depend on the site.
- PTFE or metal strainer for the end of the autosampler tubing.
- Autosampler Manual and programming methods.
- Extra ice, unless using a refrigerated unit.
- Stainless steel cable and cutters, copper sleeves and crimpers, wire cutters and a lock.
- For exposed urban sampling sites a locking metal cabinet is recommended to reduce theft and vandalism.
- The appropriate security equipment will depend on whether the equipment is left unattended and for how long.

5.7 **Field blanks:** deionized (DI) water

5.8 **Decontamination supplies (Invasive species):** See EAP Policy 1-15 and EAP070 (Parsons et al. 2018) for information.

5.9 **Decontamination supplies (Field equipment):** aluminum foil, squirt bottle with DI water, squirt bottle with methanol, lab soap and brush, waste container and bucket. See SOP EAP090 (2021) for more information.

5.10 **Instruments:** The instruments required will depend on the objective of your study and should be customized in your QAPP.

- YSI meter – for information on YSI calibrations see EAP SOP12 (Mathieu 2022).
- Rain gauge (rain bucket or weather station).
- Flow meter or gauge (nearby Ecology or USGS flow station or measure directly).

- Depth sensor (Bubbler, radar, or transducer).
- Power, control, and communications hub (telemetry continuous sampling station).

5.11 **Human and safety concerns:** 6PPD and 6PPD-q are known toxicants to aquatic life and should be assumed hazardous for humans. Use gloves and safety glasses to prevent direct contact. Print and review the safety sheet: https://cdn.caymanchem.com/cdn/msds/38247m.pdf

5.12 **Navigation and Access:** A global positioning system (GPS) device or printed maps and directions are needed to locate sampling stations and avoid private property, unless access to the property has been arranged previously. If access to private property is required, contact the landowner well ahead of time for permission.

5.13 **Personal field clothing special considerations:** To date, there is currently no special considerations for rain gear or personal care product contamination for 6PPD and 6PPD-q.

6.0 Summary of Procedure

6.1 **Sampling Considerations:** This section is intended to support occurrence sampling in waterways including streams, rivers, ponds, lakes, wetlands, and estuaries where 6PPD-q is likely fleeting in the upper water column due to dilution, settlement, sorption, or degradation. Start by selecting where, when, and how you plan to sample. The specific project objectives and most appropriate methods should be outlined in the QAPP.

Sampling considerations:

- Why are you sampling?
- Where are you going to sample?
- When are you going to sample?
- How are you going to sample?

6.2 **Sample timing considerations:**

6.2.1 6PPD-q in surface water and Urban Runoff Mortality Syndrome (URMS) events are associated with consolidation and transport of toxics by urban surface runoff (e.g. pavement). Therefore, collecting samples during storm events is recommended. Documenting information about the storm will help with result interpretation.

6.2.2 Flexible storm event criteria are recommended until more information is available regarding the fate and transport of the contaminant. Measuring concentrations across storms of variable intensities, durations, and intervals will help fill in fate and transport data gaps. Criteria will also vary depending on the size and characteristics of the watershed. Criteria for required NPDES stormwater discharge sampling typically has more specific storm criteria and reporting to accurately estimate pollutant loading. A special 6PPD-q consideration is that the peak contaminant concentration may lag the peak flow of the storm event by several hours (Johannessen et al. 2022). Additional information is available in the container considerations section.

6.3 Sample location considerations

6.3.1 Important considerations when selecting a stream sampling site include accessibility (steep slopes, private vs. public property, safety, and visibility to avoid vandalism and theft), and proximity to suspected point or non-point sources.

6.3.2 Suspected Point and Nonpoint sources: A tire contaminant interactive web map[4] provides watershed characterization information including the presence of traffic, aquatic life and impervious surfaces. There are many other GIS resources to aid in sampling site selections (Ecology 2022, Ecology 2023, ITRC 2024).

6.3.3 Understanding life histories and movements of aquatic species of interest helps estimate when, where and how often they are exposed to the pollutant. For instance, coho salmon are the most sensitive to 6PPD-q (Tian et al. 2020, Brinkmann et al. 2022, Greer et al. 2023, Montgomery et al. 2023, Ecology 2023) and reside in smaller tributaries in the middle reaches of lowland streams within a watershed. Cross referencing these priority areas of high usage with traffic and land use characteristics can help prioritize study sites.

6.3.4 Additional, higher resolution information regarding upstream stormwater conveyance systems (e.g. piping and ditches) can be obtained from the local communities. In general, stormwater conveyance systems flow downhill, although there are exceptions where it is pumped uphill to join another drainage system.

6.3.5 Obtain permission and conduct site reconnaissance prior to sampling. Conduct site reconnaissance during wet and dry weather (base flows) to determine if the waterbody goes dry during part of the year.

6.4 Sample method considerations

6.4.1 Sampling of ultra-trace toxics that are transported by stormwater and may only remain in the water column for hours is logistically challenging. The residence time of the contaminant will vary greatly across lotic (slower residence times and often more fleeting) and lentic (longer residence times, around longer, but often diluted) water types and classes. Grab sampling represents a discrete time point, while continuous active sampling provides an average concentration over time or flow (Figure 1).

6.4.2 6PPD-q fate, transport and chemical characteristics help determine the most appropriate sampling methods and study designs. The main transport mechanism for 6PPD-q is assumed to be stormwater runoff following rain or snow melt events. Tire wear particles containing tire contaminants are deposited alongside our roads and stormwater catchments. Runoff transports the tire wear particles and associated chemicals to receiving waters. The levels of 6PPD-q are measured for hours to days after a storm event in the water column (Challis et al. 2021; Johannessen et al. 2022). 6PPD-q readily sorbs to road debris and particles (Hu et al. 2023). 6PPD-q has been measured in

[4] Tire Contaminants (wa.gov)

airborne particles and road dust, but the atmospheric contribution to waterbodies is unknown (ITRC 2024; Mayer et al. 2024).

Figure 1. Left and center images are examples of grab sampling. The right image is an example of a stream station where an autosampler is set up for active sampling.

6.4.3 Active sampling, collected by discrete interval or composite sampling, increases your chances of capturing and measuring the contaminant before dispersion to the receiving waters (Figure 2). Yet, grab sampling is less complicated and doesn't require special equipment, while active sampling is more equipment intensive, and requires specialized training and more resources. Grab sampling is more effective for slower moving waters with longer retention times than fast moving waters. Study objectives, feasibility, resources, and cost will determine the most appropriate sampling method. For additional comparison of sample methods see Appendix A.

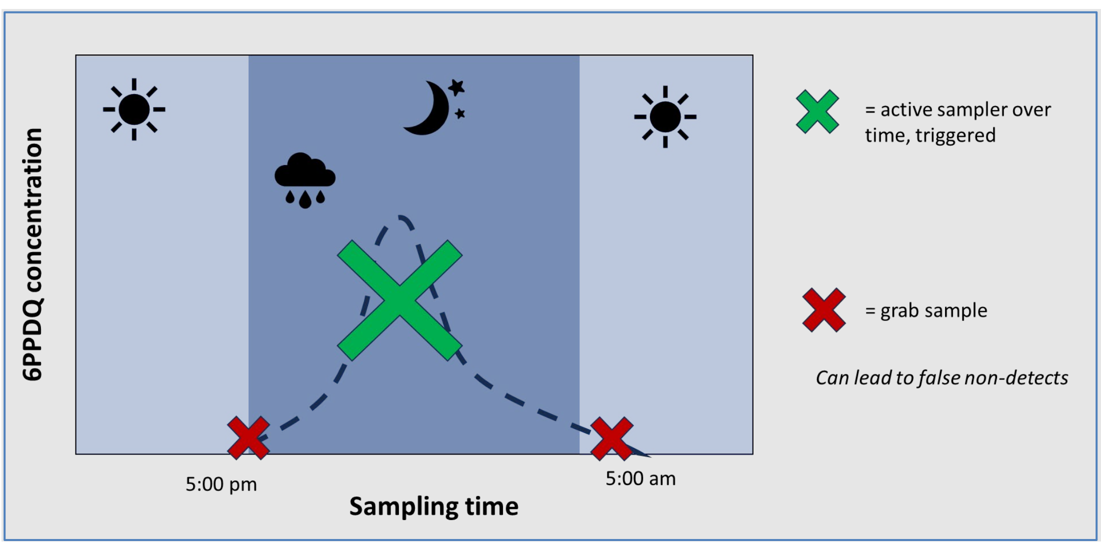


Figure 2. Conceptual model showing the often-inopportune timing of storms and typical grab sampling as a snapshot in time, which has a greater chance of missing the pollutant peak compared to active autosampling.

6.4.4 The portion of the hydrograph that lies to the left of the peak is called the rising limb, the beginning of the discharge peak following a precipitation event. The portion of the curve to the right of the peak is called the recession limb. Traditionally it is best to target sampling during the rising limb of the storm. Yet we know very little about how 6PPD-q varies among storms and watersheds. Collecting samples throughout a storm helps define the 6PPD-q pollutant peak in relation to the flow discharge peak. The pollutant peak can often lag-behind the discharge peak (Figure 3) depending on the watershed characteristics.

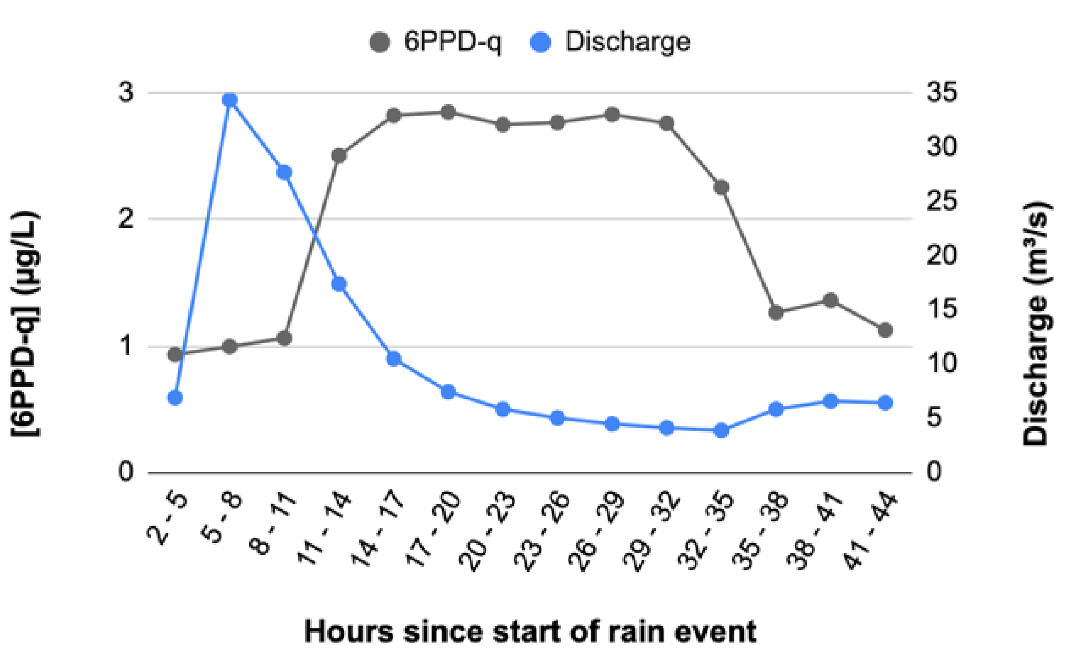


Figure 3. Data from a river in Canada that shows a delayed 6PPD-q pollutant peak from the flow peak and persistence for over 24 hours post-storm (Johannessen et al. 2022).

6.4.5 Active sampling provides many different configuration options. Composite sampling can be an effective method for toxics screening (or well-timed grab sampling). If 6PPD-q is detected, then more intensive sampling helps characterize the pollutant and discharge peaks among watersheds with variable urban uses (Figure 4). Another consideration is the permanence of the study site and available resources. Time-weighted composite sampling (or well-timed grab sampling) can be convenient for comparing the initial screening and mass loading of 6PPD-q among multiple watersheds. Flow-weighted composite sampling is effective for influent and effluent pollutant discharge comparisons.

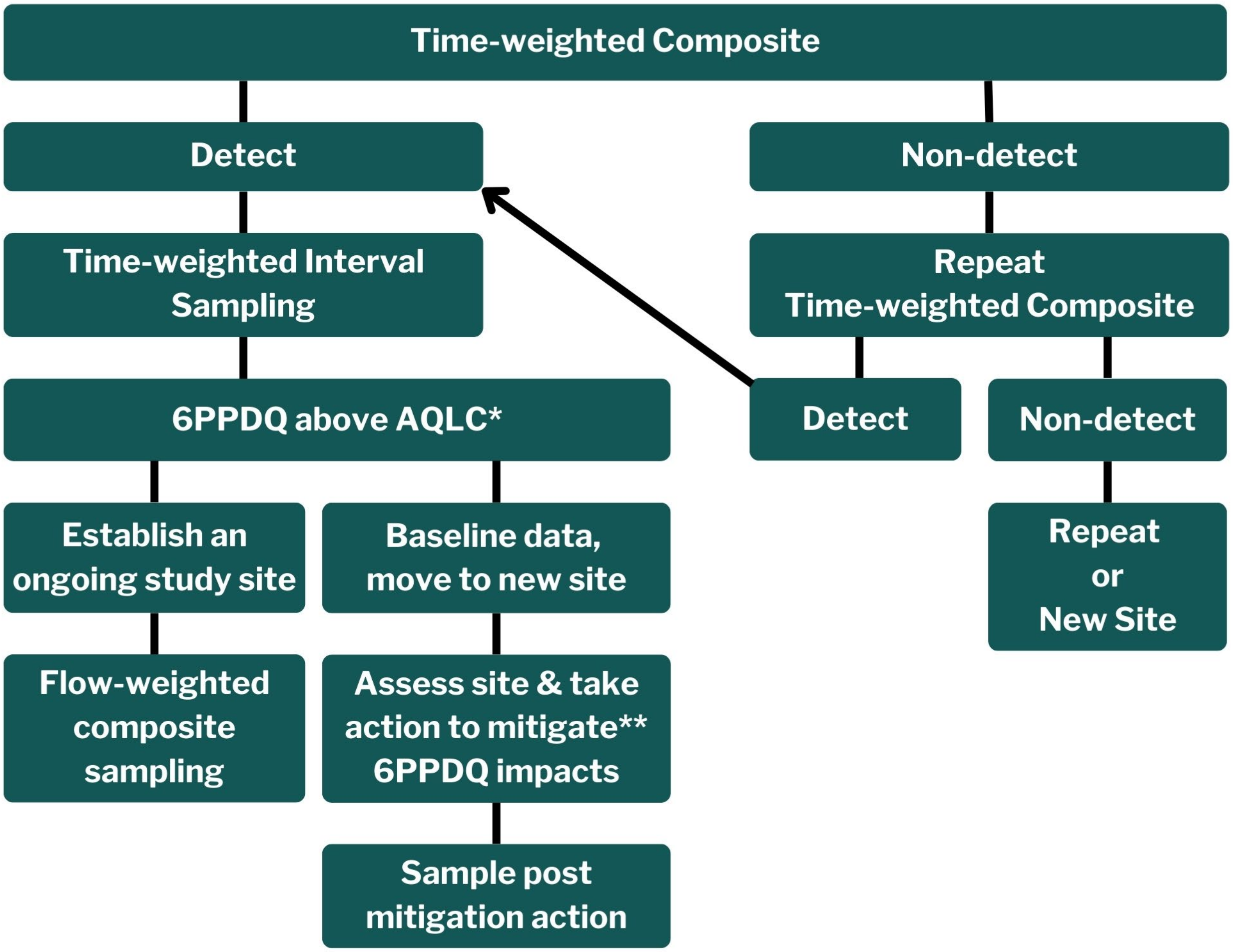


Figure 4. Example workflow for 6PPD-q sample design using an automated sampler; *AQLC refers to Aquatic life criteria threshold as an example criterion; the criteria will depend on your study design; **mitigation actions refers to most appropriate pollution prevention, reduction and control actions for the specific site.

6.5 **Pre-sampling preparation**

6.5.1 A Quality Assurance Project Plan (QAPP) is a sampling and analysis plan developed prior to field work that often includes names of responsible personnel, required training, sample and collection documentation, study design, sampling locations or site criteria, storing and transporting samples to the contract lab, equipment decontamination and storage between sampling events, and data management (Lombard & Kirchmer 2004).

6.5.2 An Approval to Begin Work form is a document that is signed by your QA officer and project lead's supervisor acknowledging that all steps have been completed and the project is ready to begin.

6.5.3 Obtain any necessary permits or permissions for accessing sample locations.

6.5.4 Submit necessary forms for participating lab. For example, pre-sampling notification form and a sample container request form are documents sent to MEL to inform lab of 1) the intent to sample and 2) request the required sampling containers and supplies. Examples are available at MEL sampling forms.

6.5.5 Notify the lab at least two weeks prior to sampling, especially if special preparations are needed for your samples or the parameters have a short hold time like 6PPD-q (14 days).

6.5.6 Coordinate with the lab to determine if the samples will be extracted within the pre-extraction hold time (14 days) or be placed in the freezer.

6.5.7 Sample collection, storage, pick up and transport between Thursday and Sunday needs to be pre-approved with the project manager and lab.

6.5.8 Reserve necessary shared vehicles, boats, and field equipment in advance using EAP's scheduling calendars.

6.5.9 A field sampling plan is a record of who, how, where and when the personnel will be collecting samples, a verification of training, what field vehicles and vessels will be used and emergency contacts and protocols. For EAP science staff, the completed form should be uploaded to the field schedule SharePoint: Field Schedules.

6.5.10 The contracted lab provides most sampling supplies. For Ecology staff, the EAP Operations Center or Headquarters provides tags, COC forms, coolers, ice, and temporary freezer or refrigerator sample storage space.

6.5.11 If shipping samples to the contract lab, avoid shipping at the end of the week. Storing samples over the weekend and shipping Monday morning may use up precious hold time days, but it is better than not having someone available to receive samples. Pre-book air transport for sample coolers if possible. For ground shipments check on delivery times and last shipment times for the day.

6.5.12 Prior to collecting samples, prepare sampling ID tags containing the project name, sample number, site, parameter, and space for date and time. Also prepare a field data sheet or notebook with similar information.

6.6 Grab sampling

6.6.1 Put on new nitrile gloves, remove stopper/lid from container just before sampling. Be careful not to contaminate the cap, neck, or inside of the bottle.

6.6.2 Face upstream in lotic waters and upwind in lentic waters.

6.6.3 Direct collection (by hand) - Hold the container near its base, reach out in front of your body, and plunge it (mouth down) below the surface to about mid-water column. Or keep the cap loose in place, then remove the cap while underwater to avoid surface contamination when feasible. Rinse the bottle three times with ambient water.

6.6.4 To rinse, fill the bottle about ½ full for each rinse, swirl and then dump downstream away from the sampling site.

6.6.5 Using the sampling extension pole – Secure the container at the end of the extension pole, remove lid while wearing gloves, extend pole, and plunge it (mouth down) below the surface to about mid-water column for shallow lotic waters. Rinse the bottle three times with ambient water.

6.6.6 Keep the sampling depth consistent from one site to another when possible. Avoid sampling the surface water to prevent floating debris from contaminating the sample. Avoid disturbing the bottom sediments.

6.6.7 If the water is so shallow that this technique will disturb sediment and contaminate the sample, it may be necessary to collect a surface water sample. Make sure to note your change of methods, if any. Collect your sample upstream from where you rinsed.

6.6.8 Once the bottle is submerged mouth downward, slowly tilt the bottle upward at an angle until the bottle is facing up and filled to the brim, slowly raise the bottle out of the water leaving no head space and replace clean lid.

6.6.9 If the receiving lab can't extract samples within the hold time and the plan is to freeze the sample, then leave at least 1/3 of the bottle as head space to avoid the water expanding and cracking the glass during the freezing process. Some labs may have you fill with no head space and then pour off water if freezing is necessary.

6.6.10 Place sampling tag on container and place in cooler with ice.

6.6.11 If there are abnormally "dirty" looking samples with lots of particulates typical of stormwater, then notify the lab, so they are prepared for longer extraction times.

6.7 Grab sampling using an intermediate device

6.7.1 Intermediate devices are not recommended for 6PPD-q, however, there are some environments where it is necessary to use special collection devices. Intermediate devices or containers should be decontaminated between each new site following SOP EAP090 (2021). When in doubt or if available, use a new container.

6.7.2 For relatively shallow waterbodies (< 1 m), collect the sample mid-depth between the surface and the bottom, unless otherwise stated in the QAPP, try to keep the collection depth consistent and record in notes.

6.7.3 For vertically (depth) integrated samples, raise and lower the sampler at a constant rate.

6.7.4 If using a Kemmerer or Van Dorn type sampler triggered by a messenger, use PTFE or FEP lined sample tubing to avoid loss of 6PPD-q when subsampling, first release ~ 50 mL from the sampler and then overfill the sample container to minimize head space and only submerge the very tip of the tubing into the sample container to avoid 6PPD-q loss from adhering. If freezing the samples has been arranged with the participating lab then only fill the sample container halfway.

6.8 Grab sampling from a bridge

6.8.1 Follow the guidelines in the EAP Safety Manual chapter, Working near Traffic and from Bridges. Sample from the bridge only if all safety precautions are taken and the risk of injury is negligible.

6.8.2 Pick a spot on the downstream side of the bridge.

6.8.3 Make sure you are over the thalweg of the water body.

6.8.4 Observe whether the current is too swift for the weight of your sampler. Do you have enough rope/rods/cables to break the water's surface and overcome the downstream current velocity? Will you be able to pull a weighted bucket up against the force of the current?

6.8.5 Are debris moving downstream or is there boat traffic moving upstream or downstream? If conditions warrant, post an observer with a clear view of upstream and downstream conditions.

6.8.6 If you do not know the depth of water at the site, roughly measure it by deploying a line with a weight on the bottom from the bridge. This is so the sampling device will not disturb bottom sediments when deployed.

6.8.7 Clear any loose debris from the bridge railing and make sure the path from the railing to the water's surface is clear of obstructions.

6.8.8 Assemble, secure, and untangle the sampler with ropes/rods/cables, and keep feet and legs clear of all ropes/rods/cables. Be aware of bridge traffic. It is best to have one person designated as an observer.

6.8.9 Place a clean intermediate container or sterilized bottle into the sampler and secure carefully while wearing nitrile gloves.

6.8.10 Remove the stopper/lid just before lowering the sampler-with-bottle down on the rope, and set it somewhere free of dirt or other sources of contamination, preferably in a plastic bag. It helps to have a "clean hand" and a "dirty hand" person during this process.

6.8.11 Wear heavy duty gloves to protect your hands from rope burns. Lower the sampler in such a manner so as not to contaminate the open bottle with dirt or dripping water.

6.8.12 When approaching the water surface, lower the sampler to where the bottom of the sampler is touching the water surface. This will clean any debris on the bottom of the sampler. If the sampler has a fin on it, the sampler will position itself with the flow. Then lower the sampler quickly to submerge and collect a sample.

6.8.13 Keep the bottle submerged long enough for the container to fill.

6.8.14 Be aware that if Kemmerer and Van Dorn bottles are being used from bridges and the river current is swift, the messenger may not be able to trigger the closing mechanism. Placing an anchor weight may help keep the line more vertical.

6.8.15 Pull up the sampler and bottle. Be careful not to contaminate the sample with dirt or water from either the rope or bridge, or other sources of contamination.

6.8.16 Swirl and pour from the intermediate device to the sample container leaving no head space.

6.8.17 Replace the stopper/lid (wearing gloves).

6.8.18 Rinse any large amount of dirt or debris from the outside of the container.

6.8.19 Place sampling tag on container and place in cooler with ice.

6.9 **Active sampling**

6.9.1 Capacity for active sampling will depend on the study's objective and available resources. When available, rain, flow, or water quality sensors can automatically detect storms and trigger sampling. A **conditional criteria start** allows more flexibility and requires less people than **manual or time delayed starts**.

6.9.2 **Composite sampling** is an effective method for capturing 6PPD-q during a storm event and minimizes the number of samples to be analyzed. There are more pros and cons for time and flow-weighted composite sampling discussed in Appendix A.

6.9.3 **Sequential interval sampling** is useful for understanding the transport timing, peak concentrations and persistence of the pollutant following a storm event. Appendix A discusses the pros and cons of composite and sequential sampling in more detail.

6.9.4 **Time delayed start:** Reference weather forecasts to estimate the start of the storm and use this information to program a delayed start. Define sample timing and storm parameters in your study QAPP when appropriate.

6.9.5 **Conditional criteria start:** Programming with a flow or rain gauge actuator provides additional convenience and standardization. Depending on the capabilities of the autosamplers, you can set a sampling criteria to detect a storm event and automatically trigger sampling. Common conditional parameters used to detect storms and trigger sampling include precipitation (rain bucket), changes in discharge volume (flow), and water quality parameters (turbidity). The most appropriate criteria and corresponding sensors will depend on the objectives and resources for your study.

6.9.6 **Program the autosampler**: There are a range of autosamplers available on the market and associated programs, the most appropriate options depends on the study's objective and available resources (Appendix A). Consult the manual for select programming procedures.

6.9.7 Once the sampler has been programmed and any corresponding sensors next set up the sampler at selected site. Look for a spot that is accessible, but not too visible. The sampler needs to sit on level ground and provide enough room to safely maneuver around when subsampling. Use the brush clearing tools if necessary to remove blackberry bushes and shrubs.

6.9.8 Adjust the length of the sample tubing to avoid curling up and low points where particles might settle. Place aluminum foil on ends during installment and where gloves when connecting the tubing. Make sure that the tubing remains below the pump.

6.9.9 Secure the strainer on the end of the tubing. This provides a nice weight to keep the tubing end in place and underwater. An alternative is to not use the strainer and hang a weight from the tubing. It is best to secure the tubing in place, so the intake end remains below the water surface and above the sediment (zip ties work well to stabilize the tubing in place).

6.9.10 If using an external battery, make sure it is in a locked, water-resistant container to protect it from rain and theft. If the sampler and battery are not secured in a sampling cabinet, then try to hide the battery in brush for short-term deployments.

6.9.11 If it's an established site, conduct routine maintenance on the autosampling station after the samples have been collected and prior to redeployment. Developing study specific methods helps track and standardize maintenance and procedures.

6.9.12 Place the composite glass jar (see container recommendations section) in the center of the autosampler base. Remove lid and place it in a clean Ziploc bag.

6.9.13 Another option when using a single composite container is to use a lined lid with a hole where the sample tubing can be secured. This helps to minimize contamination and holds the tubing in place, so pump pressure does not dislodge the tubing.

6.9.14 Connect the battery and turn on the autosampler.

6.9.15 Place the top of the autosampler over the jar opening (or thread the sample tubing into the jar lid). Make sure the tubing is secured inside the jar or lid.

6.9.16 Remove the sample container lid and carefully place the autosampler top onto the bottom autosampler section while making sure that the pump tubing is lined up with the jar opening.

6.9.17 **Rinsing:** Define the rinsing procedures for your study, for example: Find the grab sample function, and rinse the line and composite jar with 1000 mL of ambient water. Remove autosampler top, dump the rinse water out of the composite jar and replace the jar in the bottle of the autosampler.

6.9.18 Most autosamplers can be programmed to do a set number of line rinses prior to sampling. Recommend purging the line, rinsing the line three times, and purging the line prior to each sampling interval.

6.9.19 Replace the lid and recenter the composite jar into the middle of the autosampler, dump the ice over the jar to the shoulder. The ice also helps keep the bottle in place. Many autosamplers have equipment provided to secure the sample bottles in place as well.

6.9.20 Carousels are provided for interval sampling when using multiple bottles, make sure that bottle 1 is lined up correctly. Some autosamplers are refrigerated while other require ice. Follow the same procedures, remove lids prior to deployment, keep these in a clean, labeled zip lock bag.

6.9.21 Return to the main menu and press start program.

6.9.22 Secure the autosampler cover with stainless steel cable and a lock. Secure the autosampler and locked external battery housing to a nearby tree or structure when available to prevent theft and vandalism. Depending on how long you intend to leave the autosampler, it is safest to secure everything in a locked metal sampling cabinet.

6.9.23 Place sampling tag on container, it is recommended to put a label on the container as well as on a sample tag that is wrapped around the container neck in case a label falls off.

6.9.24 Place the container in a bag and in cooler with ice.

6.10 Sample Transport

6.10.1 Sample Transport will depend on the laboratory that you and your QA officer have identified for analysis in your QAPP. Check with the contracted lab on specific sample transport procedures.

6.10.2 Pack samples in regular ice or blue ice blocks. Placing sample bottles in plastic bags helps protect the labels from getting wet when using regular ice.

6.10.3 Deliver samples to the designated COC room and leave Lab Analysis Requested (LAR) forms in the “Out” box near the walk-in cooler where they will be picked up by a courier or ship samples as recommended by receiving lab.

6.10.4 Make sure the LAR (COC) form contains the work order, project name, sample numbers, site names, dates, times, and parameters.

6.10.5 Make sure that the information on the LAR matches the information on the sample tag exactly.

6.10.6 The LAR must also include a signature, date, and time in the appropriate Chain of Custody Record section. The appropriate forms are available from the contract lab.

6.11 **Samples shipped via air or ground freight service**

6.11.1 If glass containers are shipped to the lab, make sure they are adequately wrapped in packing material to prevent breakage. Place the bottles in plastic bags to protect labels.

6.11.2 Pack samples using blue ice. Cool to 4˚C and store in dark cooler. In warmer weather (80˚F and above), use eight to ten blue ice packs per cooler. In cooler weather (below 80˚F) use six to eight blue ice packs, to avoid freezing samples. If you have access to dry ice, you may use it to ship frozen samples only. Be sure to contain the dry ice in newspaper or cardboard and to use packing materials around the sample containers. Also, use a well-sealed container and include blue ice to keep the dry ice cold.

6.11.3 Follow U.S. Department of Transportation's Hazmat shipping procedures for any samples that are considered hazardous waste.

6.11.4 Put LAR form in a waterproof bag and tape it to the inside of the cooler lid and tape coolers shut after inspection. For air shipments, coolers must first be inspected by the Transportation Security Administration. If allowed, make sure that coolers are taped shut after inspection.

6.12

7.0 Records Management

7.1 Each sample collection should be fully described in the field notebook with waterproof ink (e.g., date, time, location, sample laboratory identification number, sample type, analyses to be performed, and ancillary data). Entries should be kept neat and concise. Measures should be taken to avoid losing the field notebook.

7.2 Sample locations should be described in enough detail to find in the data management system, for example, Ecology’s Environmental Information Management (EIM) System or EPA’s Water Quality Exchange (WQX) System (these databases are now linked). Otherwise, a GPS unit should be used to record an accurate location. Coordinates should be recorded as per database requirements.

7.3 Information for each laboratory sample will be entered onto a COC form when the samples are submitted to lab.

7.4 The results from the contracted laboratory will be uploaded to the appropriate database and the project manager or field lead will merge the site metadata with the analytical results and upload the data to the corresponding database following QA protocol.

8.0 Quality Assurance/Quality Control (QA/QC)

8.1 In general, QA/QC procedures will be addressed on a project-by-project basis in the QAPP. Generally, 10% of samples should be QC samples.

8.2 Minimal QC field sample type recommendations per event for 6PPD-q occurrence sampling are as follows:

- duplicate sample/sampling event
- field blank/sampling event

8.3 Additional QC field sample types include:

- field equipment blank (when using intermediate sampling equipment)
- ride along blank
- performance reference compound (PRC)

8.4 Samplers should be adequately trained in the sampling methods and QAPP.

9.0 Safety

9.1 All field staff must comply with the requirements of the EAP Safety Manual, especially Chapter 1 - General Field Work, which includes special circumstances like fall protection, working on bridges, and working in rivers and streams. Sampling from a boat requires one person onboard to be a qualified boat operator and all persons onboard must be familiar with Chapter 3 of the EAP Safety Manual, Boating.

9.2 For further field health and safety measures, refer to the EAP Safety Manual on SharePoint.

9.3 Heavy-duty gloves will protect hands from rope burns when lowering intermediate sampling equipment from bridges. Care is necessary on bridges to keep lines, ropes, and cables clear of other equipment, legs, and traffic.

9.4 Preferably, nitrile gloves should be worn to avoid bacterial or chemical exposure while performing direct sampling. If gloves are not worn, hands should be cleaned using anti-bacterial soap or hand sanitizer after each sampling station. Before ingesting food or drink, dirty clothes should be changed, and hands should be washed.

9.5 Stormwater sampling is often conducted in urban areas where samplers should be aware of their surroundings and potential threats of theft or harassment.

9.6 **Road safety:** The main transport source of 6PPD-q is pavement (e.g. roads and parking lots). It is recommended to carry road safety equipment such as triangles, cones, bridge safety control signs, and vehicle hazard lights to increase the visibility of your vehicle and personnel while sampling.

9.7 **Personal safety:** Safety vests and lines, personal floatation devices (PFDs), and boating safety equipment should be available when working near or on water. Additional safety equipment includes headlamps, ear plugs, safety glasses, hard hat, first aid kit, warm heat packs.

9.8 **Communication:** Communication devices should always be carried in case of an emergency or unsafe environment. Radios or cellular devices should be accessible in case of an emergency, along with an uploaded field trip plan with a shore contact (e.g. supervisor) and emergency contacts.

9.9 **Buddy system:** Samplers should always follow a buddy system and have an onshore contact and backup contact.

10.0 References

10.1 Brinkmann, Markus, David Montgomery, Summer Selinger, Justin G. P. Miller, Eric Stock, Alper James Alcaraz, Jonathan K. Challis, Lynn Weber, David Janz, Markus Hecker, and Steve Wiseman. 2022. Acute Toxicity of the Tire Rubber-Derived Chemical 6PPD-Quinone to Four Fishes of Commercial, Cultural, and Ecological Importance. Environmental Science & Technology Letters 9 (4), 333-338. DOI: 10.1021/acs.estlett.2c00050, https://pubs.acs.org/doi/10.1021/acs.estlett.2c00050

10.2 Challis JK, Popick H, Prajapati S, Harder P, Giesy JP, McPhedran K, Brinkmann M. Occurrences of Tire Rubber-Derived. Contaminants in Cold-Climate Urban Runoff. Environmental Science & Technology Letters. 2021 Sep 22: acs.estlett.1c00682. doi:10.1021/acs.estlett.1c00682

10.3 Ecology [Washington State Department of Ecology]: Environmental Assessment Program. 2010. EAP Policy 01-15: Minimize the Spread of Aquatic Invasive Species. Washington State Department of Ecology. Olympia, WA. http://teams/sites/EAP/EAPProcedures/01-15InvasiveSpecies.pdf

10.4 Ecology [Washington State Department of Ecology], MEL [Manchester Environmental Laboratory]. 2016. Manchester Environmental Laboratory User's Manual Tenth Edition Environmental Assessment Program. Washington State Department of Ecology. Manchester, WA. MEL Lab User's Manual

10.5 Ecology [Washington State Department of Ecology]: Environmental Assessment Program. 2019. Quality Assurance at Ecology. Environmental Assessment Program, Washington State Department of Ecology, Olympia. https://ecology.wa.gov/Quality.

10.6 Ecology [Washington State Department of Ecology]: Environmental Assessment Program. 2022. 6PPD in Road Runoff: Assessment and Mitigation Strategies. Olympia, WA. 6PPD in Road Runoff: Assessment and Mitigation Strategies (wa.gov)

10.7 Ecology [Washington State Department of Ecology]: Environmental Assessment Program. 2023. Quality Assurance Project Plan. Monitoring of Tire Contaminants in Coho Salmon Watersheds. Olympia, WA. Quality Assurance Project Plan: Monitoring of Tire Contaminants in Coho Salmon Watersheds.

10.8 Ecology [Washington State Department of Ecology], MEL [Manchester Environmental Laboratory] 2024. Standard Operating Procedure MEL 730136, Version 2.0, Extraction and Analysis of 6PPD-Quinone by EPA 1634.

10.9 Ecology [Washington State Department of Ecology]: Environmental Assessment Program. 2024. Tire Contaminant Story Map. Olympia, WA. Tire Contaminants (wa.gov)

10.10 Ecology [Washington State Department of Ecology]. 2024. Environmental Assessment Program Safety Manual. Washington State Department of Ecology, Olympia. Environmental Assessment Program Safety Manual

10.11 EPA [Environmental Protection Agency]: Office of Water. 2023. DRAFT Method 1634: Determination of 6PPD-Quinone in Aqueous Matrices Using Liquid Chromatography with Tandem Mass Spectrometry (LC/MS/MS).

10.12 Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber-Derived Toxicant 6PPD-Quinone. Environmental Science: Processes & Impacts 25, no. 5: 901–11. https://doi.org/10.1039/D3EM00047H.

10.13 ITRC [Interstate Technology and Regulatory Council]. 2024. 6PPD and 6PPD-Quinone. Washington D.C.: Interstate Technology & Regulatory Council, Tire Anti-degradants (6PPD) Team. https://6ppd.itrcweb.org/.

10.14 Greer, Justin B., Ellie M. Dalsky, Rachael F. Lane, and John D. Hansen. 2023. Establishing an In Vitro Model to Assess the Toxicity of 6PPD-Quinone and Other Tire Wear Transformation Products. Environmental Science & Technology Letters 10, no. 6 (June 13, 2023): 533–37. https://doi.org/10.1021/acs.estlett.3c00196.

10.15 Johannessen C., Helm P., Lashuk B., Yargeau V., C.D. Metcalfe. 2022. The Tire Wear Compounds 6PPD-Quinone and 1,3-Diphenylguanidine in an Urban Watershed. Arch Environ Contam Toxicol. 82(2):171-179. doi: 10.1007/s00244-021-00878-4: 34347118; PMCID: PMC8335451.

10.16 Joy, J. 2022. Standard Operating Procedure EAP015, Version 1.5: Manually Obtaining Surface Water Samples. Publication xx-03-2xx. Washington State Department of Ecology, Olympia. https://apps.ecology.wa.gov/publications/SummaryPages/xx032xx.html. (Approved or Recertified 2022.)

10.17 Lane, R.F., Smalling, K.L., Bradley, P.M., Greer, J.B., Gordon, S.E., Hansen, J.D., Spanjer, A.R., Kolpin, D.W., Masoner, R. Jason. 2024. Tire-Derived Contaminants 6PPD and 6PPD-q: Analysis, Sample Handling, and Reconnaissance of United States Stream Exposures. Chemosphere, 363, 142830 https://doi.org/10.1016/j.chemosphere.2024.142830

10.18 Lombard, S. and C. Kirchmer. 2016. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology. Olympia, WA. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies (wa.gov)

10.19 Mayer, Paul & Moran, Kelly & Miller, Ezra & Brander, Susanne & Harper, Stacey & Garcia-Jaramillo, Manuel & Carrasco-Navarro, Victor & Ho, Kay & Burgess, Robert & Hampton, Leah & Granek, Elise & McCauley, Margaret & McIntyre, Jenifer & Kolodziej, Edward & Hu, Ximin & Williams, Antony & Beckingham, Barbara &

Jackson, Miranda & Sanders-Smith, Rhea & Mendez, Miguel. 2024. Where the rubber meets the road: Emerging environmental impacts of Tire Wear particles and their chemical cocktails. Science of The Total Environment. 927. 171153. 10.1016/j.scitotenv.2024.171153.

10.20 Parsons, J. et al., 2018. Standard Operating Procedures EAP070, Version 2.2: Minimize the Spread of Invasive Species, Environmental Assessment Program, Olympia, WA. 33 pp. https://apps.ecology.wa.gov /publications/SummaryPages/1803201.html

10.21 Ecology [Washington State Department of Ecology] Quality Assurance SharePoint site: http://teams/sites/eap/qualityassurance/default.aspx

10.22 Ecology [Washington State Department of Ecology] Quality Assurance internet site: https://ecology.wa.gov/Issues-and-local-projects/Investing-in-communities/Scientific-services/Quality-assurance

10.23 Tian Z, Zhao H, Peter KT, Gonzalez M, Wetzel J, Wu C, Hu X, Prat J, Mudrock E, Hettinger R, Cortina AE, Biswas RG, Kock FVC, Soong R, Jenne A, Du B, Hou F, He H, Lundeen R, Gilbreath A, Sutton R, Scholz NL, Davis JW, Dodd MC, Simpson A, McIntyre JK, EP Kolodziej. 2021. A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon. Science. 2021 Jan 8;371(6525):185-189. doi: 10.1126/science.abd6951. Epub 2020 Dec 3. Erratum in: Science. 2022 Feb 18;375(6582):eabo5785. doi: 10.1126/science.abo5785. PMID: 33273063.

11.0 APPENDIX A – Sampling guidance and considerations

Deciding when, where and how you are going to measure 6PPD-q will depend on the objective of your study. Considerations and recommendations are discussed in this section.

Sample timing and site selection considerations

6PPD-q in surface water and URMS events are associated with urban runoff, therefore collecting samples during storm events is recommended. Collecting samples during dry periods to obtain baseline data might be appropriate for specific objectives as well. Additional considerations regarding timing are discussed in table A-1.

Table A-1. Examples of temporal study design objectives and recommended sample timing.

Objective	
Estimate exposure risk to aquatic life	Sample the corresponding habitats during spawning and rearing months. For coho that is fall to early winter for adults but could be all year round for juvenile.
Identify areas where 6PPD-q to receiving waters is storm-limited or pollutant-limited	Sample during different seasons and storm types with varying dry period. Sample the same locations many times.
Estimate mass loading across urban gradients	Sample across traffic and watershed gradients to understand what impacts the mass loading of 6PPD-q.
Understand how long 6PPD-q persists in a stream during and after storm events	Sample throughout a storm at user-defined intervals (e.g. every 2 hours)
Identify 6PPD-q discharge points and where to focus mitigation actions	Sample each stream at several points during storm events and dry periods to establish baseline concentrations.
Understand if mitigation and management actions successfully reduce 6PPD-q	Conduct status and trends sampling every few years and establish long-term probabilistic monitoring

The sampling sites will depend on the objective of the study or monitoring program. Urban runoff is assumed to be the major source of 6PPD-q to urban streams and the cause of URMS, therefore understanding the conveyance and treatment efficacy of urban runoff mitigation actions is important. Table A-2 provides examples and considerations when selecting your sampling sites.

Table A-2. Examples of site selection considerations for 6PPD-q.

Objective	Sampling type	Sampling location
Study the occurrence and source of 6PPD-q in receiving waterbodies.	Occurrence – fate & transport	Anywhere along the transport pathway from tire, road, vault, ditch, sheet-flow, soil to receiving waterbody
Measure residence time and how 6PPD-q moves through the environment	Persistence – fate & transport	Across marine and freshwater gradients, different types of waterbodies (big rivers, small streams, wetlands, lakes, ponds, etc.)
Exposure risk to target species	Risk assessments to aquatic life	Choose habitats that correspond with vulnerable aquatic life. For example, coho salmon use the middle section of smaller streams and watersheds.
Study the impact of a mitigation or management action	Before – After – Control – Impact (BACI)	Study the same site before and after the disturbance or enhancement
Study the effectiveness of new or existing structural stormwater control devices.	Mitigation monitoring	Study the influent and effluent of a control device over time to confirm that it is working as intended.
Hot spot identification	Source identification	Measure upstream and downstream from suspected point and non-point sources. Or sample at end of pipe but coordinate sampling with local permit coordinator and landowner.

Mitigation monitoring considerations

In addition to understanding where and when aquatic life of concern is exposed to 6PPD-q, understanding the transport pathway from tires to aquatic ecosystems is a high priority. Urban cities have a mix of new low impact development stormwater infrastructure that manages stormwater volume and associated contaminants AND older infrastructure that has minimal stormwater management prior to discharging to aquatic ecosystems of concern.

Sampling along the stormwater pathway may involve several types of specialized sampling methods to capture variability. This section provides considerations for measuring 6PPD-q in open and closed stormwater conveyance systems and drainage facilities.

There are many combinations of natural and constructed conveyance, and treatment and control stormwater management measures. Collecting 6PPD-q samples across these combinations will help guide 6PPD-q mitigation strategies and investments.

Natural conveyance system

- Riparian areas
- Wetlands/ponds/lakes
- Streams/rivers

Constructed conveyance system

- Catch basin – inlet
- Catch basin – manhole, flow restrictor or oil pollution device
- End-pipe
- Culvert
- Open ditch (channel)
- Curb and gutter
- Sheet flow
- Roadside flow

Influent and effluent of stormwater drainage and infiltration facilities

- Low Impact Development design
- Bioswale (flume)
- Bioinfiltration
- Rain garden
- Rain barrel, box or bucket
- Detention pond – dry
- Detention pond – wet
- Detention vault

Stormwater sampling can be implemented to satisfy NPDES permit requirements. Regulatory sampling usually has very specific storm and sample criteria to assess whether the stormwater treatment and control management is operating effectively. Please see Ecology's stormwater sampling manual and stormwater monitoring website for more information.

Stormwater sampling may also be performed for research to understand the effectiveness of existing mitigated and unmitigated stormwater management for new contaminants such as 6PPD-q.

The greatest mass loading within a piped system does not necessarily equal the greatest exposure risk. There is a lot of variability in the conveyance from the end of pipe (or ditch for open conveyances) to receiving waters.

Storm vault and pipe sampling considerations

The focus of this guidance is open conveyances, but closed conveyance vault and pipe sampling might be needed for directed studies to estimate the mass loading of the stormwater infrastructure in a given drainage area. Influent and effluent sampling are required for estimating pollutant loading.

Closed conveyance sampling should be coordinated with the associated NPDES permit coordinators and the local municipality that are familiar with the underground conveyance and can help you request and gain access. See Stormwater Autosampling (vaults & pipes) SOP for more information.

Stormwater and wastewater grab sampling considerations

Conduct a reconnaissance of potential sampling sites with assistance from facility personnel. Attend to all safety precautions. Avoid confined spaces.

Locate an appropriate sampling location representative of water being discharged to the receiving water body. In particular, the location should be below any chlorination or ultra-violet (UV) application.

Use a sampling extension pole to collect samples without contacting the effluent with your hands. Wear appropriate clothing and nitrile gloves.

Follow standard label and storage procedures.

Stormwater and wastewater active sampling considerations

There are many methods and strategies for triggering the device and programming the autosampler to accurately characterize the contaminant.

The most appropriate stormwater mitigation sampling strategy depends on 1) the objective of your study, 2) the sampling site, 3) the equipment available, 4) the duration of the study, 5) the technical experience of the field crew, and 6) the intended use of the data.

Active sampling, the use of autosamplers, is an effective method for characterizing toxics in stormwater runoff. Collection frequency approaches for active sampling include 1) user-defined (manual or delayed start), 2) time-weighted, and 3) flow-weighted. For sample intervals, there are two options: 1) composite and 2) discrete. User-defined, time-weighted, and flow-weighted collection frequencies are all commonly used with autosamplers. The pros and cons of autosampling strategies are discussed in tables A-3 and A-4. Additional autosampling logistical considerations are discussed in A-5.

Table A-3. A list of pros and cons for time-weighted and flow-weighted autosampling.

Type	Time-weighted	Flow-weighted
PROS	Can allow for loading estimation with simpler autosampler programming whether corresponding flow measurements are available or not. Can be done without a flow meter or flow station. Provides data about pollutant presence and potential exposure. Helps focus more intensive studies. There is more certainty that you will fill all bottles as designed, unless the autosampler or user programming malfunctions. Time-weighted might capture pollutant concentrations better that don't follow the rise/fall of the hydrograph (e.g. first flush or delayed pollutant peak) Samples are less impacted if sampling reach becomes backwater from downstream debris clogging When flows and/or concentrations are not known or available then time-weighted is better.	Provides more accurate data to calculate total mass during the event or an event mean concentration (EMC), which is used in pollutant load estimating. Storm can be hours later with no impact on sampling. If pollutants concentrations are known (or assumed to not be highly time-varying) flow-weighted yields more accurate characterization. If you are intentionally targeting a specific size of storm or the storm fizzles out, flow-weighted will not get triggered, flow-weighted will have a far better chance in capturing the storm Storm can be any shape and concentrations will be well captured (aside from an early first flush or bulk of pollutant occurs at the beginning of the event).
CONS	Without flow measurements, there is no data to estimate pollutant loadings per point source (effluent). With flow measurements, the loading estimates have higher uncertainty than flow-weighted sampling.	Requires flow meter and is more complicated to set-up the trigger intervals, which adds to the project cost. You need to estimate the size and duration of storm event to determine sample volumes to collect.

Type	Time-weighted	Flow-weighted
	The downstream conditions may change over time and could be mischaracterized.	If forecast under/over-estimates size of storm, sample collection will either not be enough to capture the whole storm, or spread too far apart, and timing of sample collection won't characterize how the pollutant concentrations vary over time. You must have prior knowledge of storm runoff to configure sampler. This means either flow gauge exists somewhere close enough to make an educated guess, or a hydrologic model to estimate stormwater runoff volumes. Holding times are not immediately known (unless telemetry is included). Depending on sample design, may require more site visits. If concentrations occur early on the rising hydrograph, flow-weighted may miss the pollutants peak and underestimate EMCs. Sampling can't (or shouldn't) be done in backwater conditions, lake/ponds, or large events that change channel geometry (and hydraulics). If outlet of sample reach becomes clogged with debris and starts to backwater, sample collections will be biased and not characteristic of the event.

Table A-4. A list of pros and cons for investing in sensors to remotely trigger the autosampler compared to manual start.

Type	Storm Triggered	Manual or Programmed Start
PROS	A "true" event mean concentration is more likely captured if sampler is set up and matches the forecasted storm. Have a higher certainty you will get a sample at the "beginning" of the intended event. Sampling won't start until flow rate exceeds threshold. If you are intentionally targeting a specific size of storm or the storm fizzles out, the sampler won't be triggered. If storm ends up not occurring, sampler won't trigger, thus not requiring a refresh of equipment. More likely to capture a storm of a specific size.	Holding time for sample collection is known and easier to plan accordingly for collection and transport to the lab for analysis. This helps to avoid exceeding hold times without an extra trip to determine when the sampling was started. Accuracy in size of forecasted storm doesn't degrade quality of storm characterization, only duration. Simpler, and less equipment to procure and maintain. Less things to malfunction.
CONS	The sampler may start too early or late and miss part of the storm. Requires flow meter and is more complicated to set up the trigger intervals, which adds to the project cost. There is more that can go wrong	If other sensors aren't set up to start the sampler and measure rainfall or flow, then you must rely on the weather forecast for storm timing and duration to configure sampler. If a predicted storm doesn't occur, the sampler will still collect samples and the sampler will need to refresh the equipment. The sampler may start too early or late and miss part of the storm. More difficult to target specific sized storm events by relying on the weather forecast. Requires more site visits and samplers.

Table A-5. Considerations when choosing sampling methods to suit your study objectives.

Strategy Considerations	Options
What parameters are monitored?	Rain, flow rate, flow depth, temperature, DO, turbidity, conductivity, pH
What sampling method to select?	User-defined event, time, or flow-paced
What samples are required?	First-flush, composite, or interval
How much technical support?	Are there field technicians/engineers available to help with complex programs?
Staff numbers and availability?	Are there staff available on the weekends or at night?
Site Conditions?	Easily accessible, remote, AC power on site, secure, vulnerable, exposed, protected, vegetation
Channel type?	Round pipe, lined concrete, natural ditch, smooth or rough surface, reverse flow, submerged flow, debris
Available equipment and resources?	Rain gauge (bucket), flow meter, depth gauge (radar, bubbler, sensor), weir, flume, system enclosure, refrigeration
Data retrieval	Manual – notebook, bluetooth or cellular transfer onto device on site, satellite and/or cellular modem remote data and sampling alarm, access via internet interface

Time-weighted sampling

Time-weighted sampling is commonly used for initial comparisons, or "pollutant screening" when the total discharge volume is unknown. Time-weighted sampling is often convenient for temporary sites where information on flow is not always available (e.g., many small coho salmon bearing streams).

Time-weighted composite sampling

Time-weighted composite sampling is a nice tool for initial screening of 6PPD-q. Composite sampling often employs one large container (e.g., 1000 L) with user-defined sampling intervals. An example of time-weighted conditions for 6PPD-q occurrence sampling are in Table 2. The objective of your study will determine the most appropriate criteria.

Table A-6. Example of conditions for time-weighted sampling with no flow sensor. This is not a set criterion. It will be helpful to sample a variety of storm types, yet it is important to record storm information for correlations.

Component	Recommendation
Sampling Duration	< 36 hours[5]
Manual Sampling Start	Within ± 6 hours of rising limb
Delayed Clock Start	Within ± 6 hours of predicted storm start
Trigger Start Option 1[6]	Depth or flow
Trigger Start Option 2	WQ parameter (e.g. turbidity)
Trigger Start Option 3 (rain bucket)	> 0.1 inches of rain
Remote Start	Telemetry triggered

Time-weighted interval sampling

Time-weighted discrete interval sampling is a useful strategy for sites that need further investigation following an initial screening detection. There are many different sampling schedule configurations available (Figure A-1).

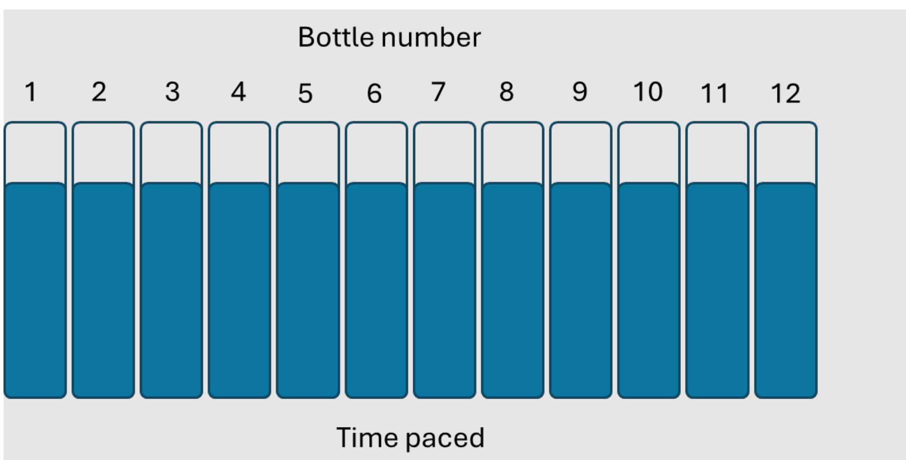


Figure A-1. An example of interval sampling with user-defined time-paced, equal volumes.

[5] If the storm lasts longer than 36 hours, change out bottle and refresh ice

[6] Volume weighted sampling is not recommended for comparing 6PPD-q mass loading across watersheds; time weighted sampling is preferred until we understand the pollutant distribution across the hydrograph. Preliminary studies have shown that there is a lag in the timing between the hydrograph peak and the pollution peak (Johannessen et al. 2022). More studies are needed that use standard time intervals and measure stream velocity and depth changes.

Flow-weighted 6PPD-q considerations

Flow-weighted sampling is preferred when measuring pollutant removal efficiency that requires discharge volume of the influent and effluent. If flow measurements are an option, then flow-weighted sampling is more appropriate for mitigation monitoring efforts, especially established at sampling sites.

The optimal flow-weighted settings will likely vary from one watershed to another. The inflow volume estimate (V) for a given drainage basin can be calculated based on the watershed area (A), the runoff coefficient (C), and historical rainfall (P):

$$V = A \times C \times P$$

Flow-weighted (flow-paced) sampling and mitigation monitoring requires equipment to measure discharge rates and volume. There are many sampling configurations to capture the first flush of a storm and characterize the rising limb section of the pollutant and discharge peak (Figure A-2). Yet, the most common method is flow-weighted composite sampling into a single container with flow-paced sampling intervals.

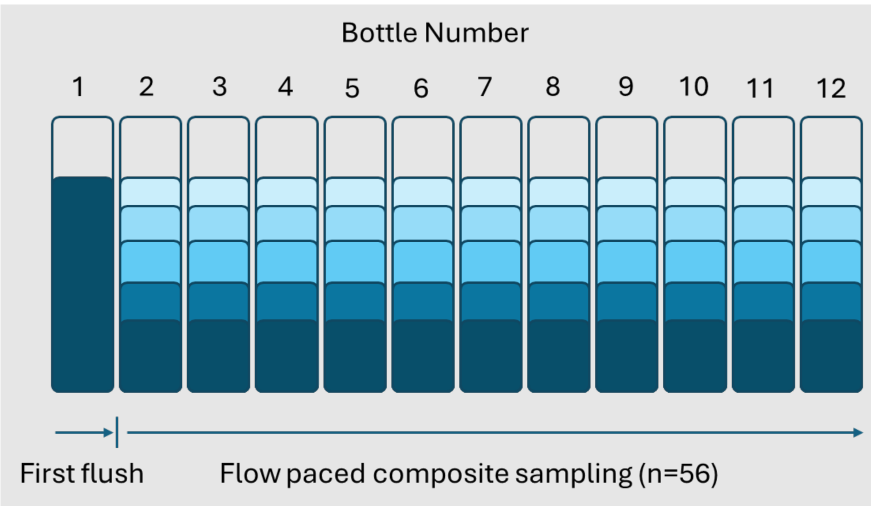


Figure A-2. An example of single first flush discrete sample and multiple composited samples that are user-defined flow paced intervals, each composite represents 5 discrete sampling events combined into one bottle.

Site scale effectiveness studies

Emerging stormwater treatment technologies (TAPE) effectiveness monitoring requires even more regimented sampling protocols at approved technology evaluation facilities. This SOP is not intended to support TAPE research and monitoring efforts. Guidance documents can be found on the TAPE website.

In addition to TAPE effectiveness studies, sampling is needed for public stormwater facilities including roadside catch basins on arterials and within residential areas, conveyance pipes, detention facilities such as ponds and vaults, oil and water separators, biofiltration swales, filter strips, settling basins, infiltration systems, and all other types of stormwater treatment systems.

Ecology and analytical partners will publish a 6PPD-q mitigation monitoring SOP once the stormwater technical community has a chance to evaluate methods. Currently, an example of a sampling schedule and storm criteria are provided in Table A-6.

Table A-6. Example of sampling conditions for flow-weighted composite autosampling. Initial flow information is needed to set the optimal volume intervals and volume change start criteria.

Component	Recommendation
Sampling Duration	> 75% of storm
Sampling Flow Interval	Site specific[7]
Sampling Flow start	Site specific[8]
Trigger Start Option 1	Flow or Depth[9]
Trigger Start Option 2	WQ parameter (e.g. turbidity)
Trigger Start Option 3	> 0.15 inches of rain
Remote Start	Telemetry triggered

[7] The average, minimum, and maximum total flows are needed to estimate the optimal volumes.
[8] The average, minimum and maximum total flows are needed to estimate the optimal threshold.
[9] Site specific estimates of flow change is needed for flow paced sampling.