6PPD in Road Runoff

Assessment and Mitigation Strategies

Prepared for

Model Toxics Control Act Legislative Program
Washington State Legislature

By the

Environmental Assessment and Water Quality Programs

Washington State Department of Ecology
Olympia, Washington

October 2022
Publication 22-03-020

Publication Information

This document is available on the Department of Ecology's website at:
https://apps.ecology.wa.gov/publications/summarypages/2203020.html

Cover photo credit: Clear Creek coho (courtesy of Wild Fish Conservancy, 2021).

Related Information

6PPD Spatial Technical Advisory Committee meeting materials[1]

WA Ecology Stormwater Strategy[2]

WSDOT Stormwater Retrofit Program Management Plan[3]

NOAA Pre-spawn coho mortality overview[4]

WA Ecology 6PPD Alternatives Legislative Report 2021[5]

CA DTSC 6PPD Safer Alternative Evaluation and Priority Product Request[6]

WA Ecology Toxic Studies Source Assessments Program - Orcas & Salmon[7]

WA Ecology & NEP Stormwater Strategic Initiative Lead (SIL)[8]

Puget Sound Regional Council Transportation Plan 2022-2050 Plan[9]

Puget Sound Regional Council Building Green Cities[10]

EPA Tire Crumb Rubber Characterization[11]

Stormwater Action Monitoring (SAM) program[12]

WA Ecology Plan to Control Nonpoint Sources of Pollution[13]

Puget Sound Stream Benthos B-IBI Restoration Decision Framework and Site Identification[14]

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[1] https://www.ezview.wa.gov/site/alias__2001/37753/overview.aspx

[2] https://apps.ecology.wa.gov/publications/documents/1810032.pdf

[3] https://wsdot.wa.gov/sites/default/files/2021-10/StormW-Retrofit-ManagementPlan030918.pdf

[4] https://www.ezview.wa.gov/Portals/_2001/Documents/Documents/Ecology_LandUse_Scholz_51822_Final.pdf

[5] https://www.ezview.wa.gov/site/alias__1962/37732/research_and_proposed_alternatives_to_6ppd.aspx

[6] https://dtsc.ca.gov/2022/05/23/news-release_t-07-22/

[7] https://ecology.wa.gov/Waste-Toxics/Reducing-toxic-chemicals/Toxics-studies/Source-assessments

[8] https://nepatlas.pugetsoundinfo.wa.gov/Award/Detail/5

[9] https://psrc.org/sites/default/files/rtp_fulldocument_ga_adopted_060222.pdf

[10] https://www.psrc.org/data-and-resources/building-green-cities

[11] https://www.epa.gov/chemical-research/public-webinar-part-1-tire-crumb-rubber-characterization

[12] https://ecology.wa.gov/Regulations-Permits/Reporting-requirements/Stormwater-monitoring/Stormwater-Action-Monitoring/SAM-effectiveness-studies

[13] https://apps.ecology.wa.gov/publications/documents/1510015.pdf

[14] https://pugetsoundstreambenthos.org/Projects/Restoration_Priorities_2014/documents/B-IBI_RestorationFrameworkSiteID.PDF

Contact Information

Environmental Assessment Program and Water Quality Program
Washington State Department of Ecology
P.O. Box 47600
Olympia, WA 98504-7600
Phone: 360-407-6000
Website[15]: Washington State Department of Ecology

Washington State Department of Ecology regions

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

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[15] www.ecology.wa.gov/contact

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Acknowledgements

The authors thank the following for their contributions to the committees that provided input used to inform this report:

6PPD Spatial Technical Advisory Committee

- Ecology would like to thank the participants of the 6PPD Spatial Technical Advisory Committee for sharing their perspectives and offering guidance on this complex and emerging issue.
- A full list of participants and presenters can be found in Appendix B. Special thanks to the many data contributors and GIS analysis support.

6PPD Best Management Practices Project Advisory Committee

- *Consultant team:* Osborn Consulting, Evergreen StormH20, TetraTech, and GeoEngineers compiled scientific and technical information and provided best management practice recommendations for 6PPD and 6PPD-q (Appendix C).
- A full list of participants can be found in Appendix C.

6PPD Partner Memo Contributors

- Technical memos from Washington Department of Transportation (Appendix A), University of Washington Tacoma and the Washington State University Puyallup (Appendix D) were requested to support this 6PPD legislative report assignment.

Stormwater Work Group 6PPD Subgroup

- *Co-Chairs:* Eli Mackiewicz (City of Bellingham) and Abby Barnes (WDNR) facilitated expert panel discussions about stormwater management approaches to address 6PPD and 6PPD-q. A full list of participants can be found in Appendix E

Puget Sound Stormwater Science Team

- The investigation that led to the discovery of 6PPD-quinone began at the Whatcom Creek Hatchery in Bellingham, WA and has since included many non-profit, local, state, federal partners over the years. Federal partners that were instrumental in the research leading to the 6PPD-quinone discovery and provided critical information for this report, have been the Northwest Tribes.
- The pre-spawn coho mortality investigations were advised and implemented by ecotoxicologists at the National Oceanic and Atmospheric Administration (NOAA) and the US Fish and Wildlife Service and funded consistently by the Puget Sound National Estuary Program, EPA. This foundational work led to a correlation between roads and pre-spawn coho mortality. The addition of the analytical expertise by the UW Tacoma team and toxicology studies at the Washington Stormwater center by WSU-Puyallup and NOAA and many others, helped the Stormwater Science Team discover the tire contaminant. This work is an inspiring example of scientific and community collaboration, everyone played a key role in the discovery to help find solutions.

The authors thank the following Ecology staff for their contributions to this report:

- Jessica Archer
- Jennifer Carlson
- Derek Day
- Karen Dinicola
- David Giglio
- Will Hobbs
- Annette Hoffmann
- Mugdha Flores
- Jeff Killelea
- Foroozan Labib
- Joan LeTourneau
- Vince McGowan
- James Medlen
- Katie Rathmell
- Keunyea Song
- Abbey Stockwell

Legislative Direction

In 2021, the Washington State Legislature passed a proviso in Engrossed Substitute Senate Bill 5092, Section 302 (23) to the Washington State Department of Ecology as follows:

> (23) $523,000 of the model toxics control operating account—state appropriation is provided solely for the department to work with the department of transportation, University of Washington-Tacoma, and Washington State University-Puyallup to identify priority areas affected by 6PPD or other related chemicals toxic to aquatic life from roads and transportation infrastructure and on best management practices for reducing toxicity. This includes developing a standard method for the laboratory measurement of 6PPD-q and related chemicals. The department will submit a report to the appropriate committees of the legislature by November 1, 2022.

Executive Summary

Vulnerable ecological areas exist across our lowlands where Pacific salmonids and untreated road runoff meet[16]. In December 2020, a Puget Sound-based stormwater science team identified the contaminant responsible for pre-spawn coho mortality[17] observed in urban areas for many decades. The contaminant is

- 6PPD: N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, a tire additive that enhances tire longevity, with
- 6PPD-q: 6PPD-quinone, the transformation product.

With this harmful contaminant identified, steps were needed to address the threat to aquatic life from roadway runoff. The Washington State Department of Ecology (Ecology) was directed by the state Legislature to seek interim strategies to address the issue until longer-term solutions could be identified. The interim strategies describe best management practices (BMPs). Priority areas were defined by their vulnerability to the co-occurrence of the contaminant and salmon.

In collaboration with Washington State Department of Transportation (WSDOT), University of Washington Tacoma (UW Tacoma) and Washington State University - Puyallup Extension (WSU-Puyallup), two expert workgroups convened to form technical advisory committees to help review scientific and technical information in order to inform next steps for assessment strategies and mitigation actions.

For the assessment strategies workgroup, a letter was sent to Washington Tribes with interests residing in Washington watersheds and streams to solicit information and request participation to develop a prioritization process of next steps for state action and implementation. Federal and state agencies, local governments, universities, and non-governmental organizations also provided the most up-to-date scientific information regarding 6PPD-quinone and discussed data gaps. Collectively, this group provided technical recommendations based on vulnerabilities of salmon to the contaminant at the sub-watershed level. This group also created a process that could be used for future efforts to inform implementation prioritizations for reducing tire contaminants exposure to vulnerable aquatic areas.

Ecology recognizes that our salmon bearing watersheds and streams have Treaty Rights and reserved rights attached to them by federally recognized tribes. This sets a high priority for Ecology and other state agencies to quickly determine and implement remedial efforts on 6PPD-q in consultation with Indian Tribes.

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[16] Additional Pacific salmonid species are sensitive to 6PPD-quinone, see Appendix D, coho are the most sensitive thus far and represent the extent of field mortality observations. Species-specific prioritizations are recommended when considering natural resource management and funding decisions.

[17] Pre-spawn coho mortality is commonly referred to as urban runoff mortality syndrome (URMS). Future research will help correlate pre-spawn coho mortality events with land use and delivery mechanisms.

For mitigation and stormwater management approaches, the participants of the project advisory committee represented state agencies, local governments, and universities. This group reviewed a stormwater management evaluation report completed by a contracted consultant group.

The assessment strategy workgroup found that the amount of stormwater mitigation needed to address the tire pollution problem varies considerably from watershed to watershed. Identifying areas for finer-scale assessments based on vulnerability will require more coordination and research. This report provides an initial assessment of vulnerable ecological areas in order to inform planning efforts (Figure 1).

Stormwater treatment infrastructures that use infiltration, sorption, filtration, and/or effectively capture tire wear particles are expected to reduce the toxicity from 6PPD-q. Preventive operation and maintenance, such as street sweeping and catch basin cleaning, are likely helpful in preventing the transport of tire wear debris and reducing the magnitude of the problem.

The development of 6PPD-q analytical methods at Ecology's Manchester Environmental Laboratory (MEL) can support future experiments and monitoring to assess research areas. To date, MEL has completed method development for 6PPD-q in water samples, with accreditation pending. MEL has begun the development of a method for measuring 6PPD-q in sediments.

This report is an initial assessment to help with reconnaissance (monitoring and science) of a new contaminant of emerging concern. A prioritization process was cooperatively developed amongst the committee members and future research opportunities were identified.

Ecology has submitted budget requests for the 2023-2025 biennium to continue research in the following areas:

1. Mitigate road runoff in previously inventoried areas using approaches that slow and infiltrate stormwater runoff. Where infiltration is not possible, allow soils, vegetation, or sorbent materials time to filter pollutants before the stormwater enters surface waterbodies. *(2023-25 Stormwater Financial Assistance Program[18]).*
2. Conduct studies to test BMP effectiveness to reduce toxicity in runoff. *(Ecology 2023 Policy Level – PW – Toxic Tire Wear in Stormwater decision package[19]).*
3. Support coordination to assess, fund, design, implement, and monitor stormwater mitigation projects that effectively protect aquatic life. *(Ecology 2023 Policy Level – PW – Toxic Tire Wear in Stormwater decision package).*

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[18] http://teams/sites/FS/Budget_Managers/Budget%20Development/40000539%202023-25%20Stormwater%20Financial%20Assistance%20Program.pdf

[19] http://teams/sites/FS/Budget_Managers/Budget%20Development/PL%20PW%20Toxic%20Tire%20Wear%20in%20Stormwater.pdf

4. Continue related efforts to identify safer alternatives to 6PPD and to eliminate its use. *(Ecology 2023 Maintenance Level – AK – Address Toxic Tire Wear Chemical decision package[20]).*

In addition, Ecology and partners have identified areas for subsequent research and collaboration:

5. Support continued local and regional research to further our understanding of the main sources, pathways, persistence, and harmful impacts of motor vehicle tire additives to vulnerable waterbodies. This includes science-based actions for (1) continued coordination to refine the scoring criteria and apply to finer geographic scales, and (2) continued research to reduce the assumptions made in this assessment and to develop additional field and laboratory methods.
6. Support ongoing 6PPD geographical information system (GIS) mapping strategies to inform and track mitigation efforts and to identify cost-effective, feasible projects that result in optimal habitat benefits and support self-sustaining Pacific salmonid populations.
7. Help coordinate and conduct baseline physical and chemical stream assessments prior to fish barrier and stormwater retrofit projects in order to inform an adaptive management approach.

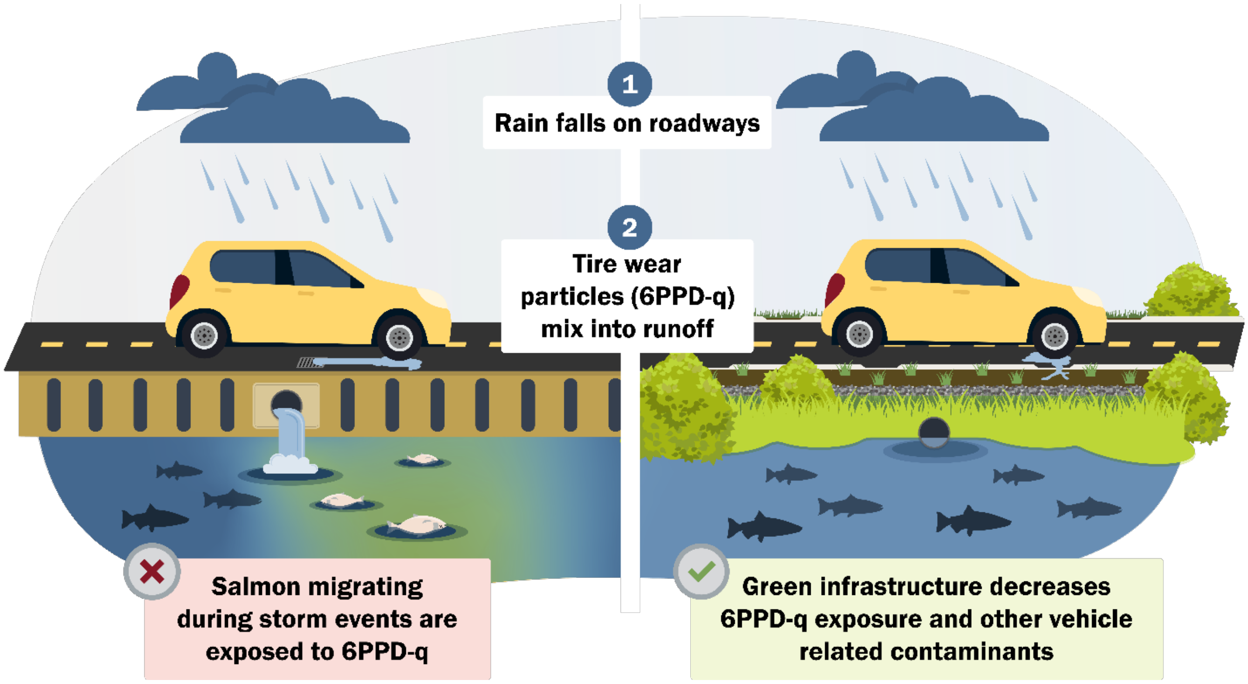

Figure 1. Vulnerable ecological areas: waterways near transportation infrastructure that support species sensitive to 6PPD-quinone.

Roads crisscross our lowland streams. 6PPD-q source control and treatment can help protect aquatic life from harmful tire pollutants. Stormwater facilities that mimic natural filtration processes is an effective approach to treating 6PPD-quinone discharge. (*Graphic courtesy of Amanda Johnson.*)

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[20] http://teams/sites/FS/Budget_Managers/Budget%20Development/ML%20AK%20Address%20Toxic%20Tire%20Wear%20Chemical.pdf

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Chapter 1: Introduction

Purpose of this Report

This report provides our approaches for evaluating how and where to mitigate 6PPD-q in the environment.

A summary of strategies and preliminary recommendations:

1. Assessment strategies to identify priority areas where vulnerable aquatic habitats are most likely exposed to road runoff to help focus tire wear studies.
2. Mitigation strategies that are likely to help prevent and reduce 6PPD and 6PPD-q in stormwater runoff from the built environment.
3. Analytical capability to accurately measure 6PPD-quinone in environmental samples including water, sediment, and tissue to support reconnaissance and mitigation efforts.

Assessment Strategies

A 6PPD spatial technical advisory committee (STAC) was convened in response to this proviso to help develop an approach for identifying ecological areas vulnerable to untreated road runoff to guide future reconnaissance (see Table 1 for affiliations and Appendix B for a full list of participants).

Preliminary sub-watershed scale evaluations were performed to help focus stream assessment and mitigation efforts. The continued engagement of salmon recovery, water quality and transportation communities are needed to strategically locate, plan and fund tire pollutant source control and treatment measures to protect the most vulnerable aquatic ecosystems.

Objectives and scale of the 6PPD priority area evaluation

Watershed scale - 2022 – this report: Produce a sub-watershed scale assessment of vulnerability and exposure including
(1) transportation, (2) ecosystem, and (3) watershed attributes.

Stream scale - Continuous: Incorporate stream health and habitat benefits on a stream catchment scale, while supporting field and lab based 6PPD research. Share information via a web-based 6PPD hot spot interactive webmap, to help standardize, collect, and share data across interest groups.

Project scale - Continuous: Incorporate latest information regarding the scope and scale of 6PPD-quinone in the environment and BMP effectiveness studies. Cross-reference and coordinate fish passage barrier and local and state transportation stormwater retrofit, and salmon recovery project prioritizations. Consider Pacific salmonid habitat and population assessments when weighing the cost and benefits of proposed projects.

The new urgency that 6PPD-q toxicity adds to the suite of sustainability challenges facing our transportation infrastructure provides an opportunity to re-envision these systems. Project prioritization decisions that consider both physical and chemical habitat benefits and avoid undesirable consequences, such as creating ecological traps[21], will best support ongoing salmon recovery efforts.

Mitigation Strategies

Understanding the hazards, dominant source, and delivery pathways of 6PPD-quinone to vulnerable aquatic habitats will inform future decisions on which mitigation approaches and treatment options are feasible for particular sites. The Washington State Department of Transportation (WSDOT), Ecology, and regional scientists have made significant investments in stormwater treatment studies that measure the effectiveness of various best management practices (BMPs) and inform mitigation strategies. However, few studies have yet directly evaluated 6PPD-q.

National Oceanic and Atmospheric Administration (NOAA), U.S. Fish and Wildlife Service (USFWS), Suquamish Tribe, and WSU-Puyallup have conducted stormwater treatment experiments in the laboratory and found that filtration of road runoff through engineered soil mixes used for bioretention prevent pre-spawn mortality (Spromberg et al. 2016).

More recently, UW Tacoma and WSU-Puyallup retrospectively analyzed stored samples from a compost-amended bioswale (CABS) along a WSDOT roadway and found reduced 6PPD-q concentrations. This treatment uses horizontal runoff filtration through the blades of grass and was moderately effective at preventing sub-lethal impacts in zebrafish embryos (Tian et al. 2019). Altered stormwater wattles containing bioretention soil mix placed in an existing stormwater detention pond appeared to provide greater toxicity reduction benefits than CABS, with overall performance similar to bioretention (Appendix D).

Ecology's Stormwater Management Manuals (Ecology's Manuals) define design standards and other minimum requirements for the actions specified in the permits intended to control runoff from roadways and other developed surfaces. The manuals provide guidance used by the stormwater general permits by outlining the needed source control or treatment BMPs based on land use and pollution generating impervious surfaces. WSDOT maintains the Highway Runoff Manual[22] to guide stormwater management for transportation projects.

Analytical Capabilities

Analytical methods for reliable measurements of 6PPD-q in water are now available at Ecology to allow direct quantification of 6PPD-q in the environment and evaluate the performance of BMPs. Ecology's Manchester Environmental Lab (MEL) has funding to continue method development for the analysis of 6PPD-q in sediment and could expand to fish tissue matrices

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[21] Ecological trap refers to addressing fish barriers and inadvertently exposing salmon to impaired water quality.
[22] https://wsdot.wa.gov/engineering-standards/all-manuals-and-standards/manuals/highway-runoff-manual

with additional funding. Currently, there are no labs accredited for 6PPD-q analysis; however, UW Tacoma and Ecology's MEL are in the process of applying for accreditation.

Ecology's Approach to Implementing this Proviso

Given that 6PPD-q is a newly discovered toxic contaminant, Ecology staff sought the advice of leaders in ecotoxicology, stormwater management, urban and transportation planning, modeling, and salmon recovery. The following is a summary of our efforts to capture and summarize the evaluated information including (1) literature and spatial data reviews, (2) strategies developed by Ecology staff and contractors, and (3) input from Washington Tribes and our other local, regional, federal partners.

- WSDOT provided a memo to Ecology that explains their adaptive stormwater retrofit planning approach to mitigate 6PPD-q and how they plan to invest the $500 million dedicated to stormwater treatment (Appendix A).
- Ecology formed a 6PPD spatial technical advisory committee to help focus source assessment and mitigation efforts (Table 1). Spatial information – including salmon distribution as well as watershed and transportation characteristics – was gathered and mapped to identify watersheds vulnerability to the co-occurrence of the contaminant and salmon.

Table 1. Affiliation of members participating in the 6PPD spatial technical advisory committee (Presented).* A full list of participants is in Appendix B.**

WA Department of Transportation*	National Oceanic and Atmospheric Administration*
UW Tacoma	WA Department of Natural Resources
WSU Puyallup	WA Department of Fish and Wildlife*
The Washington Stormwater Center	Northwest Indian Fisheries Commission*
Nisqually Indian Tribe*	Geosyntec Consulting*
Suquamish	Tulalip Tribe
The Puget Sound Partnership Working Groups	Washington Nature Conservancy*
Squaxin Island Tribe	Muckleshoot Tribe
Hoh Indian Tribe	Puyallup Indian Tribes
US Environmental Protection Agency	Stormwater SIL
Pierce County	King County
Wild Fish Conservancy*	Salmon Safe
US Geological Survey	US Fish and Wildlife Service

- Vulnerable areas are proposed for pilot studies using the following approaches:
    - GIS experts presented an overview of their innovative work, and the group assessed what methods and information would be most effective at indicating 6PPD hot spots prior to having direct 6PPD-quinone data (Appendices B and D). A map of sub-watersheds with greater traffic activity and distribution of salmon bearing streams and impervious surface was produced.
        - *Product* – map of sub-basins scored for vulnerability of exposure to 6PPD-quinone for further assessment and planning.
    - Technical coordination with Washington Tribes
        - A letter to the Tribes of WA State soliciting information and participation in developing a vulnerability scoring process.
        - Ecology staff presented the proposed process to the Tribal water quality working group coordinated by the Northwest Indian Fisheries Commission (NWIFC), the support staff for the Northwest Tribes, to share updates and collect information.
        - Chapter 43.376 RCW requires that Washington State agencies collaborate and partner with several federally recognized sovereign Indian tribes on shared interests and issues. These recognized Indian Tribes have reserved rights on their reservation lands or usual and accustomed territories associated with their Treaties with the federal government or by Executive Order of the President of the United States.
        - *Product* – feedback regarding areas of particular concern within usual and accustomed fishing areas are found in Appendix B.
    - Personal interviews with regional fish biologists and water quality professionals.
        - *Product* – list of areas for further assessment and planning to help guide mitigation actions.
    - Cross-referencing fish barrier, transportation stormwater retrofit plans, and NWIFC salmon distribution.
        - *Product* – list of previously prioritized major highway transportation stormwater retrofit projects coordinated with WSDOT.
- Ecology procured support from engineering consultants to prepare a report that evaluates which stormwater BMPs are expected to reduce concentrations of 6PPD and 6PPD-q in stormwater runoff. Consultants reviewed BMPs published in Ecology's Manuals, WSDOT's Highway Runoff Manual, and other stormwater manuals across the country. Their report, *Stormwater Treatment of Tire Contaminants – Best Management Practices Effectiveness,* is provided in Appendix C. The BMP project advisory committee and the consultants' work will inform future updates to Ecology's Manuals.
- Ecology procured technical memos from UW Tacoma and WSU-Puyallup to capture the most up-to-date science information for this report (Appendix D).
- The Stormwater Work Group 6PPD Subgroup reviewed and shared information and provided recommendations to Ecology staff and the larger stormwater community (Appendix E).
- A more detailed overview of the sources of 6PPD and transformation products are summarized in Appendix F.

- Links to information regarding low impact development and innovative stormwater treatment approaches are available in Appendix G.
- A brief history of pre-spawn mortality observations and the efforts that led to the identification of 6PPD-quinone as the cause is provided in Appendix H.

Chapter 2: Assessment Strategies

This chapter provides an overview of the priority area identification strategy that to inform assessment actions. There are over 33,000 stormwater outfalls in the Puget Sound area alone and more than 9,000 are discharged to streams, many of these are managed by WSDOT. The number of mapped outfalls around Puget Sound is an underestimate considering the thousands of undocumented stormwater outfalls outside of municipal stormwater permit areas. Washington State has over 150,000 lane miles, and WSDOT administers 7,000 miles of highways, with the remaining managed by local jurisdictions (WSDOT 2021[23]). Transportation infrastructure crisscross the lowland landscape and Pacific salmon bearing streams.

Despite the widespread use and presence of 6PPD in tires and on roadways, the prevalence of 6PPD-q in aquatic areas is unknown (Appendix B and C). WSDOT and local jurisdictions are ready to adapt and re-assess previously prioritized transportation stormwater retrofit projects to address tire toxicant impacts on Pacific salmon (Appendix A). In parallel with conducting more research to confirm the physical and chemical properties of 6PPD-q, we also need to research the persistence and pathways of 6PPD-q to inform ongoing prioritizations and mitigation planning.

Despite our limited understanding of 6PPD-q fate and transport of tire wear particles and contaminants in the environment, data are available for the Puget Sound area showing multi-year, pre-spawn coho salmon mortality observations (Appendix B and H). Most of these observations have been in the greater Seattle area in highly urbanized areas; however, streams characterized by less urbanization and within transportation corridors have experienced reoccurring pre-spawn coho mortality as well (Appendix B and Appendix H). Therefore, the exposure of 6PPD-q is not necessarily isolated to urbanized areas and is correlated with traffic and roads (Feist et al. 2017).

Prioritization Approach

After an extensive literature review and an inventory of regional data, the use of desktop spatial (GIS mapping) analysis was found to be an effective approach to assess priority areas at this early, 6PPD data poor stage (Appendix B). This report defines priority areas as aquatic habitats that support species known to be sensitive to 6PPD-q and are near transportation supporting infrastructure. Spatial analysis can allow natural resource scientists and managers to visualize conservation and restoration action plans (Ettinger et al. 2020, Puget Sound

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[23] https://wsdot.wa.gov/sites/default/files/2022-02/Statewide%20Highway%20Log%202021.pdf

Watershed Characterization Project[24]). The 6PPD STAC provided guidance and inspiration for the development of a multi-scalar prioritization approach (Appendix B; Figure 2).

A spatial evaluation identified existing tools designed to inform conservation, restoration, and Low Impact Development (LID) actions (Appendix B: Table 4). However, no stand-alone visualization tool provided the information needed to identify vulnerable aquatic ecosystems and 6PPD-q exposure. Furthermore, many of the most relevant tools are unavailable beyond the Puget Sound region.

Prioritization approach

1. Sub-watersheds were scored using indicators of vulnerability and exposure (ecosystem-salmon habitat, transportation, and watershed attributes).
2. Fish biologists, environmental scientists, stormwater professionals, and urban planners were interviewed to capture professional advice.
3. A spatial technical advisory committee was formed. It included many of the curators of existing spatial resources as well as stormwater and fish professionals.
4. A letter was sent to each of the Washington Tribes requesting local information on streams or areas suspected to be most impacted by transportation-related water quality impairments to help further focus pilot study areas.
5. Vulnerable streams were cross-referenced with the Washington State Department of Transportation previously prioritized stormwater retrofit projects. These stormwater projects were reviewed using an extensive stakeholder and Tribal government process that scored projects by habitat benefits, cost effectiveness, feasibility, environmental and social co-benefits, and community support.
6. A literature review and spatial information evaluation was conducted to help us understand the best methods for identifying priority areas where the most vulnerable species (species-specific priority method) are most likely exposed to stormwater pollution.

For this report, preliminary maps are presented to help visualize the initial sub-watershed scoring process that relies on primary indicators (ecosystem, transportation, and watershed attributes). The sub-watershed scores, habitat benefits, tribal input, as well as prioritized fish passage and transportation projects need to continually be cross-referenced to help focus reconnaissance efforts and improve our understanding of 6PPD-q in the environment (Appendix A and B; Tables 1, 2, and 3).

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[24] https://ecology.wa.gov/Water-Shorelines/Puget-Sound/Watershed-characterization-project

Prioritization Scale and Process

A watershed scale approach was employed *"to identify priority areas affected by 6PPD or other related chemicals toxic to aquatic life from roads and transportation infrastructure [ESSB 5092, Section 302 (23)]"* to help focus future 6PPD-q assessments and mitigation pilot studies.

Watershed-scale refers to Washington's National Hydrography Dataset [25] that represents 2,730 designated sub-watersheds within Washington State (HUC12: Appendix B). Salmon Recovery Watersheds refers to the 25 salmon recovery lead entity watersheds as designated by the Governors Salmon Recovery Office[26] and the Recreation and Conservation Office[27] (Appendix B. Figure B2).

Ongoing planning and reconnaissance are needed at each spatial scale using the most appropriate tools and processes.

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[25] https://ecology.wa.gov/Research-Data/Data-resources/Geographic-Information-Systems-GIS/NHD
[26] https://rco.wa.gov/salmon-recovery/governors-salmon-recovery-office/
[27] https://rco.wa.gov/salmon-recovery/

A Summary of the Proposed Prioritization Scale and Process:

✓

1. **Regional scale** – Regional information assessment, this has been completed for the Puget Sound area by the Watershed Characterization Project as an initial screen of general conservation and restoration planning. – ***Completed for Puget Sound***

✓

2. **Watershed scale** - Use existing data and best professional judgement to identify vulnerable ecological areas on a watershed scale (most traffic, salmon, and stormwater) – ***This report for Washington State***
3. **Stream scale** - Use existing data and best professional judgement to identify vulnerable ecological areas on a stream and reach scale, seek input from natural resource agencies and tribes. – ***Ongoing***
4. **Project scale** - Augment the above with considerations for water quality enhancement with partner prioritization efforts including transportation stormwater management, fish passage and stream habitat enhancement projects. – ***Ongoing***
5. **Community scale** - Support and coordinate stakeholder and tribal government engagement of the proposed priority areas and stormwater treatment projects. Salmon Recovery Community Lead Entity project prioritization process provides a good framework. Collect and assess local information and level of support. – ***Ongoing***
6. **Funding** - Support federal and state funding coordination. – ***Ongoing***
7. **Monitoring and mapping** - Support efforts to inventory, standardize and map stormwater infrastructure and facilities needed for pollution reduction modeling and stream recovery planning. Collect baseline biological, physical, and chemical data before and after habitat enhancement projects to assess effectiveness and the reduction of harmful impacts using standardized biological stressor procedures. – ***Ongoing***

Indicators of Vulnerability

The watershed evaluation highlighted several primary indicators from three main characteristic features to help identify vulnerable areas exposed to road runoff pollution: (1) ecosystem, (2) watershed, and (3) transportation (Table 2).

Table 2. Primary indicator of vulnerable ecological areas exposed to road pollution for this report.

Characteristics	Indicator Type	Primary Indicators
Ecosystem	Vulnerability	Salmon habitat type by species Salmon habitat distribution by species Salmon stocks per watershed all species Salmon reach habitat length
Transportation	Exposure	Traffic counts (AADT) Road distance Road type Vehicle type Road and stream crossings
Watershed	Transport	Land cover Land use Stream characteristics Precipitation

Ecosystem: Indicators of Vulnerability

Understanding Pacific salmon distributions and population dynamics across life stages helps evaluate habitat benefits when prioritizing projects. Furthermore, understanding the range of sensitivity of 6PPD-q toxicity to salmonid species allows refined focus to species-specific priority areas. Among the Pacific salmonid species, coho salmon are the most sensitive to 6PPD-quinone and the most exposed to vehicle pollutants given their lowland small stream habitat preference (Spromberg and Scholz et al. 2011, Feist et al. 2017, French et al. 2022, Appendix D).

Transportation: Indicators of Exposure

Greater traffic and heavier vehicles lead to increased 6PPD-q pollutant loading on roadways and presumably to streams (Tian et al. 2020). Traffic counts and vehicle weight are measured by Annual Average Daily Traffic (AADT) and vehicle type, respectively. Other suspected hot spots include parking lots, park and rides, ferry terminals, bridges and industrial transportation facilities that are represented in this preliminary analysis by percent impervious land cover and road length per sub-watershed defined by a 12 digit hydrologic unit code (HUC12[28]) and the

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[28] https://developers.google.com/earth-engine/datasets/catalog/USGS_WBD_2017_HUC12

National Land Cover Database (NLCD[29]). Additional transportation support activities such as bridge washing, car washing, street sweeping, and tire disposal are regulated activities in the State of Washington. For instance, tires are no longer allowed at landfills and must be disposed of properly in secondary containers. Old tires are reused and recycled into a variety of new products.

Watershed: Indicators of Transport

Watershed characteristics can help identify areas that are more likely to be impacted by stormwater pollution. Watersheds characterized by greater impervious surfaces and limited natural infiltration processes are more likely to carry harmful pollutants to streams. Stormwater volume and contaminant loading are driven by a combination of land use, land cover, and precipitation (Appendix B). For example, bare roads versus tree-canopy-covered roads may produce different amounts of 6PPD-q driven by greater heat and light exposure. Urban heat and ozone syndrome could cause faster whole tire and tire wear particle degradation and 6PPD-q production.

Stream and watershed hydrology not only affect chemical dilution, fate, and transport, but can also impact the natural substrates of the stream and biological communities (Larson et al. 2019). Understanding watershed and stream characteristics will help identify areas of pollution retention and corresponding water quantity impacts. High, low, and flashy streamflow most likely affect the retention and resuspension of tire wear particles and other pollutants in sediments. The elevation, gradient, size, and complexity of a watershed lead to greater risk of flooding and overloading old stormwater systems. Finally, regional climatic variability such as temperature and precipitation intensity and frequency most likely affect the tire wear particle and chemical release rates to the environment.

Integration of Indicators

The primary indicators were integrated to calculate a score for each of the 2,730 sub-watersheds for vulnerability, exposure, fate, and transport (Figure 2). Appendix B provides a more detailed overview of the initial, broad-scale scoring process. Sub-watersheds that lacked indicators of both exposure and vulnerability were removed from the map. The higher the score, the greater the indicators of vulnerable ecological areas exposure to tire wear particles and chemicals. Vulnerable areas for this initial broad-scale assessment included coho salmon, rainbow trout and steelhead chosen for their sensitivity to 6PPD-quinone (Appendix D). GIS layers are available for additional species-specific prioritizations.

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[29] https://www.usgs.gov/centers/eros/science/national-land-cover-database

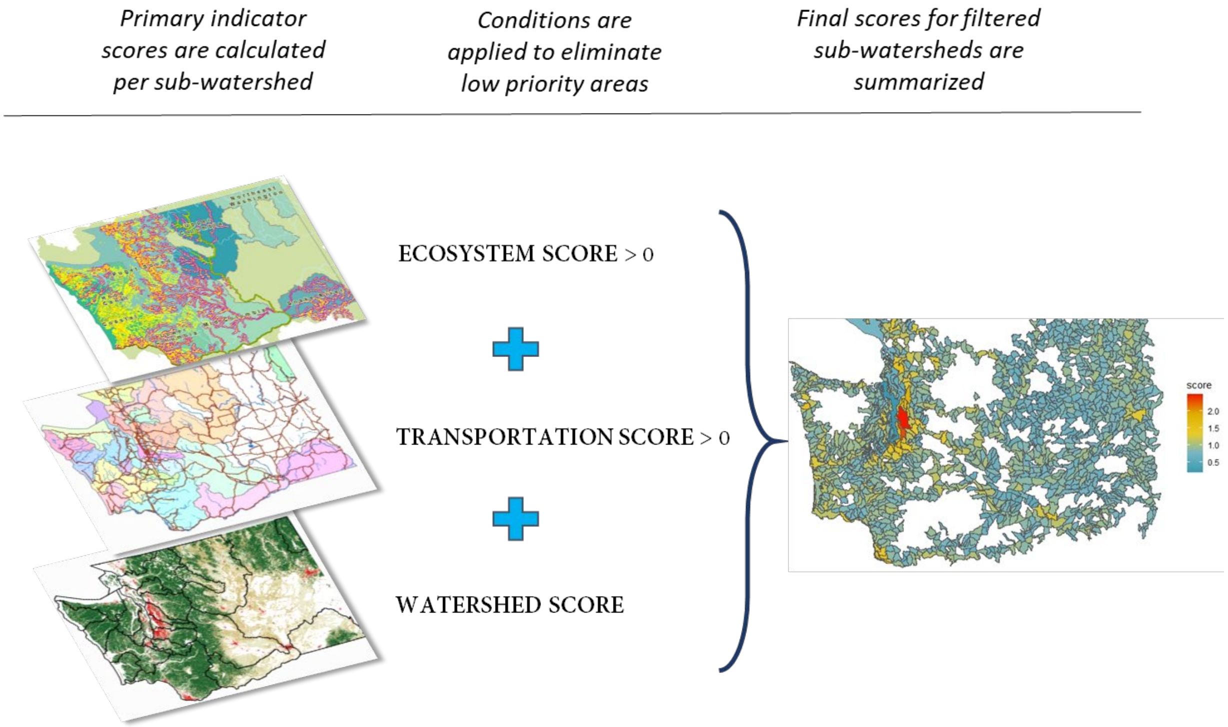


Figure 2. Scoring and integration of sub-watersheds to help focus efforts on vulnerable ecological areas for 6PPD-q assessment and mitigation studies.

The integration of primary indicators binned by indicator type and nested into sub-basins provides mapping results to help visualize and focus reconnaissance efforts (Figures 3). There are hundreds of sub-basins with a combination of Pacific salmonid habitat and tire wear particle and chemical sources.

Areas where broad-scale and mid-scale assessments have been completed are natural areas for communities to identify projects that strategically replace old stormwater systems with new stormwater management facilities that satisfies or exceeds current regulations. Areas with the most available and reliable monitoring information, data rich areas, are ideal to evaluate mitigation planning to improve salmon habitat water quality.

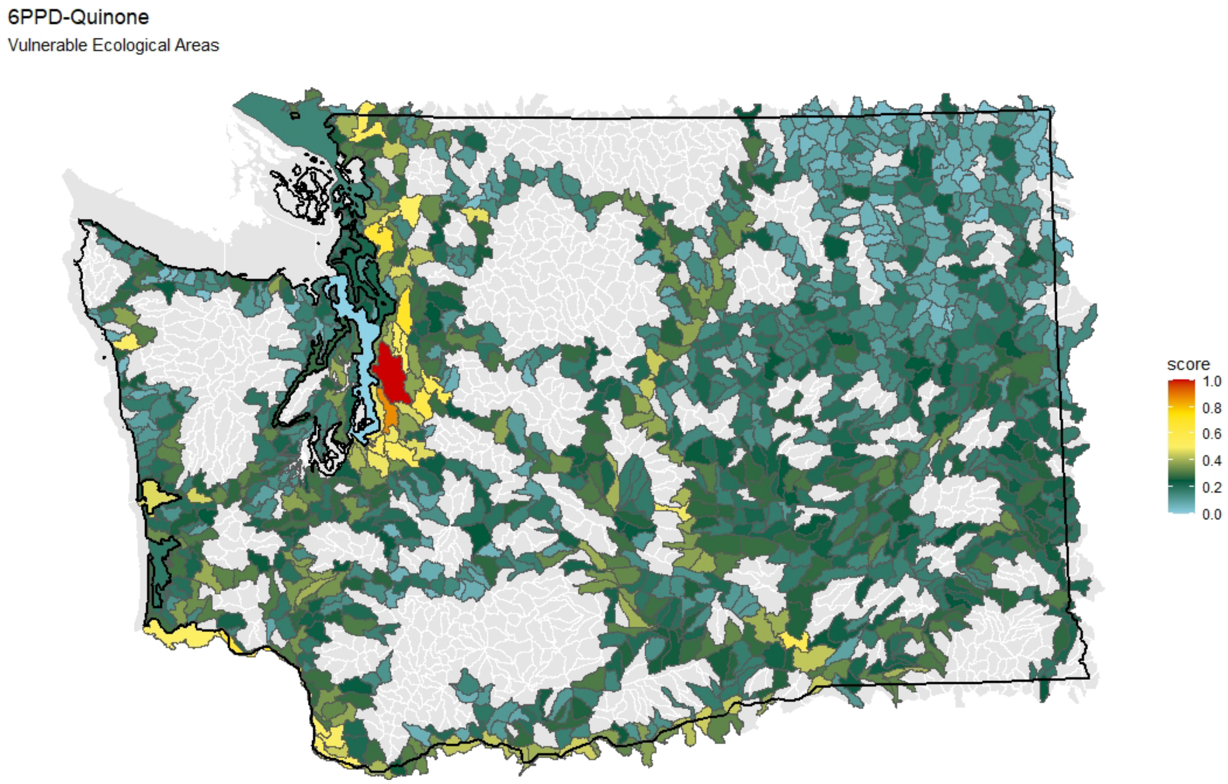
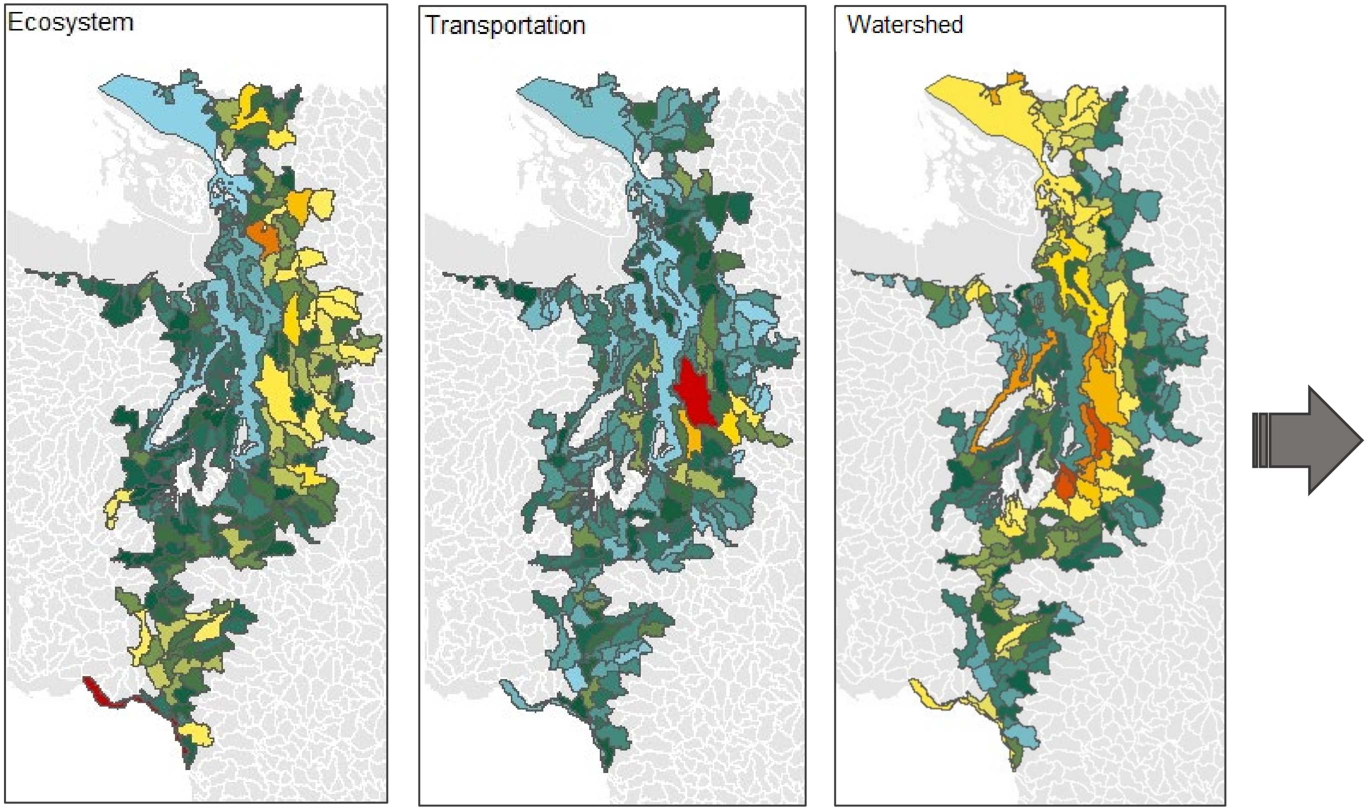


Figure 3. A GIS assessment of vulnerable ecological areas for coho, steelhead, and rainbow trout that are potentially exposed to transportation runoff.

However, source ID reconnaissance is needed to verify these broad-scale assessments that employ indicators of tire wear and chemical exposure.

The Puget Sound ecoregion currently has the most available monitoring information to inform strategic stormwater retrofits of outdated infrastructure, while data deprived areas need further inventories to support strategically focused mitigation actions. The inequality of available monitoring data around the State of Washington is the primary reason that this mapping exercise is considered an initial step to help focus local reconnaissance support and resources. The Puget Sound ecoregion represents a range of ecosystem, transportation, and watershed indicators of vulnerability and exposure that, when combined, help visualize priority areas (Figure 4).



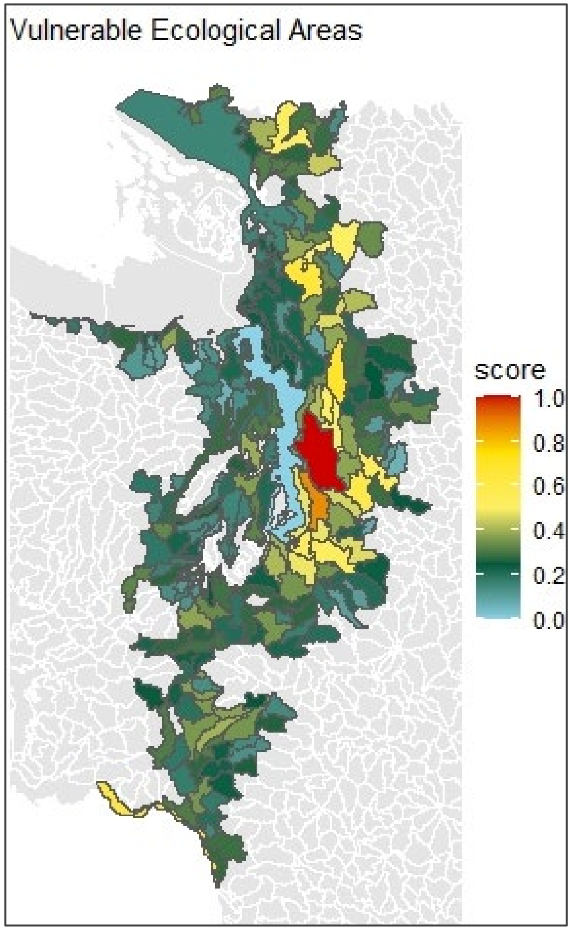
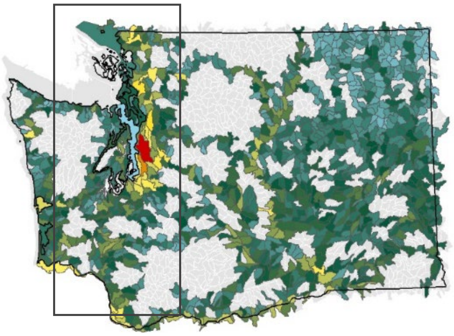


Figure 4. Puget Sound Ecoregion sub-watershed 6PPD-q mapping process. Ecosystem, transportation, and watershed scores are integrated for a 6PPD-q exposure to vulnerable ecological areas score.



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A more detailed account of the primary indicator prioritization analysis is in the spatial technical advisory committee report (Appendix B). The 6PPD-q vulnerable ecological area watershed map allows us to focus our tire contaminant studies to assess 6PPD-q in the environment (Appendix B). One caveat regarding this preliminary analysis is that the available data represents presence data not absence data, so there could be additional vulnerable areas that may represent an under monitored watershed. The variable monitoring information available from one watershed to another further supports the need for ongoing technical coordination with salmon recovery and stormwater management communities.

Streams and roads run through a gradient of human land uses including industry, agriculture, urban development, and forestry. 6PPD-q contamination presents different risks under different circumstances. There are some places where 6PPD-q may act as a limiting factor and render habitat unusable due to acute toxicity, where the physical habitat has been conserved. Therefore, it is critical to assess the ecosystems most sensitive to 6PPD-q toxicity and help identify the most vulnerable aquatic habitats for conservation and restoration planning (Appendix B).

Fortunately, many natural resource groups conduct long-term monitoring to assess and inventory stream health (Appendix B). One of the most effective metrics to assess watershed health is the Benthic Index of Biotic Integrity (B-IBI). A consortium of local and state monitoring programs conducts B-IBI monitoring to help inform recovery efforts in the Puget Sound[30]. As part of the Freshwater Quality Implementation Strategy, the Stormwater Strategic Initiative, 2020[31] uses B-IBI to help guide protection and restoration actions to improve stream health. This is a collaborative effort among the Department of Ecology, Washington Stormwater Center, Washington Department of Commerce, Puget Sound Partnership, Puget Sound communities, and the Puget Sound Institute. Expanding existing local and regional monitoring efforts to measure 6PPD-q as a limiting factor may help with ongoing and future prioritizations for conservation and restoration actions.

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[30] https://pugetsoundestuary.wa.gov/freshwater-quality/

[31] https://pspwa.app.box.com/v/PublicISBIBI/file/902443964294

Further assessment tools instructive to identify streams impacted by motor vehicle and tire pollution:

1. A web-based interactive 6PPD-q vulnerability map to help visualize, track, and scope suspected transportation pollution near vulnerable areas to help inform mitigation actions.
2. Mid-scale stormwater mitigation action planning assessment tool to incorporate selected stream characteristics and planning information. The mid-scale assessment units (e.g., stream catchment) would apply the Watershed Characterization Project (WCP) framework to incorporate (1) spatial resources curated by natural resource partners and (2) recommendations of the 6PPD-q spatial technical advisory group.
3. Field-based assessments of pre-spawn coho mortality observations and direct 6PPD-q measurements are needed to renew a 6PPD-q risk map (this effort is led by NOAA and funded by the Puget Sound National Estuary Program). Meanwhile, employing watershed health monitoring more intensely to local streams will help support limiting factor analysis and ongoing prioritization process.
4. Finally, once the focal streams have been evaluated for tire wear exposure, stormwater modeling may help locate placement and type of stormwater treatment. For example, a new model called Visualizing Ecosystem Land Management Assessments (VELMA) developed by EPA and Oregon State University has conducted a pilot study in West Seattle to model 6PPD-q mass loading and pathways to help plan mitigation actions. (Appendix B).

Ongoing adaptive prioritization processes are needed to incorporate and adjust plans as added information emerges. In addition to continuing related research on 6PPD hazards and potential alternatives, some of the key research data gaps that would help inform prioritizations, planning, and funding efforts are listed below.

Additional Research Questions to Inform Priority Areas for 6PPD Source Control Planning

1. How long do tire wear particles continue to leach 6PPD-q in the environment?
2. How long does 6PPD-q persist under variable environmental conditions?
3. Are there additional delivery pathways of 6PPD-q to aquatic systems (e.g., atmospheric deposition of tire wear dust)?
4. Are tire wear particles (TWPs) and 6PPD-q toxicity an isolated urban problem or does it occur along transportation corridors outside of urban areas?
5. How much and what type of motor vehicles and transportation infrastructure lead to toxic amounts of 6PPD-q?
6. What level of treatment is needed to mitigate 6PPD-q; is a grass strip along a roadway enough to filter out tire wear particles and 6PPD-q?
7. Where has stormwater been effectively treated or diverted to protect sensitive aquatic habitats? (BMP effectiveness)
8. Are there additional tire chemical transformation products to consider beyond 6PPD-q?
9. What other species-specific habitats should be protected, beyond coho-bearing and steelhead-bearing streams, from transportation runoff?

The identified vulnerable areas may shift as these research questions regarding the distribution and persistence of 6PPD-q in the environment are answered. For now, it is known that untreated stormwater impacting sensitive aquatic systems should be managed and that coho have been proposed as an ecological sentinel to help measure our stormwater management and treatment progress (Scholz et al. 2011; Spromberg and Scholz 2011; Spromberg et al. 2016).

Stormwater and Salmon Recovery Partners

Embracing adaptive management strategies, fostering partnerships, and applying all our tools and resources is critical to support ongoing water quality improvements in lowland streams and estuaries and the timely recovery of self-sustaining salmon populations. The Stormwater Strategic Initiative Lead (SIL)[32], a program supported by the National Estuary Program's Puget Sound funds[33], focuses on three priority actions, which include reducing the impacts of stormwater throughout Puget Sound. The program is led by the state Department of Ecology in partnership with the Washington Stormwater Center at Washington State University and the state Department of Commerce.

Ecology and partners plan to coordinate, support, and track the NOAA-led 6PPD-q and coho mortality field surveys.

The discovery of 6PPD-q, after decades of research and reports of pre-spawn coho mortality, was a culmination of a dedicated science team with consistent funding. EPA's Puget Sound Geographic Program provided the most consistent funding source for pre-spawn coho mortality research to date. Continued tire contaminant research will require flexible and accessible local, state and federal funding[34] and coordination between agencies to successfully leverage resources and secure support.

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[32] https://pugetsoundestuary.wa.gov/stormwater-strategic-initiative/
[33] https://www.pugetsoundinfo.wa.gov/Fund/Detail/227
[34] https://www.epa.gov/system/files/documents/2022-06/puget-sound-federal-task-force-action-plan-2022-2026.pdf

Chapter 3: Mitigation Strategies

This section describes *"…best management practices for reducing toxicity. [ESSB 5092, Section 302 (23)]"* and the current state of knowledge about the processes by which 6PPD-q may be managed both physically and chemically, using available stormwater BMPs. Preventing pollutant transport and providing stormwater treatment will be needed for the near future to lessen the impacts from tire chemicals to salmonids.

As a result of this proviso assignment and funding, Ecology procured professional engineering input on effective approaches for stormwater managers to employ to prevent or reduce 6PPD-q toxicity in receiving waters (Appendix C). This section summarizes existing BMP functions that are expected to effectively reduce concentrations of 6PPD and 6PPD-q in stormwater runoff at the site or basin scale, given what is currently known about the chemical properties, sources, and probable pathways to stormwater. This section also provides the rationale for assumptions used in our analysis, research uncertainties, and data gaps that should be addressed to help us better understand and control these pollutants of concern.

Our understanding of what eventually happens to 6PPD and 6PPD-q in the environment is incomplete. The following evaluation is based on EPA's chemical behavior models for 6PPD and 6PPD-q, a few key pilot environmental studies, and the best professional judgment of scientists and engineers. Currently, the most effective BMPs to reduce 6PPD-q concentrations in stormwater include (1) stormwater source controls and (2) treatment approaches that use infiltration, sorption, filtration, and settling. Both 'gray' and 'green' stormwater infrastructure BMPs found in Ecology's Manuals[35] provide these treatment approaches. Source control BMPs, including operational source control BMPs such as street sweeping, are expected to help reduce 6PPD-q concentrations particularly in low (traffic) pollutant loading areas. In high pollutant loading areas, source control BMPs are not likely enough on their own but will help reduce the magnitude of the problem and may work well in combination with treatment BMPs.

Prior to this report, there was no information about 6PPD or 6PPD-q in Ecology's Manuals or WSDOT's Highway Runoff Manual. In July 2022, the consultant's BMP report (Appendix C) has been added to Ecology's Manuals as supplementary guidance. WSDOT is in the process of incorporating 6PPD-quinone into their stormwater retrofit plans (Appendix A).

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[35] https://ecology.wa.gov/Regulations-Permits/Guidance-technical-assistance/Stormwater-permittee-guidance-resources/Stormwater-manuals

Stormwater Management Using BMPs

Permittees and other regulatory agencies have already asked Ecology for best professional judgment guidance on source control and runoff treatment BMPs to address 6PPD and 6PPD-q. Stormwater managers want clarity on Ecology's regulatory expectations for upcoming capital facility projects, retrofits of older infrastructure, and construction of new development and redevelopment projects.

Ecology's Manuals define BMPs:

> *"The method by which the manual controls the adverse impacts of development and redevelopment is through the application of Best Management Practices. [BMPs] are defined as schedules of activities, prohibitions of practices, maintenance procedures, and structural and/or managerial practices, that when use singly or in combination, prevent or reduce the release of pollutants and other adverse impacts to waters of Washington State. The types of BMPs are source control, treatment, and flow control. BMPs that involve construction of engineered structures are often referred to as facilities."*

Stormwater is managed to control runoff volumes and flow rates as well as minimize the discharge of stormwater pollutants. Some larger facilities, such as regional treatment facilities or stormwater parks, are built to handle runoff from large drainage areas; these facilities use the same, scaled up principles as site-scale facilities. Street sweeping (a stormwater source control BMP) is an example of a BMP that works well at larger geographic scales, such as a small city, where a route is developed to maximize efficiency of driver time and waste handling.

BMPs to Reduce Toxicity of 6PPD and 6PPD-q

Local, state, federal, and international researchers have conducted stormwater treatment BMP effectiveness studies for over two decades. Lessons learned from these studies focused on metals and organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCBs), and pesticides, yet these lessons are all relevant to reducing 6PPD-q. In 2014, Ecology launched the Stormwater Action Monitoring (SAM) program, a regional cooperative effort between Ecology and local municipal governments, to conduct studies that improve effectiveness of stormwater management efforts here in Washington. Several SAM studies have gathered information on treating organic contaminants in stormwater, with several of them specifically evaluating toxicity reduction.

Our working BMP assumptions

1. Vehicle-dominated impervious surfaces are a major source of tire wear particles, 6PPD, and 6PPD-q in runoff.
2. All sizes of tire debris and particles are pollutants themselves and presumed to contain 6PPD and potentially release 6PPD-q for an unknown but not indefinite amount of time.
3. 6PPD-q prefers binding to soils, particles and surfaces as opposed to remaining dissolved in water (Appendix C consultant report and Appendix D EPI Suite model output).
4. Persistence of 6PPD and 6PPD-q depends on chemical properties like reactivity or half-life. The modeled half-life for 6PPD and 6PPD-q are relatively short, minutes to days, respectively (Appendices B and C) and will depend on environmental conditions like pH, temperature and oxygen gradients.
5. A wide range of stormwater management strategies are needed to control road runoff. Functional reduction of toxicity from tire wear particles, 6PPD, and 6PPD-q will come in varying degrees from all three types of stormwaters BMPs in Ecology's Manuals: source control, flow control, and runoff treatment.

Using Ecology's Manuals

Stormwater permittees, stormwater grant recipients, and others look to Ecology's Manuals to provide up-to-date information on how to effectively manage stormwater with BMPs to prevent adverse water quality impacts. Ecology's general National Pollutant Discharge Elimination System (NPDES), including municipal stormwater, permittees must follow the BMPs in Ecology's Manuals for both eastern and western Washington. Fortunately, impervious surfaces that support vehicle use are already a focus for stormwater runoff for all new development and re-development projects; therefore, WQP policy believes this focus already helps to control 6PPD-q.

Ecology's Manuals currently include treatment performance standards for total suspended solids, oil, grease, phosphorus, and metals such as zinc and copper. Information to develop new treatment thresholds is collected and reviewed (1) as part of Ecology's grants, and (2) by the Technology Assessment Protocol-Ecology (TAPE) and SAM programs. The use of pollutant surrogates for modelling and treatment is common, and the rationale is that any BMP will reduce concentrations of other pollutants that have chemical behaviors and pathways similar to the pollutant for which the BMP is designed. The information gathered for this report and in ongoing evaluations will inform future updates to Ecology's Manuals on this topic. The categories below will provide more detail on how these BMPs will work to manage the tire wear and 6PPD-q in stormwater runoff.

Post-Construction Soil Quality and Depth

As part of implementing LID, this BMP ensures that the soil at a project site has ample sorptive and plant-supporting characteristics after construction to provide effective soil ecosystem function, sediment capture, treatment and encourage infiltration. This is required in areas covered by the municipal stormwater permits if the site was graded and the naturally occurring topsoil was removed. The refurbished soils will have some added capacity to control contaminants, including 6PPD-q, from runoff directed to the vegetated areas and to allow infiltration of the stormwater on site.

Source Control BMPs

Even if a safer alternative were identified today, 6PPD and 6PPD-q would continue to be released from existing tires for many years to come. This means source control will continue to be extremely important for the near future. All stormwater source control BMPs are intended to prevent pollution from contaminating rainfall or runoff and are based on the land use or pollution-generating activities that take place at a given site. Ecology manuals state, *"It is generally more cost effective to use source controls to prevent pollutants from entering runoff, than to treat runoff to remove pollutants."*

Source control BMPs for 6PPD and 6PPD-q can include actions that prevent tires, tire pieces, and tire wear particles from contacting rainfall, entering runoff, and/or being further transported in the stormwater system. Analyzing the traffic network can help identify where to strategically use source controls. Examples of stormwater source control BMPs for tire chemicals include:

- Roadside tire, tread, and trash clean up.
- Routine schedules for maintenance of stormwater infrastructure such as sweeping streets and parking surfaces as well as cleaning out catch basins and stormwater conveyance pipes.
- Not hosing down streets or parking lots but sweeping them instead.
- Changing truck routes to reduce tire wear from tight turns and pivots or to reduce stops and starts by vehicles near a particular catch basin or stream.
- Use of berms or stormwater wattles to protect inlets and mulches to slow flows across soil or grassy areas.
- Changes to vehicle washing practices at public and private facilities including auto sales lots.
- Coverings to prevent rain or runoff from interacting with tires, crumb rubber, or piles of street waste.
- Education and outreach for garbage pick-up programs including "Adopt a Highway."

Source control BMPs like these will help manage this widely distributed contamination problem. Source control BMPs are typically implemented at broad-scale and will play an important role in meeting receiving water goals. Well-implemented source control activities can make progress toward goals shared with other environmental initiatives such as improving air quality and reducing carbon footprints. Local source control programs and policies can add focus on more specifically addressing 6PPD-q with these practices. However, source control BMPs alone cannot prevent all 6PPD-q impacts. To achieve toxicity reduction, a combination of stormwater source control and treatment approaches will likely be needed in basins with heavy vehicle use or other 6PPD sources.

Flow Control and Runoff Treatment BMPs

Many of the physical and chemical processes used by the flow control and runoff treatment BMPs in Ecology's Manuals will help reduce concentrations of 6PPD, 6PPD-q, and tire wear particles in stormwater. BMPs frequently employ two or more of these processes to reduce contaminants from stormwater.

Size exclusion

Stormwater flow control and runoff treatment BMPs are designed to address most storm events in the Pacific Northwest. Storm events can transport substantial amounts of water and sediment as well as large material like trash, rocks, and branches – or in this case, tires, or large tire tread pieces – to ditches, pipes, and structural BMPs. Examples of size exclusion in road runoff include catch basin inlets or grates, screens on the inlet of manufactured treatment devices, or bars on overflow openings. In the case of tire debris, big pieces would be left on the street, shoulder, or parking surface by inlet bars for crews or sweepers to pick up.

Settling

The highly variable size range of solid particles carried in stormwater systems is a function of: (1) flow rate, in other words, energy to carry the particle, (2) readily available sources of particles, including the build-up of particles between rain events, and (3) maintenance programs, such as street or parking area cleaning.

Tire particles, except for the smallest microplastics, are dense, heavier than water, and will settle out when given the chance (Figure 6). The larger the tire particle, the more surface flow is required to transport from roads to stormwater systems. Specific BMPs or in-system features like ditches or catch basins where stormwater slows and is pooled will allow particles transported by surface runoff to settle. Many factors influence particle settling including water depth, time, associated sediments, and deposition rates, and if applicable, the BMP design for either dead storage or location of emergency overflows.

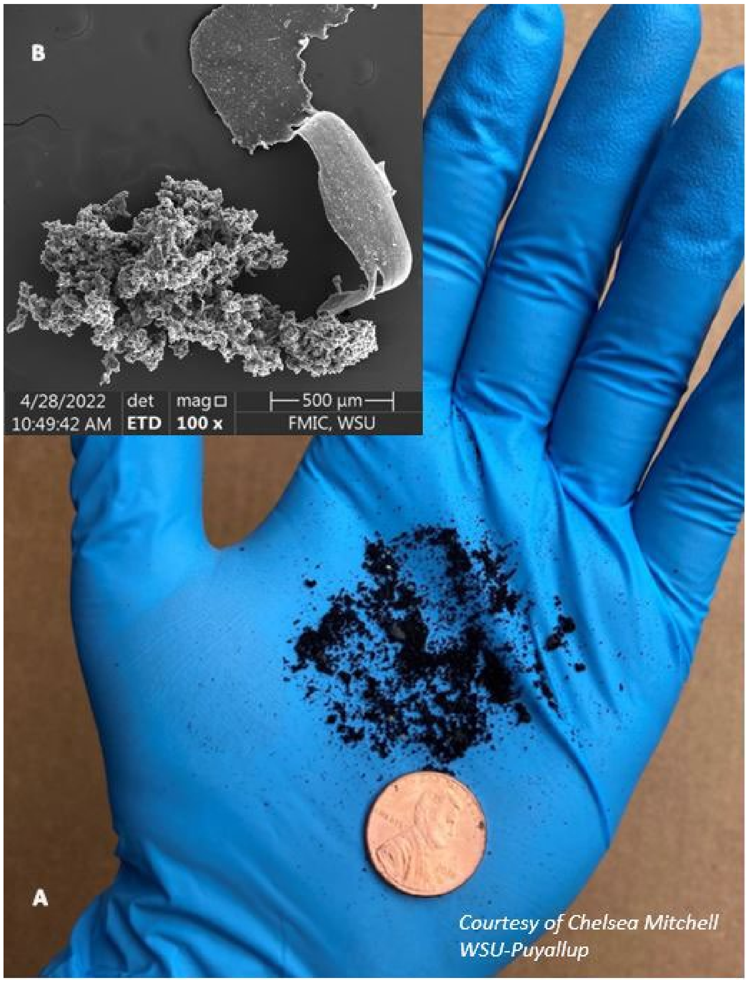

Figure 5. (A) Abraded tire particulates from a nine-tire mixture made at WSU-Puyallup and used in their research; (B) Scanning electron microscope of two of the tire particles from the nine-tire mixture.

The particles that settle in the stormwater conveyance system may be re-suspended during the next rainfall event. However, BMPs with water storage and sedimentation trapping are designed to retain all but the smallest tire particles. Flow control BMPs such as detention and retention ponds, tanks, or vaults are designed for (1) controlling stormwater flow rates and volumes, and (2) capturing suspended solids transported by stormwater. Routine maintenance is required to maintain BMP performance. For example, regularly removing accumulated solids layer which is presumed to contain tire particles along with other trash.

The smallest, microscopic tire particles are not expected to settle out in these temporarily pooled areas of flow and treatment BMPs or in catch basin sumps. Field studies indicate that microscopic tire particles are found in stream sediments. It is unknown whether microscopic tire particles are neutrally buoyant, or if they are removed from additional stormwater management approaches.

Filtration and sorption

Filtration BMPs physically separate particles from water while sorption media in BMPs use physical and chemical processes to attract the chemicals to the media. This “sorptive” media (commercial or natural-based) will likely be effective at separating dissolved constituents like 6PPD, 6PPD-q, and other tire-derived constituents from road runoff. These will be useful for early or low flow runoff, or direct conveyance where runoff is relatively free from suspended particulate and likely to have recently washed off vehicle or tire surfaces. The effectiveness of intercepting runoff containing 6PPD-q with sorbent media has not yet been studied.

Filters that focus on reducing suspended particles (e.g., total suspended solids) will be effective at capturing tire particles and any other particulate matter with sorbed contaminants including 6PPD-q. Filters, such as commercial catch basin inserts, reduce solids prior to entering stormwater conveyance systems in settings where a larger than normal amounts of soils and solids are expected in the flows. Such filters are frequently used at construction and industrial sites and, to a lesser extent, in urban environments. Most of these devices capture trash, soil, and solids and can likely capture tire wear particles.

Contaminants, particularly fecal coliforms, organic chemicals, nutrients, and some metals, preferentially travel through the environment bound to particles of soil, plastic, or organic matter such as leaves. As these particles travel in stormwater systems, they tend to get smaller in physical size due to weathering and grinding by cars or abrasion on concrete pipe walls, often resulting in surface area increases. The increased surface area leads to more binding or sorption potential of the smaller particles. Whether engineered or natural in origin, these small, weathered particles can potentially bind a substantial amount of 6PPD-quinone. If the particle is tire rubber, the same weathering and grinding is anticipated, but this will be a source of 6PPD to the other particles.

Based on the modeled chemical characteristics (Appendices B and C; Table 2, and Ecology 6PPD Alternatives Report 2021[36]), 6PPD-q is presumed to be bound to particulates if enough time or material is available for the sorption to occur. Sorptive media used in stormwater treatment BMPs vary widely among natural to commercial materials. Stormwater treatment compost[37] is specified in Ecology’s stormwater manuals as a plant-based material that does not contain manure or biosolids, has a strictly limited amount of post-consumer meat and food waste, and is not used to grow food. This compost is intended to support a few native or decorative plants, so much less nitrogen and phosphorus are needed.

Researchers have not measured the effectiveness and capacity of any filtration media to reduce 6PPD-q toxicity except the local bench scale studies on the 60% sand and 40% stormwater compost (60:40 mix) bioretention soil mix (Appendix D). The long-term ability of healthy soil and engineered soil mixes to capture and retain 6PPD-q is a research need and is currently unknown. Naturally occurring topsoil or amended soils that meet post-construction soil quality and depth suitability requirements are both likely to capture and retain 6PPD-q.

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[36] https://www.ezview.wa.gov/site/alias__1962/37732/research_and_proposed_alternatives_to_6ppd.aspx

[37] Stormwater compost is specified in Ecology’s stormwater manuals and is not the same product used by gardeners.

Commercially available sorptive media with carbon content, organic matter, and lots of surface area are expected to be effective at controlling 6PPD-q in the environment. These media may be present in a manufactured treatment device or incorporated into site soils or into custom BMP mixes for testing. Additional research is needed to confirm the sorption potential to reduce microscopic tire particles as well as dissolved 6PPD-q and other tire-derived chemicals.

Some solids suspended in stormwater are so small they are considered “dissolved” solids. Presumably 6PPD-q will sorb to these solids just list any other solids and remain very mobile. Knowing if sorptive media or filters can capture this bound dissolved fraction of 6PPD-q, and the extent to which this fraction contributes toxicity, will guide our understanding of how much treatment is needed to prevent toxicity in surface waters.

Infiltration

A key principle of present-day stormwater management is to limit the alteration of the local water cycle and better protect ecosystem function. Infiltration BMPs are those that allow rainfall and stormwater runoff to percolate into the ground. These BMPs keep the water cycle intact by promoting consistent streamflow, preventing erosion or stream downcutting, reducing water temperatures, and providing natural filtration of pollutants.

Infiltration into the ground employs filtering and capturing of tire wear particles and associated toxic chemicals. Stormwater designers look for suitable locations for infiltration BMPs as close as possible to where the rain falls on impervious surfaces, minimizing opportunities for the stormwater to pick up and carry additional pollutants. Also, drywells have been used for many decades to infiltrate runoff.

By design, infiltration BMPs in Ecology’s Manuals filter out the solid material transported by stormwater and are anticipated to perform well to capture tire wear particles, bound 6PPD and 6PPD-q, and dissolved 6PPD and 6PPD-q at the surface layer. Other key considerations include designing for adequate capture of runoff volumes, slowing water down, and infiltrating water into the ground. Infiltration BMPs listed in Ecology’s Manuals and the HRM include dispersion, bioretention, bioswales, and other green stormwater infrastructure (GSI) that include native soil, plants. Infiltration occurs when these BMPs are not lined or under drained to prevent infiltration into the ground. Although it would be ideal to put bioretention and other infiltration GSI everywhere, there often is not enough space or appropriate soils or geology for these highly effective BMPs.

Bioretention

Bioretention is the only GSI in Ecology’s Manuals that meets all three of Ecology’s onsite stormwater management requirements; it is LID, it can be sized to meet flow control requirements, and it also provides runoff treatment. The engineered soil mix used in the bioretention BMP is regionally well studied and prevents acute mortality to coho salmon from highway runoff, and retrospective analyses of frozen post filtration water samples collected during this study did not detect 6PPD-q itself in the filtered water (Appendix D).

Bioretention is sometimes generalized to the term “bioinfiltration” in the literature and other states manuals, and it is often confused or conflated with rain gardens. Bioretention BMPs are designed and sized by engineers to treat a specific volume of runoff and use specified soil mixes. Rain gardens function similarly but have no requirements to be sized or use specific soil mixes and are often constructed by homeowners. Rain garden soils, like native soils, will probably adsorb 6PPD-q, presuming some carbon content and the road and parking area runoff infiltrates and does not bypass the rain garden.

Summary: BMPs for Controlling Tire Contaminants

Ecology procured Osborn/Evergreen StormH20, engineering consultants, to prepare a report compiling and synthesizing current knowledge of 6PPD and 6PPD-q, including physicochemical properties, sources, and fate and transport within the built environment (Appendix C). Table 3 is a summary of these findings, which BMP functions are most likely to help prevent and reduce tire wear particles, 6PPD, or 6PPD-quinone from being carried by stormwater runoff, and therefore reduce the toxicity of stormwater.

Table 3. The BMP functions to target for stormwater management of tire wear particles, 6PPD, and 6PPD-q in runoff.

Estimated BMP Effectiveness	Functions associated with stormwater source control BMPs	Functions associated with treatment and flow control BMPs
High	BMPs that completely separate a 6PPD source (e.g., tire wear from roads, parking, high vehicle turning areas) from precipitation and stormwater.	Sorption, infiltration, dispersion, and filtration (e.g., bioinfiltration swales).
Medium	BMP partially separates 6PPD source from stormwater (i.e. education and outreach efforts). This may prevent 6PPD from entering stormwater from a smaller source (i.e. uncovered new tires).	BMPs that provide sedimentation (removal depending on size/detention time) or filtration (removal dependent on particles size). May need a polishing layer/treatment train including sorption (i.e., sand filter with zero valent iron in layers). May be less feasible due to maintenance, other feasibility. For 6PPD-q, may need to modify BMP to retain in solids for a residence time equivalent to the half-life of 6PPD-q.
Low	Unlikely to provide any measurable separation between 6PPD and stormwater. Unlikely to reduce generation or deposition of tire wear in vehicle land uses.	BMP does not provide infiltration, sorption, filtration, or sedimentation. BMP cannot retain solid longer than the half-life of 6PPD-q.

Specific BMP names and descriptions, and their estimated performance effectiveness, are listed in Appendix C, Chapter 4. Stormwater managers can use this information in planning new, re-development, and retrofit projects, particularly for vehicle infrastructure (roads and parking areas).

Addressing Tire Contaminants in Road Runoff Using this New Information about BMPs

Regional stormwater and natural resource managers seek enough information and certainty to confidently select and implement road runoff treatment strategies that will specifically address 6PPD-q impacts on salmonids in their jurisdictions. At the same time, they must make strategic planning decisions and allocate resources to accommodate population growth and maintain economic and transportation infrastructure.

In July 2022, Ecology made available via our webpage and stormwater manuals the report on BMPs for reducing 6PPD and 6PPD-q (Appendix C). All BMPs in the categories of *high* or *medium* BMP Effectiveness (Table 3) should be considered for development and retrofit projects. There are many assumptions and information gaps to be evaluated and BMPs may change categories with more knowledge in the coming years.

Ecology is working to incorporate the current state of knowledge about 6PPD and 6PPD-q sources, transport, and treatability into Ecology's Manuals to provide a more complete set of information and guidance for stormwater practitioners. The 2024 reissuance of the municipal stormwater permits, as well as future updates to other relevant stormwater permits and to Ecology's Manuals, will provide the most updated information and practicable implementation framework possible. Ecology expects that to successfully address this issue many if not most local jurisdictions will need additional information, resources, and funding sources.

Implementing the BMPs

Stormwater source control BMPs are a cost-effective approach to prevent pollution from entering the stormwater system. Routine maintenance practices preserve the intended function of the stormwater infrastructure. Catch basin cleaning and street sweeping are implemented infrastructure-wide, typically on a schedule with more frequent emphasis on higher traffic areas. These source control BMPs are not anticipated to provide enough reduction of 6PPD and 6PPD-q to prevent toxicity alone. Because existing road crews are fully committed to these operation and maintenance activities, additional resources and capacity will be needed to plan and implement new, innovative measures focused in vulnerable areas.

The flow control and treatment functions most anticipated to provide capture and treatment of 6PPD and 6PPD-quinone are provided by both 'gray' and 'green' BMPs. GSI or other LID approaches, techniques that are usually scalable and provide other habitat and community co-benefits, can be incorporated into retrofit designs. The BMPs described in Appendix C can be used in any combination in an approach called a treatment train.

In rural settings, enough space is anticipated for complete management of runoff in the site, even for transportation projects. But for the more space constrained urban settings, especially roads and highways, fewer BMP options will be available. Further evaluation of commercial treatment devices and sorptive media BMPs are needed. Local jurisdictions often find opportunities to retrofit by adding or upgrading stormwater infrastructure using BMPs and treatment trains when other utility, maintenance, or development work is occurring.

Chapter 4: 6PPD-q Analytical Capabilities

As part of the legislative proviso ESSB 5092, Section 302 (23), Ecology and partners must *"develop[ing] a standard method for the laboratory measurement of 6PPD-q and related chemicals."*

The 6PPD-q toxicant was identified by the University of Washington –Tacoma (UW Tacoma), Center for Urban Waters group. Commercial labs were quick to develop research methods to directly test 6PPD-q in water. Similarly, Ecology's Manchester Environmental Laboratory (MEL) developed a 6PPD-q method for analysis in water for Ecology and others to use. MEL will use the developed method for water to support a monitoring pilot study in the winter of 2023.

Briefly, the method developed by MEL takes 250 mL of water concentrated using solid phase extraction (SPE) and analyzed by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS). The method is optimized for sensitivity and selectivity and includes robust quality control to assure valid and defensible quantitative data. Quantitative analysis is performed using isotopic dilution. MEL purchased analytical standards for 6PPD-Quinone from Cambridge Isotope Laboratories (Tewksbury, MA, USA) and HPC Standards (Cunnersdorf, Germany). D5-6PPD-Quinone and 13C6-6PPD-Quinone serve as internal standards. The current Lower Level of Quantitation (LLOQ) for the analysis is 1 ng/L which is about one hundred times less than the 95 ng/L LC50 concentration for coho salmon.

Reliable measurement of 6PPD-q will allow us to directly quantify concentrations and loading of 6PPD-q in the environment and support source control method effectiveness. MEL and UW-Tacoma methods for water are currently going through the lab accreditation process for Washington State. EPA is also developing an analytical method for 6PPD-q including protocols for sample preservation. MEL will continue method development for the analysis of 6PPD-q in sediment. Method development could be expanded for tissue with additional funding.

The ability to measure 6PPD-q in water, sediments and fish tissues will enable studies to assess the bioaccumulation potential of 6PPD and 6PPD-q in fish and shellfish tissues, fate, and transport of 6PPD and 6PPD-q in the environment, and development of monitoring programs to measure 6PPD, 6PPD-q, and other potentially toxic tire contaminants in Puget Sound. Monitoring data may help field test assumptions used in this assessment. NOAA analytical laboratory is in the process of developing a method for 6PPD-q rapid tissue testing to support Puget Sound 6PPD-q monitoring efforts as well.

Analytical 6PPD-q capacity at MEL and partner labs will support the research needed to fill in the many data gaps that will provide more information on how and where to control tire contaminant exposure to vulnerable aquatic habitats.

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Chapter 5: Recommendations

The coordination and research to organize and synthesize information for this report was conducted during an early stage of knowledge about 6PPD-q. Additional research, synthesis, adaptation, communication, and coordination across disciplines, agencies, states, governments, and countries is needed. This report is the first step towards the identification of priority areas at a fine scale. The following are recommended actions to advance this work, some of which are larger than Ecology as we learn about this new pollutant and its sources and impacts.

Ecology and partners identified subsequent research needs and collaboration in the following areas[38]:

1. Invest in research to further understand the main sources, pathways, persistence, and harmful impacts of motor vehicle tire additives to vulnerable waterbodies. The answer to the many remaining questions regarding tire toxicity will help inform where and how to manage releases of tire wear particles and chemicals.
2. Conduct baseline stream assessments prior to fish barrier and stormwater retrofit projects to inform an adaptive management approach and to support restoration and conservation decision-making efforts to strategically reduce the impact of transportation related pollutants to vulnerable ecological areas. Watershed stewards are needed in the most impacted areas to support local efforts in filling data gaps needed to effectively control and treat transportation related pollutants to vulnerable habitats.
3. Invest in tools to further identify and refine impacted streams and toxic source control areas. These tools can help focus and track mitigation efforts and identify cost-effective, feasible projects:
    - Develop a web-based interactive 6PPD-q vulnerability map to help inform mitigation actions.
    - Develop a mid-scale stormwater mitigation action planning assessment tool to incorporate the stream scale attributes and planning information.
    - Conduct field-based assessments of pre-spawn mortality observations and direct 6PPD-q measurements for the development of a 6PPD-q risk map. This effort is already underway and led by the National Oceanic and Atmospheric Administration (NOAA) and funded by the Puget Sound National Estuary Program (EPA), but continued support and coordination is needed to support our partners' efforts.
    - Adapt or develop modeling tools to help locate placement and type of stormwater treatment. For example, a new model called Visualizing Ecosystem Land Management Assessments (VELMA), developed by EPA and Oregon State University, was used to conduct a pilot study in West Seattle to model 6PPD-q mass loading and pathways to help plan mitigation actions (Appendix B).

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[38] Items 1-3 are collaborative research recommendations between our local, State, and Federal partners; a State and Federal Puget Sound Transportation Task Force has been formed to help coordinate future actions and funding gaps. Budget requests have been submitted for Items 4-6 for the 2023-2025 biennium.

4. Support coordination to assess, fund, design, and implement stormwater mitigation projects that effectively protect aquatic life. (Ecology 2023 Policy Level – PW – Toxic Tire Wear in Stormwater decision package[39])
5. Mitigate road runoff using approaches that slow and infiltrate stormwater runoff. Where infiltration is not possible, allow soils, vegetation, or sorbent materials time to filter pollutants before the stormwater enters surface waterbodies. (Ecology 2023-25 Stormwater Financial Assistance Program[40]*)*
6. Continue related efforts to identify safer alternatives to 6PPD and to eliminate its use. (Ecology 2023 Maintenance Level – AK – Address Toxic Tire Wear Chemical decision package[41]*)*

Understanding the persistence, prevalence, and transport of 6PPD-quinone and tire wear particles (TWPs) will help focus where and how much toxic source control measures are needed to reduce the impacts to aquatic life. As additional studies are conducted and more information is learned, the research priorities and recommendations may change.

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[39] http://teams/sites/FS/Budget_Managers/Budget%20Development/PL%20PW%20Toxic%20Tire%20Wear%20in%20Stormwater.pdf

[40] http://teams/sites/FS/Budget_Managers/Budget%20Development/40000539%202023-25%20Stormwater%20Financial%20Assistance%20Program.pdf

[41] http://teams/sites/FS/Budget_Managers/Budget%20Development/ML%20AK%20Address%20Toxic%20Tire%20Wear%20Chemical.pdf

Chapter 6: Conclusions

This report summarizes our current understanding of 6PPD-q, identifies where to begin conducting tire emission studies to help protect salmon bearing streams, and provides an evaluation of available stormwater treatment and control strategies. The report appendices provide details on our current understanding of 6PPD-q toxicity and contain supplemental information gathered during our geographic and best management practice (BMP) evaluations.

This is an initial assessment to help with reconnaissance (monitoring and science) of a new contaminant of emerging concern. A prioritization process was cooperatively developed amongst the committee members and future research opportunities were identified.

The management and assessment of 6PPD-q cannot be tackled with one tool; it requires a multi-disciplinary approach using planning, science, regulation, and funding strategies in concert with ecosystem, transportation, and watershed management partners. The extent of planning, monitoring, and available resources will vary from watershed to watershed.

Employing source control measures strategically along transportation corridors will support salmon recovery efforts and provide co-benefits from other contaminants.

Advancing tire emission mitigation work along transportation corridors will require additional long-term funding support for research, planning, and project implementation. For now, there are many potential high-return, low-risk stormwater treatment projects that can be done with more near-term funding for planning and construction. The spatial technical advisory committee (STAC) cross-referenced salmon distribution, stormwater retrofit, and fish barrier correction plans to inform on salmon vulnerabilities (Appendix B).

Analytical development and capacity building are high priorities to support field and laboratory research aimed to help us understand 6PPD-q’s harmful impacts to aquatic life, the fate and transport in the environment, and BMP effectiveness.

Glossary and Acronyms

Definitions

6PPD is the chemical N-(1,3-Dimethylbutyl)-N’-phenyl-p-phenylenediamine

6PPD-quinone (6PPD-q) is the chemical 2-anilino-5-[(4-methylpentan-2-yl)amino]cyclohexa-2,5-diene-1,4-dione)

Best Management Practice (BMP) – The schedules of activities, prohibitions of practices, maintenance procedures, and structural and/or managerial practices, that when used singly or in combination, prevent or reduce the release of pollutants and other adverse impacts to waters of Washington State.

Bioretention is a commonly used stormwater best management practice (BMP) to treat and infiltrate runoff onsite. Bioretention is an example of green stormwater infrastructure (GSI) that supports natural habitat connection and uses biologically active soils and plants to help filter runoff.

Green Stormwater Infrastructure (GSI) is a subset of low impact development (LID) practices that reduce impacts of human development on the natural world. GSI is infrastructure that use more natural features such as plants and soils to manage runoff close to where it falls. GSI terminology is used in contrast to traditional “gray infrastructure” that focuses on systems including curbs, gutters, and pipes to transport water away from the site as quickly as possible. A combination of gray and green infrastructure exists in many if not most areas of Washington State.

Low Impact Development (LID) is a development strategy that protects and uses natural features and/or engineered, small-scale methods to manage stormwater as near as possible to where it falls and more closely mimic pre-development functions. LID strategies focus on reducing disturbance of native soils and vegetation and on evaporating, transpiring, and infiltrating stormwater onsite through native or amended soils, vegetation, and bioengineering applications to reduce and treat runoff.

Polychlorinated biphenyls (PCBs) are a group of engineered organic chemicals consisting of carbon, hydrogen, and chlorine atoms. The number of chlorine atoms and their location in a PCB molecule determine many of its physical and chemical properties. The intentional manufacture of PCBs is banned, but these chemicals continue to be created in the production of many household and building products (e.g., paints and dyes, lightbulb ballasts).

Sediment – Soil in water deposited at the bottom of waterways.

Soil – Soil on land.

Sorptive – Take up and held, as by absorption or adsorption.

Wattle – Stormwater erosion control wattles are a reliable way to filter water as it flows into a drain system**.** Designed in a tubular structure, these wattles stretch across drains to remove unwanted materials as they enter the system. This helps to effectively control sediment on job sites and prevent pollution from entering a drain system.

Acronyms and Abbreviations

BMP	Best management practice
DNR	Washington State Department of Natural Resources
DOH	Washington State Department of Health
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
ESA	Endangered Species Act
GSI	(see Glossary above)
HRCD	High Resolution Change Detection
HRM	Highway Runoff Manual
IDDE	Illicit Discharge Detection and Elimination
LID	(see Glossary above)
MEL	Manchester Environmental Laboratory
NHD	National Hydrology Database
NOAA	National Oceanic Atmospheric Administration
NWIFC	Northwest Indian Fisheries Commission
PCBs	(see Glossary above)
PPD	p -phenylenediamine
PSEMP	Puget Sound Ecosystem Monitoring Program
PSRC	Puget Sound Regional Council
RCO	Washington State Recreation and Conservation Office
SAM	Stormwater Action Monitoring
SIL	Strategic Initiative Leads
SWMM	Stormwater Management Manual
SWMMWW	Stormwater Management Manual for Western Washington
TMDL	Total maximum daily load
TNC	The Nature Conservancy
TRWP	Tire and road wear particle
TWP	Tire wear particle
URMS	Urban Runoff Mortality Syndrome
USFW	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
UW Tacoma	University of Washington Tacoma
VELMA	Visualizing Ecosystem Land Management Assessments
WDFW	Washington Department of Fish and Wildlife
WRIA	Watershed Resource Inventory Area
WSC	Washington Stormwater Center
WSDOT	Washington State Department of Transportation
WSU-Puyallup	Washington State University - Puyallup Extension

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Appendices

The following appendices are linked to this report on Ecology's website at:
https://apps.ecology.wa.gov/publications/summarypages/2203020.html

Appendix A. Washington Department of Transportation Memo
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Appendix A.

Washington Department of Transportation Memo

Washington State
Department of Transportation

Environmental Services Satellite Office
Mottman Office Building
2214 RW Johnson Blvd SW
PO Box 47332
Olympia, WA 98504-7332

360-570-6635
TTY: 1-800-833-6388
www.wsdot.wa.gov

August 1, 2022

WSDOT prepared this document, in coordination with the Department of Ecology, to be included in the *6PPD and Road Runoff Assessment and Mitigation Strategies Report* as required by the Washington State Legislature Proviso ESSB 5092 Section 302(23) of the Model Toxics Control Operating Account.

WSDOT is committed to improving water quality and protecting aquatic species and habitat from stormwater impacts. Our efforts in this area are necessary to meet regulatory obligations but are driven primarily by our agency's values. WSDOT recognizes the connections between stormwater management and salmon recovery, as well as the wide array of stakeholders involved with these efforts. We actively seek to align priorities with external partners and are coordinating with Department of Ecology, other state and federal agencies, and many other stakeholder groups on the emerging research related to urban runoff mortality syndrome (URMS) and 6PPD-quinone, including identifying affected species, evaluating geographic scope, and prioritizing affected areas. WSDOT is also participating in, and closely tracking, efforts to gather critical additional information on this topic, such as the fate and transport of 6PPD-quinone in the environment as well as related research on bioretention and compost effectiveness in removing or reducing toxicity.

WSDOT understands 6PPD-quinone is a source of pollution generated primarily through use of the transportation system and is detrimental to multiple species of salmon, particularly coho. Existing research on stormwater pollution in general has shown that many roadway pollutants are significantly reduced through implementation of stormwater best management practices (BMPs) and other measures that enable stormwater infiltration, pollutant settlement, biofiltration, adsorption of pollutants to organic matter and soil media constituents, and other biophysical and chemical processes. WSDOT's current approach to stormwater design begins with considering low impact development (green infrastructure), infiltration, and biofiltration facilities, and employs additional treatment options that may be necessary based on the characteristics of stormwater run-off at a particular location. WSDOT is partnering with the Department of Ecology and other public and private organizations to conduct research on the effectiveness of these types of treatments in reducing 6PPD-quinone toxicity. Additional measures necessary to address 6PPD-quinone toxicity will be determined based on this research and other developments on this emerging subject.

While this research is being conducted, WSDOT continues to manage stormwater impacts in accordance with regulatory requirements using best management practices. This includes constructing treatment facilities for new and existing pavement, performing ongoing maintenance of those facilities to remove contaminants before they reach nearby waterbodies and to help ensure they work as intended, and conducting and supporting stormwater research.

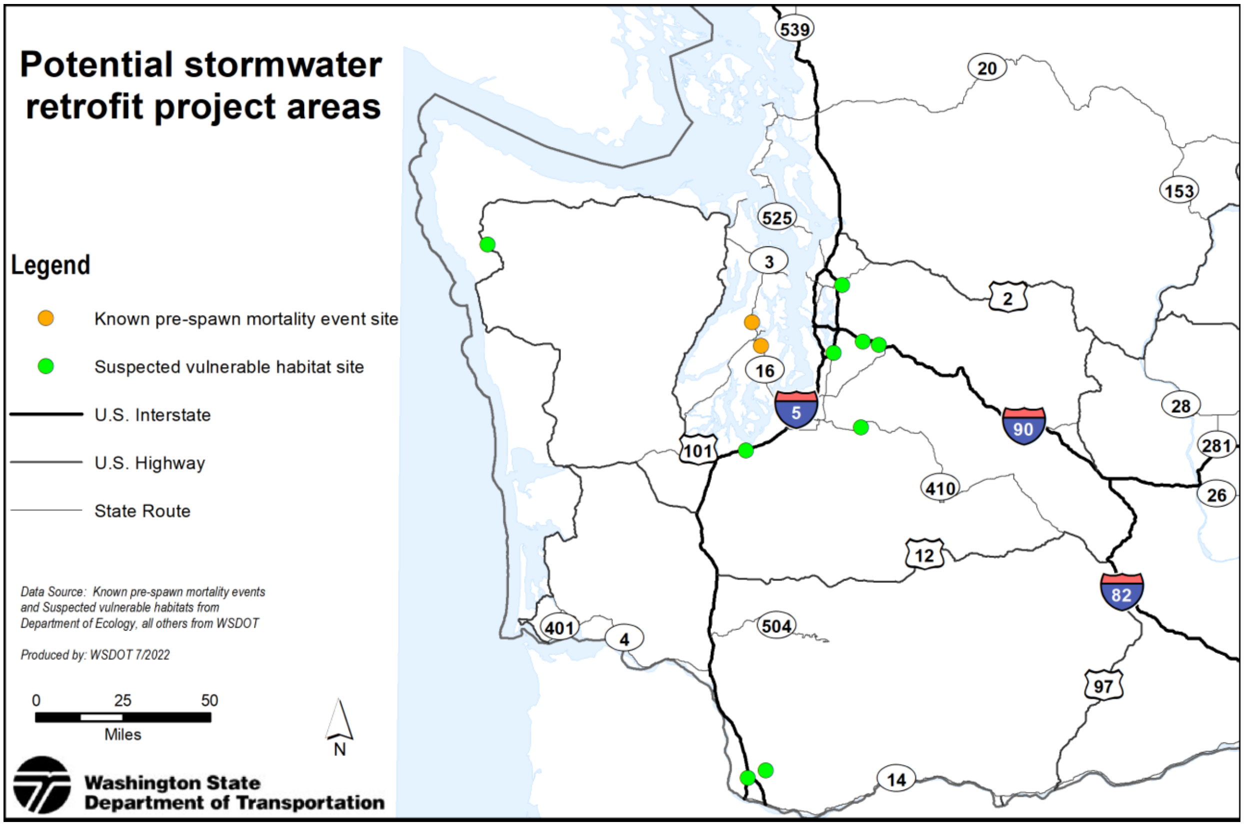
WSDOT’s stormwater retrofit program addresses stormwater impacts from existing transportation infrastructure through three main approaches. (1) Project-triggered retrofits add stormwater treatment for existing impervious surfaces as a part of transportation improvement projects and as required by regulations. (2) Opportunity-based retrofits add treatment for existing impervious surfaces as a part of transportation projects when it makes sense and is cost-effective, even when not required by regulation. WSDOT specifically looks for these types of opportunities to retrofit with every fish passage project so that fish can return to higher quality habitat after a barrier is removed. (3) Stand-alone retrofits add treatment for existing impervious surfaces at prioritized locations and are not part of a larger transportation project. WSDOT completed its initial stormwater retrofit prioritization in 2017 with a substantial outreach effort to tribes, partners, and stakeholders including other state and local agencies.

This year, the Legislature authorized $500 million for WSDOT as part of the Move Ahead Washington funding package to enhance stormwater treatment from existing roads and infrastructure, with an emphasis on green infrastructure retrofits over the next 16 years. $6M of the funding will be dedicated to the I-5 Ship Canal Bridge Pilot Project in Seattle. This is part of a larger partnership with The Nature Conservancy, Department of Ecology, and local agencies in the Seattle area, to develop a green infrastructure stormwater park to treat stormwater from the Ship Canal Bridge and surrounding area. While this new funding to WSDOT will provide incredible benefits to water quality and salmon recovery impacted by state highway runoff, we understand there are also impacts from local roadways which will need additional funds for prioritization and retrofitting. WSDOT is seeking input from regional partners including federal, state, local governments, tribes, and non-profits to prioritize locations on WSDOT infrastructure to address 6PPD-quinone and to best prioritize and spend the legislative funding while focusing on benefits to salmon recovery and ecosystem health, reducing toxic pollution, addressing health disparities, and cost effectiveness.

WSDOT still has a lot of work to do to address our existing priorities for stormwater retrofit, however, we have begun efforts to add new prioritization criteria based on the requirements in the funding package as well as more recent information learned about 6PPD-quinone. In particular, there are several streams that have been verified to have 6PPD-quinone-related pre-spawn mortality events as well as several streams suspected of being vulnerable habitat for coho and/or steelhead exposed to road runoff. By cross-referencing these locations with WSDOT’s existing prioritization for stormwater retrofits, we were able to identify the locations in the table below as potential opportunities to address these emerging issues more quickly. WSDOT will continue to work with regional partners in planning and research as described above to ensure that combined efforts are aligned and that we are positioned to incorporate emerging scientific knowledge to continually update policies and priority models for the best possible outcomes for improving ecosystem health.

Potential stormwater retrofit project areas

Creek Name	6PPD-quinone criteria	State Route	Milepost	Lat	Long
Chico Creek	known pre-spawn mortality event	003	40.9	47.601492	-122.70613
Blackjack Creek	known pre-spawn mortality event	016	25.2	47.50362	-122.646171
East Fork Issaquah Creek	suspected vulnerable habitat	090	18	47.532002	-122.021937
Raging River 2	suspected vulnerable habitat	090	23.4	47.518566	-121.924646
White River	suspected vulnerable habitat	410	22	47.174024	-122.023284
Salmon Creek 2	suspected vulnerable habitat	005	6	45.705957	-122.654361
McCallister Creek	suspected vulnerable habitat	005	114	47.068135	-122.719878
Untitled Placemark	suspected vulnerable habitat	101	184.6	47.881235	-124.352055
Weaver Creek	suspected vulnerable habitat	503	5.1	45.740769	-122.551441
Little Bear Creek	suspected vulnerable habitat	522	12.5	47.763881	-122.157475
Cedar River	suspected vulnerable habitat	405	3.7	47.480838	-122.199874

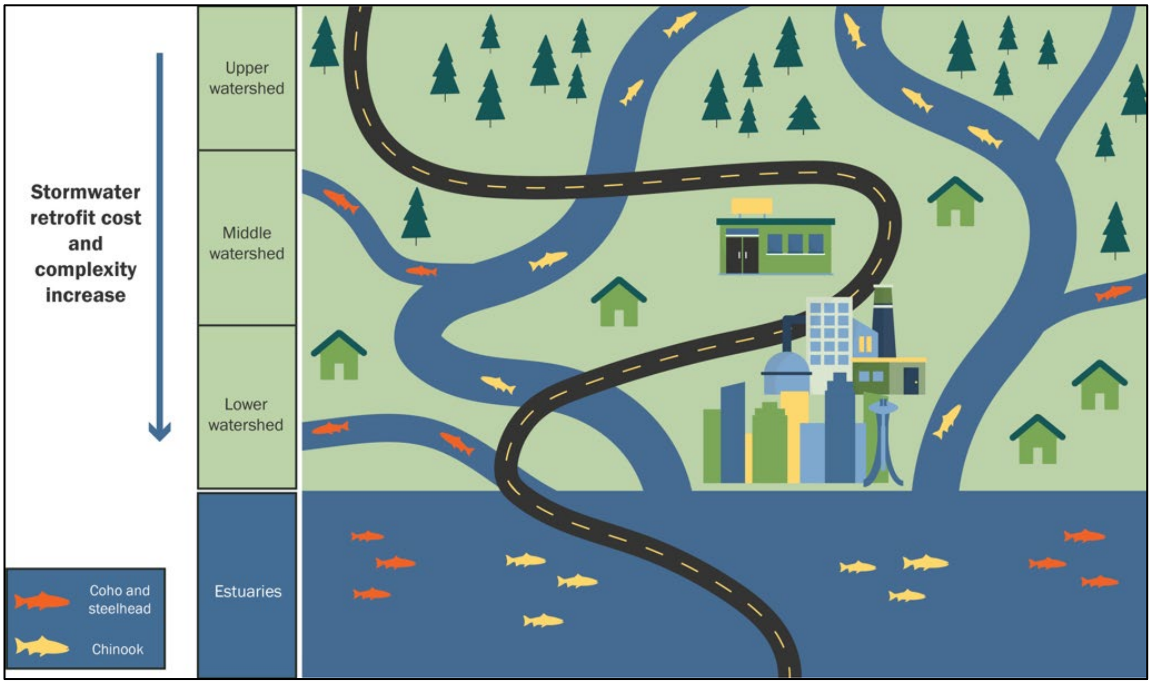


Appendix B.

6PPD-q Spatial Technical Advisory Committee Overview

Vulnerable Ecological Areas and 6PPD-quinone Exposure

Spatial Technical Advisory Committee Overview



Cover Photo: ***Courtesy of Mugdha Flores***

Vulnerable Ecological Areas
6PPD-quinone

Spatial Technical Advisory Committee Overview

Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington

Supplemental Information

6PPD Meeting materials

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Acknowledgments

We thank the following people for their contributions to this spatial proviso overview:

- The 6PPD Spatial Technical Advisory Committee (STAC), Table 1
- The 6PPD STAC presenters, Table 2
- The 6PPD Spatial Technical Advisory Committee Summary contributors:
    - Susan Cormier
    - Arleta Agun
    - Christopher Clinton
    - Keisha Chinn
    - Jessie Alton
    - Colin Hume

6PPD Spatial Technical Advisory Committee Approach

A 6PPD Spatial Technical Advisory Committee was formed in response to the 2022 6PPD Legislative Proviso Report assignment to help gather the best professional advice from stormwater and natural resource professionals in response to the discovery of tire additive toxicity to coho salmon. The anti-degradant used to enhance tire safety and duration, 6PPD (parent compound) and 6PPD-quinone (transformation product), causes coho mortality, potentially anywhere there is untreated transportation stormwater discharging to salmon bearing streams. The frequency and intensity of rainfall in the Pacific Northwest combined with the number of vehicles, and roads that crisscross salmon bearing streams pose a formidable challenge for addressing 6PPD contamination of Washington waters. The state of our urbanized lowland streams and aging transportation stormwater infrastructure demands strategic actions that simultaneously addresses multiple goals. The scope and scale of the problem requires a multi-scalar prioritization approach to support effective conservation and restoration planning and actions.

Discussions, Evaluations, Presentations and Interviews

In December of 2020, a paper published in Science established that 6PPD-quinone from tires is an extremely potent causal agent proposed to be responsible for pre-spawn mortality of coho and potentially other Pacific salmonid species (Tian et al. 2020). The meticulous evidence provided a clear and compelling target to galvanize federal, state, tribal, and other interested groups to better understand the scope of the problem and to effectively reduce toxicity.

In response to the discovery of 6PPD-quinone, and its acute toxicity to coho salmon, a legislative proviso was assigned to assess the significance and geographic scope of untreated road runoff to salmon bearing streams:

> *(23) …state appropriation is provided solely for the department to work with the department of transportation, University of Washington-Tacoma, and Washington State University-Puyallup to identify priority areas affected by 6PPD or other related chemicals toxic to aquatic life from roads and transportation infrastructure and on best management practices for reducing toxicity. This includes developing a standard method for the laboratory measurement of 6PPD-quinone and related chemicals. The department will submit a report to the appropriate committees of the legislature by November 1, 2022.*

In response, a 6PPD spatial technical advisory committee (STAC) of stakeholders, state and federal agencies, and tribal government representatives was assembled (Table 1). In February of 2022, virtual science presentations and discussions informed the development of a multi-scalar approach to share and visualize available information and identify data gaps using GIS (Table 2). Table 3 provides an overview of the discussions and shared presentations during a series of STAC meetings.

Table 1. List of participants to the spatial technical advisory meetings; this does not include participants to the final 6PPD science share meeting on May 18th. Many additional individuals unable to attend the meetings, provided Ecology with best professional advice.

Participant	**Role**	**Affiliation**
Arleta Agun	SWIFD GIS Analyst	WDFW
Ron McFarlane	SWIFD GIS Analyst	NWIFC
Tyson Waldo	SSHIAP Biologist and GIS Analyst	NWIFC
David Troutt	Natural Resource Director	Nisqually Indian Tribe

Participant	Role	Affiliation
Tony Bush	Stormwater planner	WSDOT
Keisha Chinn	Environmental IT	WSDOT
Jesse Alton	Environmental GIS	WSDOT
Christopher Clinton	GIS Analyst	Ecology
Sheena Pietzold	Stormwater	WSDOT
Blake Feist	Biology Statistician	NOAA
Nat Scholz	Ecotoxicology Program Manager	NOAA
Julann Spromberg	Research Fish Biologist	NOAA
Ailene Ettinger	Quantitative Ecologist	TNC
Christian Nilsen	Senior Water Resources Engineer	Geosyntecs Consultants
Braeden Vandeynze	Natural Resource Economist	WDFW
Marisa Litz	Fish biologist	WDFW
Colin Hume	Watershed ecologist	Ecology
Derek Day	Stormwater SIL Team Lead	Ecology
Catherine Gockel	Puget Sound Geographic Program Lead	EPA
James Medlen	Toxics Studies Unit	Ecology
Cecilia Gobin	Conservation Policy Analyst	NWIFC
Susan Cormier	Senior Scientist	EPA
Eli Mackiewicz	Stormwater Program	City of Bellingham

Participant	Role	Affiliation
C. Figueroa-Kaminsky	Environmental Engineer	Ecology
Abbey Stockwell	Municipal Stormwater Permit Writer	Ecology
Emma Trewhitt	Water Quality Planner	Pierce County
Karen Dinicola	Policy and Technical Lead (retired)	Ecology
Brandi Lubliner	Stormwater Engineer	Ecology
Chad Larson	Stream Ecologist	Ecology
Christy Rains	Fish Barrier Inventory Manager	WDFW
Valerie Chu	Contaminants Biologist	USFWS
Abby Barnes	Environmental Scientist	DNR
Anand Jayakaran	Faculty	WSU-Puyallup
Jen McIntyre	Faculty	WSU-Puyallup
Ed Kolodziej	Faculty	UW Tacoma
Bob Black	Hydrologist	USGS
Bob McKane	Ecologist	EPA
Jonanthan Halama	Faculty	OSU & EPA
Ken Pierce	HRCD Project Lead	WDFW
Jamie Glasgow	Director of Science	WFC
Jennifer Vanderhoof	Senior Ecologist	King County
Tim Beechie	Fish Biologist	NOAA

Participant	Role	Affiliation
Brian Muegge	Certification Specialist	Salmon Safe
Thorsten Reemsta	Faculty	UFZ Germany
Markus Hecker	Faculty	USASK Canada
Markus Brinkmann	Faculty	USASK Canada
Philip North	Conservation Scientist	Tulalip Tribe

Table 2. List of presentations given during the spatial technical advisory committee Spring 2022. Note - presentation titles are linked to the presentation.

Presenter	Co-authors	Presentation Title	Affiliations
Ron McFarlane	Arleta Agun and Tyson Waldo	State Wide Integrated Salmon Distribution Map	NWIFC & WDFW
David Troutt		WA Tribal Treaty Rights & Salmon BMP Pilot Project	Nisqually Indian Tribe
Tony Bush & Keisha Chinn		Stormwater Retrofit Prioritizations	WSDOT
Nat Scholz	Blake Feist & Julann Spromberg	Toxic stormwater threats to Puget Sound at the watershed and landscape scales: priority information gaps for the recovery of ESA-listed species	NMFS
Ailene Ettinger	E. R. Buhle, B. E. Feist, E. Howe, J. A. Spromberg, N. L. Scholz & P. S. Levin	Prioritizing Conservation Actions in Urbanizing Landscapes	TNC
Christian Nilsen		Stormwater Heatmap	Geosyntecs Consultants

Presenter	Co-authors	Presentation Title	Affiliations
Braeden Vandeynze		Analyzying and applying cost information in restoration planning	WDFW
Colin Hume		Phase 2 Development of a Hydrologic Condition Index for the Puget Sound Basin	WA Ecology
Chad Larson		Examining the direct and indirect impacts of anthropogenic stressors on stream macroinvertebrate communities at multiple spatial scales: a structural equation modeling approach	WA Ecology
Christy Rains		WDFW's Fish Passage Barrier Inventory & Assessment Program - An Overview	WDFW
Bob McKane & Jonathan Halama	Jonathan Halama, Robert McKane, Vivian Phan, Allen Brookes, Kevin Djang, Edward Kolodziej , Katherine Peter, Zhenyu Tian	VELMA model green insfrastructure applications for reducing 6PPD-quinone concentrations in Puget Sound urban streams	EPA
Ken Pierce		WDFW's High Resolution Land Cover program and alternatives	WDFW
Jamie Glasgow		Addressing URMS Data Gaps - a View from the Field	Wild Fish Conservancy
Jennifer Vanderhoof		Beavers, Salmon rearing, Toxic reservoirs and Water flow	King County

Presenter	Co-authors	Presentation Title	Affiliations
Tim Beechie	Alex Stefankiv, Arianna Goodman, Britta Timpane-Padgham, Jeff Jorgensen, Aimee Fullerton, Peter Kiffney	Habitat Assessment and Restoration Planning (HARP) Model	NOAA
Thorsten Reemtsma		Tire Wear Particles and associated chemicals in the environment	UFZ Helmholtz, Germany Center for Environmental Research
Markus Hecker	Steve Wiseman, Markus Brinkmann	Occurence of 6PPD-quinone in cold-climate urban runoff and acute toxicity to four fishes of commercial, recreational, and cultural relevance	University of Saskatchewan, Saskatoon, SK, Canada University of Lethbridge, AB, Canada
Brandi Lubliner		Evaluating 6PPD BMPs	WA Ecology
Craig Manahan		Evaluating 6PPD Alternatives	WA Ecology

Table 3. Local information was requested and gathered by interviews and correspondence in the Spring of 2022 to capture best professional judgement from regional fish biologists, water quality experts and stream ecologists to collect local salmon habitat benefits and suspected high impact areas (areas where vulnerable ecological areas are exposed to untreated road runoff).

Recommended Focal Areas	**Local Information**
White River; Muckleshoot and Puyallup Indian Tribes.	White rivers hosts one of the few remaining wild stocks of coho and should be a high protection priority.
Cedar Creek (WRIA 8)	Significant restoration efforts have led to salmon returns, most work has focused on chinook habitat enhancement. They want to know whether Sockeye are sensitive to 6PPD and 6PPD-q or not.
Green River and Lake Washington	Regional fish biologist suggested focusing on medium sized streams with 10-20 ft. bank width and to focus on streams with adequate flow all year round for rearing.
Snohomish; Quilceda; Coho creek – lots of recovery efforts	Coho populations in Snohomish are doing well, they had diminished returns during the warm blob that led to poor food availability in the ocean, but numbers have sprung back to expected sizes (>50,000). The fish look good and there is extensive good habitat. Treating water quality in the lower reaches of the Snohomish will support the returns further up the watershed. Despite the extensive low impact development guidance, development is occurring quickly and too close to the streams. This is a common concern and observation from local jurisdictions and regional fish biologists that development needs to be controlled and done sustainably.
Bear creek and little bear creek, Issaquah creek,	Lake Washington area regional fish biologist suggested that areas new development, or urban fringe areas should be a priority to preserve the remaining good habitat. New development is encroaching on the undisturbed habitat and some of the last wild salmon refuge areas left in the Puget Sound lowlands. Habitat degradation and riparian loss is happening faster than can be restored it.
Upland rivers and streams	Natural resource scientists suggested using forestry conservation planning that provides methods for diverting water completely away from streams.

Recommended Focal Areas	**Local Information**
Salmon streams	A fish scientist highlighted the importance of more coho population assessments and the need to incorporate a combination of newer technology such as pit tags small enough for juvenile tagging and the traditional smolt and adult trapping to estimate whether populations are self-sustaining or not. In addition, genetics, toxic screening and life history studies are needed to further define "conservation stocks". Understanding population trends will help us measure our success to achieve our goal of living sustainably with salmon in the Pacific Northwest.
Salmon streams	A stream ecologist suggested incorporating stream temperatures into the prioritization process, many of the streams with limited canopy cover reach harmful temperatures to hatching and rearing salmon.
Lake Washington, Cedar Creek & Sammamish Watershed (WRIA 8)	King County is one of the salmon recovery managers and coordinates with 25 lead salmon recovery entities to assess and prioritize salmon restoration and conservation actions on a watershed scale. The salmon recovery community has developed a limiting factor approach to prioritization that employs both a technical advisory group and a community advisory group to help choose projects that balance, habitat benefits, cost, logistics, and local community support. The salmon recovery community suggests more coordination between the physical and chemical (toxic reduction) project prioritization process.
South Sound = (Squaxin Island Tribe); Skookum Creek; Little Creek (101 at Kamilche and North Bound off ramp to old 101) – both creeks are also subject to low flows in summer, but exposed to road runoff from 101 during storms; Shelton and Goldsborough Creeks;	Usual and accustomed fishing area of the Squaxin island Tribe (south of the Tacoma Narrows Bridge). All salmon bearing streams are important to us. Many federal, state, county and city road and highway drainage features discharge directly to lakes, wetlands, rivers and streams and eventually flow to the Salish Sea. Small coastal catchments, right next to the Salish Sea, that are crisscrossed by roads, are of particular interest. All of these creeks support coho salmon. Sites where: • Highway 101 crosses streams between Olympia and Shelton • Highway 3 crosses streams between Shelton to Allyn • Highway 108 crosses streams between Kamilche to Mcleary. • Highway 302 and 144th st. NW Pierce County

Recommended Focal Areas	**Local Information**
Squaxin Island Tribe U&A	“The potential risk areas for 6PPD Quinone in the usual and accustomed fishing area of the Squaxin Island Tribe is the Tribe's entire U&A”….”The problem of tire dust getting into stream systems is endemic to any location where roads cross-streams. Essentially, that is everywhere within a watershed.”
Hoh Indian Tribe U&A	The Hoh Tribe’s DNR is concerned about runoff from Highway 101 and the Upper Hoh Road entering rivers and creeks within the Hoh River Watershed. The Hoh River and its tributaries support runs of steelhead, chinook, coho, pink and chum salmon. The Hoh Rainforest entrance is one of the most visited trailheads in the Olympic National Park. Park visitors must take Highway 101 and the Upper Hoh Road to reach the entrance. Due to the Hoh River's proximity to these roads and the high volume of visitors traveling to the park each year, there is concern about the potential effects of 6PPD and 6PPD-Quinone on salmon runs in the Hoh River Watershed.

In addition, spatial resources and modeling efforts were reviewed that were designed to help natural resource managers to identify vulnerable aquatic areas and plan conservation and restoration actions to protect them (Table 4 and 5). Much of this work was specific to Puget Sound and relied on the general acceptance of coho salmon being a sentinel species most sensitive to 6PPD-q. Pre-spawn mortality is currently associated with major transportation and urban areas.

Table 4. A selection of mapping tools and resources to help visualize conservation and restoration planning.

Spatial Resource	**Developer**	**Region**
Puget Sound Stormwater Heatmap	TNC | Geosyntecs	Puget Sound
Puget Sound Watershed Characterization Project	Ecology	Puget Sound
Freshwater Explorer	EPA	Statewide | US
StreamCAT	EPA	Statewide | US
Puget Sound Stream Benthos	King County	Puget Sound
SWIFD | Salmonscape	NWIFC | WDFW	Statewide
Washington State Fish Passage	WDFW	Statewide
High Resolution Change Detection	WDFW	Statewide
Water Quality Atlas	Ecology	Statewide
Washington Geospatial Open Data Portal	WA State	Statewide
Urban Canopy	City of Seattle	Puget Sound
NorWeST project	USDA	Statewide
Stream flow	USGS	Statewide
WSDOT Online Map Center	WSDOT	Statewide
Washington Geospatial Open Data	WOCIO	Statewide
Puget Sound Mapping Project	WDOC	Puget Sound
WA's National Hydrography Dataset Program	Ecology | USGS	Statewide
Visualizing Ecosystem Land Management Assessments	EPA	Flexible

Table 5. Examples of prioritization frameworks and opportunities for coordination.

Affiliation	Prioritization Resource	Description
WSDOT	Stormwater Retrofit Program (2013 to present)	Framework developed to prioritize transportation stormwater retrofit projects.
Ecology, NEP	Puget Sound Watershed Characterization Project (2011 to present)	Water and Habitat Assessments to identify areas to protect, restore and develop (using LID).
Ecology Chehalis Basin, WDFW, Quinault Nation and Chehalis Tribes	Aquatic Species Restoration Plan	Chehalis Basin plan to restore and enhance aquatic species habitatand improve local communities. Joint task force to prioritize and fund projects.
WDFW	Fish passage inventory, assessment and prioritization	To prioritize fish passage barriers for correction, you must know the habitat conditions and barriers upstream and downstream.
The Nature Conservancy of WA & NMFS	Prioritizing conservation actions in urbanizing landscapes	
King County	Stormwater Action Planning for Green/Duwamish Watershed	

Rain, Tires and Salmon Converge

The timing of salmon movement and rains that wash tire emissions into creeks is somewhat synchronized. Juvenile salmon leave their natal streams during freshets, large and sustained rain events, during high tides that lead to high flow stream levels that often cause riparian flooding (Downen and Mueller 1999). Similarly, adult salmon return to natal streams during high tides and freshets because some spawning areas are more difficult to access during low flows. These same intense rain events, as well as less intense events throughout the year when juvenile salmon are rearing in streams, wash tire wear particles and additives into streams when stormwater is not adequately treated. Much of our existing, older stormwater treatment infrastructure and pipes are not designed to accommodate large storms and have minimal if any treatment prior to discharge regardless of storm intensity, leading to direct conveyance of road pollutants to our waterways. This culmination of large storm events, during salmon migrations returning or leaving their natal streams in areas with minimal stormwater treatment and control is most likely when salmon are at greatest risk of dissolved 6PPD-quinone exposure, however, tire wear particles and 6PPD-quinone are assumed to be a potential source year round (Figure 1).

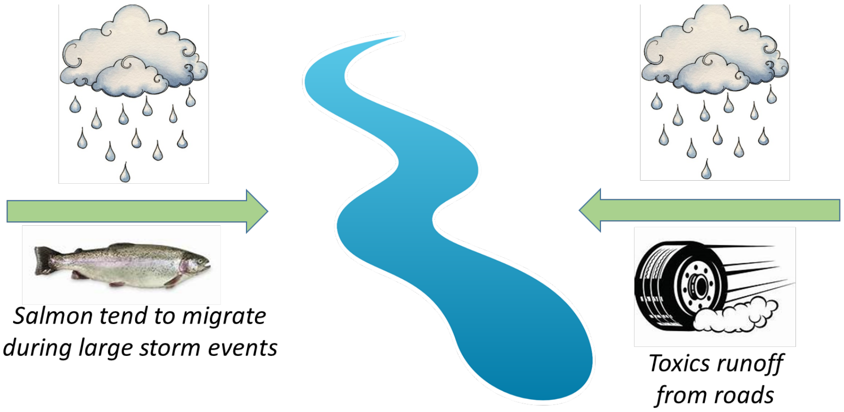

Figure 1. The risk of pre-spawn and juvenile coho mortality is heightened by the co-occurrence of storm washed road pollutants and salmon migrating up streams during the wet season freshets that can occur between October to June[1].

Because wild coho salmon populations have declined and habitat loss has occurred over the last several decades, direct observations of symptomatic salmon are challenging to survey. Associations between coho occurrence and 6PPD-q in toxic amounts therefore may not truly reflect the full extent of toxic impacts.

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[1] cliparts.com, graphic by R. Smith

Pre-spawn mortality surveys, to date, have been added to ongoing spawning surveys within and outside urban areas as part of salmon recovery monitoring efforts. Spawning surveys take an extensive amount of coordination and require well-trained community scientists or regional biologists to implement properly, safely and avoid trampling on salmon eggs. Despite these challenges, more pre-spawn mortality assessment efforts and a certified training program are critical to support risk assessments and help guide stream reach protection prioritizations utilizing water, sediment and bioassays, which are less staff-intensive to measure, in addition to coho mortality surveys of both adult and juveniles.

Previous assessments conducted by NOAA for understanding the causal agent of pre-spawn mortality relied on a combination of field intensive pre-spawn coho mortality surveys and the State-Wide Integrated Fish Distribution (SWIFD) database, also known as the Salmonscape, a publicly available interactive web-map to help identify coho watersheds. The resource is co-curated by the Northwest Indian Fisheries Commission (NWIFC), and the Washington Department of Fish and Wildlife (WDFW). Salmon distribution reports from regional biologists are gathered, quality assured, and uploaded to the map regularly by hosting local community mapping workshops. This resource provides valuable visualizations of salmon distribution and vulnerable areas to road runoff.

Following years of intensive pre-spawn mortality surveys and stormater ecotoxicology research, the NOAA and USFW led a mapping study to visualize the problem (Scholz et al. 2011, Spromberg & Scholz 2011, Spromberg et al. 2016). The Feist et al. (2017) broad scale spatial study was instrumental in linking road runoff as the source of the contaminant responsible for coho pre-spawn mortality, however, it was not intended to be a 6PPD-q risk assessment tool. The study provides a framework for future 6PPD-q risk assessments and GSI planning to reduce the impacts of tire emissions to coho salmon.

Ettinger et al. (2021) created a broad scale visual mapping product that applies the pre-spawn mortality correlation model across an urban gradient to prioritize areas for conservation and restoration actions based on effort to restore and salmon habitat. The study modeled a coho habitat degradation gradient and set a threshold of where to restore and where to protect streams. The study provides a conceptual model to help inform further restoration and conservation action planning once more 6PPD-q and pre-spawn mortality information becomes available. These authors are working with Ecology staff to further develop and integrate these concepts to (1) identify and evaluate priority vulnerable areas and (2) recommend focus areas for stormwater mitigation.

Prioritization Objectives and Strategies

STAC and Ecology staff evaluated the available spatial attributes most relevant for priority area identification through a combination of interviews, presentations, and group discussions. The diversity of expertise and perspectives enriched the discussion while defining priority areas of the 6PPD legislative assignment.

The 6PPD spatial technical GIS workgroup recommends the integration of two well-known approaches for restoration planning, 1) limiting factor analysis, and 2) process-based restoration (Booth et al. 2016). Limiting factor analysis is traditionally used to identify physical habitat limitations to salmon recovery, for example, if the optimal sized pebbles are added to a degraded stream, salmon will return to spawn. Water quality degradation of a stream can present chemical habitat limitations to salmon recovery and should be included as a factor in ongoing analyses.

In the case of 6PPD-quinone, reconnaissance is needed to prioritize coho streams that are impacted by untreated road runoff. Site-based monitoring and source identification studies can be time and resource intensive, but are critical for verifying hot spots and prioritizing stormwater mitigation actions. Green infrastructure is promoted globally as an effective method for controlling stormwater flow and pollutant loading. The optimal type and placement of green infrastructure is still being developed therefore collecting baseline information is crucial for measuring effectiveness and guiding future installments.

Process-based restoration refers to protecting and restoring watershed scale processes, like habitat connectivity to support salmon recovery. For example, stormwater retrofit planning may want to focus on one stream catchment at a time rather than spreading restoration efforts too thinly across several basins, a series of partially restored streams could inadvertently lead to ecological trapping. Ecological traps refers to exposing salmon to legacy impacts despite best intended physical habitat restoration efforts, such as low or high water flows or water quality impairments. Pacific salmonids, coho salmon in particular, require both spawning (shallow areas with pebbles) and rearing habitat (deeper pools and structures to hide from predators) nearby, providing spawning habitat with no rearing habitat causes habitat driven mortality of hatched salmonids. Optimal stream health needs to support the required prey and ecosystem engineers, such as beavers, as well.

This spatial technical report provides a recommended pathway towards developing an integrated limited factor analysis (bottom up, fine scale) and process-based restoration (top down, broad scale) approach to strategically placing green infrastructure and stormwater retrofits to best mitigate 6PPD-quinone to fish bearing streams (Figure 2).

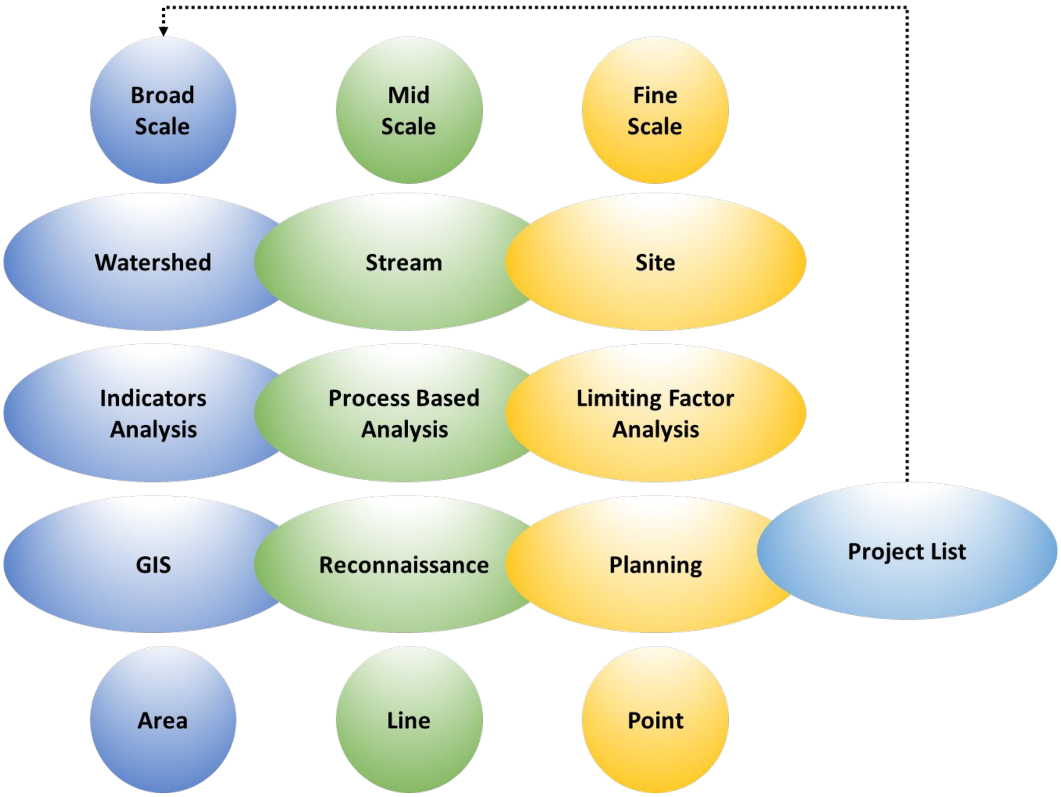
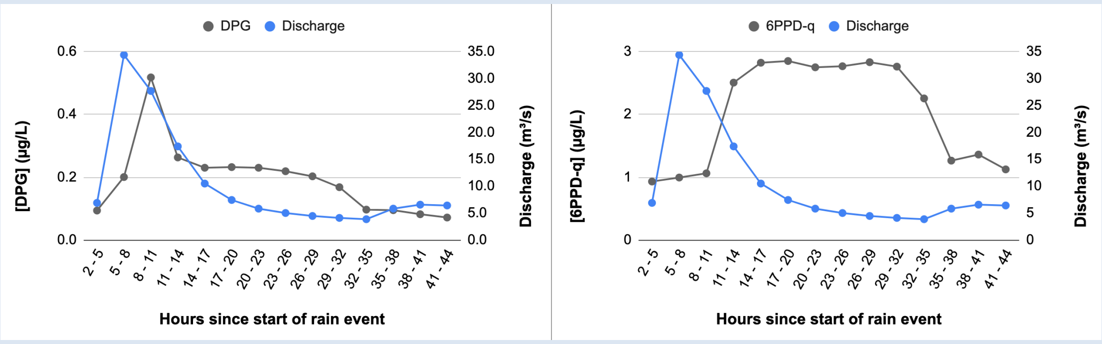


Figure 2. Integrated limiting factor and process based prioritization approaches to address tire emission and stormwater impacts to aquatic ecosystems.

Assumptions and questions at this early stage of 6PPD discovery that define the scope and scale of 6PPD in the environment

1) Adult and juvenile coho salmon are acutely toxic to low levels of 6PPD-quinone and result in mortality within hours (0.8 ± 0.16 micrograms per liter, Tian et al., 2022).
2) Once coho are exposed to 6PPD-quinone in toxic amounts, they do not recover, making the standard bioassay and sublethal assessments more challenging. **More research is needed to identify the most effective monitoring strategies for 6PPD and tire related contaminants.**
3) Coho mortality events are difficult to assess given the suspected fleeting nature of 6PPD-quinone in the environment and majority of re-occurring observations are in urban areas. One study in Toronto showed approximately a 4-hr. lag between maximum stream discharge and a 24-hour plateau of elevated 6ppd-q (Figure below). **Automated samplers need to be deployed to collect samples to characterize patterns in different types of streams.**



Source: (Johannessen et al. 2022)

4) A low percentage of pre-spawn mortality events are natural and expected, but the multi-year, high mortality rate observed in the Puget Sound area exceed natural mortality. **More research is needed in suburban and rural areas along transportation corridors to understand the pollution pathways leading to mortality in less urban areas where observations have more recently been reported.**
5) Very low amounts of traffic can lead to 6PPD-quinone mass loading along county roadways and public highways. Untreated road runoff has the potential to exceed lethal concentrations of 6PPD-quinone, however, it is reasonable to assume that the greater the mass loading of contaminants, the greater the exposure and the more likely pre-spawn mortality will occur. **More research is needed to empirically model mass loading of 6PPD-quinone with traffic attributes.**
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 suspected to be less persistent in the environment compared to 6PPD-quinone that is estimated to persist for days. **More research is needed on the persistence of 6PPD and related tire contaminants.**

7) Tire wear particles (TWP) shed from tires into the environment are suspected to be the most persistent and to continue releasing 6PPD and transformation products under certain environmental conditions. **More research is needed to measure the fate and transport of TWP.**

8) Coho 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. **More resources are needed for coho population assessments and stream inventories to enable us to measure the efficacy of the physical and chemical mitigation actions to restore degraded salmon habitat.**

9) The majority of remaining coho runs are a combination of hatchery stocked and wild populations. Watersheds that support wild coho runs are a high priority for conservation and restoration actions to support self-sustaining populations and genetic diversity. **More research is needed to support genetic diversity, stock origin, and natal stream return (smolt and adult traps and tagging) assessments.**

10) The majority of lowland streams in the Pacific Northwest that support coho populations have multiple physical and chemical disturbances to address. Ecology and many local and federal partners have accrued a substantial amount of data on the health of waterways, including small streams that support coho and steelhead. More analysis of existing stream, transportation, and salmon data is planned for an initial phase II spatial analysis effort, however, more resources are needed to maintain and continue this work. **Work has begun, but a sustained effort is needed for research, planning, and implementation.**

11) Tires are the main source of 6PPD; however, it is suspected to be used in other products such as tire crumb rubber, roofing materials, sealants, asphalt, rain gear, wipers, shoe soles, and camping gear. **More research is needed to evaluate additional sources and loadings of 6PPD in other rubber products.**

12) Stormwater is believed to be the main delivery pathway of 6PPD and related chemicals, however, there may be additional pathways. **More research is needed to evaluate additional pollution pathways (e.g., atmospheric).**

Multi-scalar GIS Approach at this Early Stage

The complexity, multi-disciplinary, and multi-jurisdictional nature of the transportation and stormwater infrastructure will require ongoing prioritization efforts at multiple scales and varying objectives to achieve the prime goal of protecting salmon fisheries. This initial, tip of the iceberg, framework needs ongoing resources to maintain and refine as data improves and our many assumptions at this early stage regarding 6PPD and related chemicals in the environment are evaluated.

In response to this legislative report, the following criteria are proposed to identify priority areas:

Priority Area: Vulnerable ecological areas that support sensitive species and are subjected to (potential) 6PPD-quinone in toxic amounts.

Vulnerable ecological areas: Pacific salmonid species that are acutely sensitive to 6PPD-quinone (e.g., coho, steelhead, species list will need to be updated as new research is published; French et al. 2022).

6PPD-quinone exposure: The latest LC-50 for coho suggests that small amounts of traffic of any sized road near a coho bearing stream has the potential to deliver toxic amounts of 6PPD-quinone (Tian et al. 2020, 2022). Current models predict that: 1) more traffic, 2) heavier vehicles, 3) more lanes, 4) higher speeds, 5) more turning and stopping, and 6) more impervious surface and absence of natural infiltration processes will lead to higher rates of stormwater exposure (Cappiella et al. 2012).

Scale: In Scope 1 (Broadscale), the assessment will use the HUC 12 or sub-watershed scale, followed by Scope 2 (Midscale) and 3 (Finescale; Figure 3).

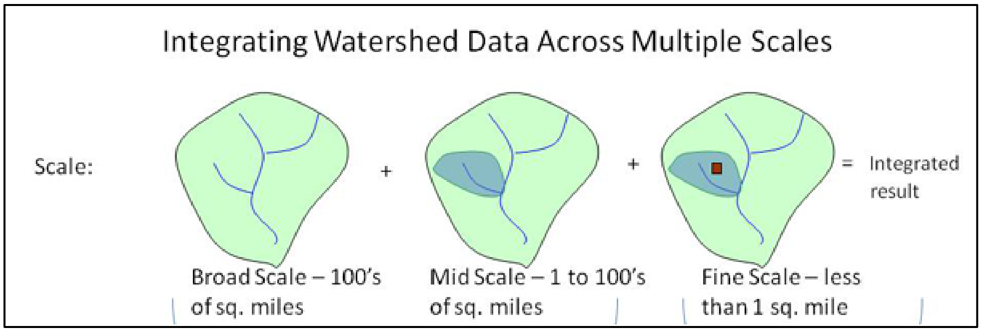


Figure 3. Example of a multi-scale framework for integrating data across scales from the Puget Sound Watershed Characterization Project (Volume 3).

6PPD priority area assessment strategies:

Scope I – Watershed scale (Summer of 2022 – this report): Produce a sub-watershed broad scale assessment of priority areas that consider primary indicators including transportation, and ecosystem and salmon attributes (The focus of this proviso).

Scope II – Stream scale (Starting in Winter, need ongoing support) - Incorporate stream attribute information on a catchment scale, while funding and coordinating field and lab based 6PPD assessments. Complete a web-based coho mortality, water quality, salmon recovery and stormwater treatment interactive map (storymap) that will help standardize, collect and share data across interest groups. Support assessment, modeling, and mapping efforts to hone our joint road runoff mitigation strategies and salmon bearing stream water quality enhancement efforts.

Scope III – Project scale (Future work support needed) - Incorporate new information regarding the scope and scale of 6PPD-quinone in the environment. Cross-reference and coordination fish passage barrier and local and state transportation stormwater retrofit, and salmon recovery project prioritizations. Consider Pacific salmonid habitat and population assessment when weighing the cost and benefits of proposed projects.

The multi-scalar framework relies on a series of spatial indicators of watershed, stream, and site-level conditions, and value to watershed processes and salmon habitat. As programs and projects develop to address 6PPD-q, they may want to consider what's occurring at landscape to site-scales to ensure that the work is going to occur in the most valuable areas, and account for limiting factors that may be occurring at different scales.

The framework does not necessarily imply a sequence of prioritization going from coarse (Scope I) to fine-scales (Scope III). Rather, whatever scale the program is working at prioritizing work in, can use these indicators to understand the processes at play, which could inform the timing, sequence, and location of specific projects. For example, a jurisdiction may be in the process of updating their transportation improvement plan. It has site-level locations where work could occur (e.g. culverts), and to prioritize this work should consider the stream, and watershed-scale factors which could leverage this work for the most ecosystem gain, and 6PPD-q mitigation.

The Scope I strategy was inspired by Feist et al. 2017 and Ettinger et al. 2021 and the Watershed Characterization Project where characterization attributes were summarized to produce a score that represents vulnerability and potential exposure to road runoff. Primary attributes were selected and the STAC GIS working group helped gather and condition the selected data (Table 6). The amount of data available, prioritization efforts, and the mitigation required to reduce the impact of water quality on Pacific salmon will vary from watershed to watershed. Multiple tools and monitoring efforts are needed at local, state and regional scales to keep mitigation planning and implementation flexible and customizable.

Table 6. Primary indicators of vulnerable habitats exposed to road pollution for this report.

Primary Indicators	Indicator Type
Salmon habitat type by species	Ecosystem
Salmon habitat distribution by species	Ecosystem
Salmon stocks per watershed all species	Ecosystem
Salmon stream habitat length	Ecosystem
Traffic counts (AADT)	Transportation
Road distance	Transportation
Road type	Transportation
Vehicle type	Transportation
Road and stream crossings	Transportation
Land cover	Watershed
Stream characteristics	Watershed
Land use	Watershed
Precipitation	Watershed

Given the limited number and extent of direct measurements of 6PPD-q, spatial information is useful for local stormwater managers to identify vulnerable salmon habitats with suspected 6PPD-q exposure from motor vehicles and impermeable surfaces to help focus their stormwater retrofit inventories. Indicators such as roads, traffic, salmon distribution, water quality, quantity and physical impairments, and land changes can help prioritize areas where stormwater is untreated and harming sensitive aquatic species. For example, coho spawn and rear in small lowland tributaries and are nearest to the source of 6PPD-q from road runoff and other contaminants. Therefore, freshwater habitats used by coho salmon are considered priority areas for protection and road runoff mitigation actions.

A watershed scale characterization can provide the necessary first step in identifying existing conditions that can, or have, resulted in degraded waterways used to identify areas that are high priority for protection or restoration. Initial assessments for conservation and mitigation on a watershed scale also support salmon population diversity and connectivity. Mitigation and restoration projects are often done on a site-specific scale without fully understanding the source of the problem. Permit, funding, or policy deadlines make it difficult to conduct broad-scale assessments in a timely manner and result in projects based on opportunity and convenience, rather than habitat benefits and cost effectiveness.

A considerable amount of spatial and chemical information was gathered during this proviso, including interviews with the stormwater and salmon recovery communities. Recommended next steps are to determine how to continue this multi-disciplinary and multi-agency approach and momentum to combining salmon, road, land cover, and stream information to help visualize non-point source pollution mitigation priority areas. This presents an opportunity to develop a data sharing and visualization platform to support ongoing non-point source reduction efforts to vulnerable aquatic habitats. Further mapping and assessment of vulnerable areas will help focus local site evaluations for road runoff mitigation measures covered in the section above.

Ecology plans to continue working with the committee and other interested partners and stakeholders to address these issues and develop technical guidance to help with prioritizations of mitigation actions and refine the scope II (streams) and scope III (sites) approaches.

This STAC summary provides an initial analysis at a sub-watershed scale meant to guide 6PPD-quinone reconnaissance efforts to develop a stormwater retrofit planning process using 6PPD-quinone exposure as a limiting factor to create a list of potential priority sub-watersheds. Once the multi-scalar green infrastructure and stormwater retrofit planning process is developed to protect coho salmon, it would hopefully help guide local communities to optimize multiple ecosystem services and help enhance urban sustainability and resilience.

Under the 1989 State/Tribal Centennial Accord and the 2012 State/Tribal Relations Act (Chapter 122, Laws of 2012), Ecology maintains a government-to-government relationship with Tribes. We are fully committed to the principals of government-to-government consultation and cooperation with Tribes consistent with our mission to protect, preserve, and enhance Washington's environment, and promote the wise management of our land, air, and water for the benefit of current and future generations. The preliminary sub-watershed prioritization maps are to inform reconnaissance efforts throughout the State of Washington and is not meant to guide implementation. Reconnaissance efforts and pilot studies will be coordinated with regional Tribal water quality and salmon scientists.

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Appendix C.

Consultant Report on Best Management Practices for 6PPD and 6PPD-q

Washington State Department of Ecology

STORMWATER TREATMENT OF TIRE CONTAMINANTS BEST MANAGEMENT PRACTICES EFFECTIVENESS

Final Report | June 2022

STORMWATER TREATMENT OF TIRE CONTAMINANTS BEST MANAGEMENT PRACTICES (BMP) EFFECTIVENESS

FINAL REPORT

PREPARED FOR:

Washington State Department of Ecology

PREPARED BY:

Aimee S. Navickis-Brasch, PhD, PE
Evergreen StormH2O

Mark Maurer, PE, PLA
Evergreen StormH2O

Taylor Hoffman-Ballard, PE
Evergreen StormH2O

Susan Bator, LSP
GeoEngineers

Jerry Diamond, PhD
Tetra Tech

PROJECT BACKGROUND AND ACKNOWLEDGEMENTS

In the fall of 2021, the Washington State Department of Ecology (Ecology) released a request for qualifications and selected a Consultant Team with staff from Osborn Consulting, Inc., Evergreen StormH2O, Tetra Tech, and GeoEngineers to complete this work. The consultant team was advised and supported by a project advisory committee made up of researchers and staff from Ecology, the Washington State Department of Transportation (WSDOT), Washington State University (WSU), the University of Washington (UW), and the Technical Assessment Protocol - Ecology (TAPE) Program, who recommended literature to review, provided research updates, and comments on the draft versions of the report that were incorporated into this document.

Project Advisory Committee Members

Brandi Lubliner (Lead), PE
Washington State Department of Ecology

Karen Dinicola
Washington State Department of Ecology

Rhea Smith
Washington State Department of Ecology

Ed Kolodziej
University of Washington

Jenifer McIntyre, PhD
Washington State University

Doug Howie, PE
Washington State Department of Ecology

Foroozan Labib
Washington State Department of Ecology

Alex Nguyen, PE
Washington State Department of Transportation

Carla Milesi
University of Washington

Ani Jayakaran, PhD, PE
Washington State University

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CHAPTER 1: PROJECT OVERVIEW AND SUMMARY OF FINDINGS

Project Purpose

The antioxidant 6PPD and its byproduct 6PPD-quinone (6PPD-q) are chemicals recently discovered to come from tires and enter waterways through roadway runoff (stormwater). 6PPD-q has been linked to high mortality rates in coho salmon on the west coast of the United States. The goal of this project was to synthesize current knowledge of 6PPD and 6PPD-q, including physicochemical properties, sources, and fate and transport within the built environment, to assess which stormwater best management practices (BMPs) are expected to reduce concentrations of 6PPD and 6PPD-q in stormwater runoff. The objectives completed to achieve this goal included:

- Identify and review literature related to physicochemical properties, sources, fate and transport, and potential effective treatments of 6PPD and 6PPD-q (Chapters 2 and 3).
- Develop a basis from the literature for how to evaluate BMPs for their ability to capture, contain, and treat bound and dissolved 6PPD and 6PPD-q (Chapter 4).
- Apply the basis for how to evaluate BMPs to existing BMPs in the Washington Stormwater Management Manuals and stormwater design manuals from other states (Chapter 4).
- Summarize and prioritize research needs (Chapter 5) regarding physicochemical properties, sources, fate and transport, and potential effective BMPs for treating 6PPD and 6PPD-q.

Summary of Findings

The following paragraphs provide a summary of the findings organized by chapter followed by a summary of recommendations for future research.

Chapter 2. Key Physicochemical Properties

Summary and Synthesis of Current Knowledge - Of the sources reviewed and synthesized, 14 sources reported physicochemical properties for 6PPD and 6PPD-q. Half of the 14 sources reported modeled properties or a combination of model and lab or field data (e.g., CompTox Chemicals Dashboard, National Center for Biotechnology Information PubChem website). Fewer sources reported properties of 6PPD-q (5 of 14 sources) than 6PPD.

Findings Summary - The following properties and findings were identified through the review of sources.

- Both 6PPD and 6PPD-q appear to have an affinity for soil and organic matter, based on their relatively high log K_{ow} and log K_{oc}.
- The density and solubility of 6PPD suggest that it is likely to remain undissolved and will float, assuming it is not attached to another particle.
- 6PPD-q is more likely to travel in the dissolved phase than 6PPD. No density information was available for 6PPD-q.
- The degradation of 6PPD appears to vary in different environmental media with sources reporting short half-lives of a few hours in biologically active water, and longer half-lives of nearly a year in sediment (soils in water). The degradation of 6PPD-q also varies significantly (from just over a day in water to nearly a year in sediment) in different environmental media.

Knowledge Gaps - Because model data are based on assumed inputs and are generally used only as screening tools, we consider the limited amount of lab or field data on the following to be research gaps to test and understand:

- The affinity of 6PPD and 6PPD-q to soil and organic matter under different environmental conditions.
- The half-life of both parameters in soil and sediment as well as 6PPD-q in water.
- The reaction dynamics of 6PPD transforming into 6PPD-q.
- The prevalence of the contaminants in the dissolved phase compared to that adhered to particles.
- The lethality of 6PPD-q for fish related to particle size distribution and either attached to particles or dissolved phases.

Chapter 3. Anticipated Fate and Unmitigated Transport

Summary and Synthesis of Current Knowledge - A literature search was conducted to identify articles and studies with information about 6PPD and 6PPD-q sources and their anticipated fate, and unmitigated transport to determine how they get into and move through the MS4 system. Literature was located by reviewing databases and search engines that included Web of Science, PubChem, Science Direct, European Chemicals Agency (ECHA), and Google Scholar. Ecology also provided a compilation of articles, memos, and reports that covered these topics as well. 18 studies had relevant information. Of the 18 studies, 13 focused on transport in the environment.

Findings Summary **-** The following information was identified through the review of sources.

- The primary pathway of 6PPD-q transport is most likely via runoff from roads and parking areas to BMPs or through conveyance systems (storm drainpipes and catch basins) to surface waters or direct discharges to surface waters.
- 6PPD-q and other chemicals associated with tire wear particles (TWPs) are present in roadway runoff and in surface waters near highways, particularly in urbanized areas. However, more TWPs are found on roads and roadside ditches compared to receiving water columns or sediments.
- TWPs smaller than 10 μm tend to be air borne with larger TWP deposited onto and along roadways.
- Snow melt contains relatively high concentrations of 6PPD and 6PPD-q.
- Conflicting research has been reported regarding the temporal distribution of 6PPD-q and other TWP contaminants during a wet weather event. Some studies have reported that 6PPD-q transport exhibits a first flush phenomenon while other studies indicate tire wear chemicals concentrations peak several hours after the wet weather event starts, suggesting that these chemicals are transport-limited rather than mass-limited.
- The peak concentration of some tire wear chemicals may be delayed at a site due to many factors such as distance to the source(s), the type of source and its hydraulic behavior (e.g., stormwater outfall, drains from retention basins, drains from bridges) and or the extent of road traffic from which the chemical originates.

Knowledge Gaps **-** The main gaps in the fate and transport of 6PPD and 6PPD-q are as follows.

- Most studies have been conducted during wet weather events and less is known about the impact of 6PPD-q and other TWP contaminants that are deposited on roadways and accumulate during dry weather until the next runoff event. Research is needed to examine 6PPD-q deposition, how long it remains bioavailable and toxic, and how it's transported outside of wet weather events. This is particularly important in Washington State with a long dry summer season on the west side and semi-arid environments on the east side.

- Some key chemical properties of 6PPD-q (e.g., half-life on surface roads and partitioning to soils) are still uncertain.
- Better information is needed to determine the deposition of TWP in all sizes from dust via air deposition to larger particles thrown from tires onto the roadside: what is the distribution of these particles and what are their effects on fate and transport of the particles and 6PPD and 6PPD-q to surface waters?
- The temporal distribution of 6PPD-q and other TWP contaminants in the stormwater system and delivery to water bodies during wet weather events is poorly understood; we need to study 6PPD-q transport dynamics at different distances from roadway sources.

Chapter 4. BMP Evaluation Process

Development of the BMP Evaluation Basis **-** Two categories of BMPs were identified: Stormwater Flow and Treatment BMPs and Source Control BMPs. An evaluation criteria and process were developed to rank BMPs (Table 1.1) in terms of potential ability to provide treatment or prevent 6PPD and 6PPD-q from mixing with stormwater. The evaluation criteria are based primarily on treatment processes provided by the BMP and likely to reduce 6PPD and 6PPD-q. These treatment processes were identified after reviewing literature on physicochemical properties and lab or field testing of a BMP or as defined in stormwater manuals. The evaluation process included applying the criteria to an inventory of BMPs from 8 stormwater design manuals nationwide and BMPs approved through TAPE to identify which are most likely to reduce 6PPD and 6PPD-q from entering stormwater runoff.

Table 1.1 BMP Evaluation Criteria for 6PPD and 6PPD-q

Treatment or Prevention Potential Category	Flow and Treatment BMPs Definition of Category	Source Control BMPs Definition of Category
High	Dispersion, Infiltration, or some biofiltration BMPs (that use bioretention soil media or compost) where the underlying soils meet soil suitability criteria, or BMPs that provide the treatment process sorption.	BMP separates a source (i.e., roadway, parking, etc.) from stormwater.
Medium	BMPs provide sedimentation (removal depending on size/detention time) or filtration (removal depending on size of particles). May need a polishing layer/treatment train including sorption; i.e., sand filter with zero valent iron in layers.	BMP partially separates 6PPD and 6PPD-q from stormwater (i.e., E&O efforts); prevents 6PPD and 6PPD-q from entering stormwater from a minor source (i.e., traffic at a construction site)
Low	BMP does not provide infiltration, sorption, filtration, or sedimentation.	BMP is unlikely to provide any measurable separation between 6PPD and stormwater.

Findings Summary **-** The BMP evaluation criteria was applied to 93 flow and treatment BMPs and 84 source control BMP that were identified in the stormwater design manuals. For flow and treatment BMPs, 28 BMPs ranked high, 51 medium, and 14 low. For source control BMPs 9 ranked high, 3 medium, and 72 low. A complete list of the BMP evaluated along with the assigned rank is in Appendix 4-1.

Knowledge Gaps **-** Based on knowledge gaps from Chapters 2 and 3, these gaps were identified for better understanding the most effective flow and treatment BMPs and source control BMPs:

- Whether and what types of sorption remove 6PPD and 6PPD-q from stormwater.
- Whether 6PPD and 6PPD-q will remain adhered to soil or organic matter and not be exported to groundwater or downstream when stormwater flows over the soil.
- Whether infiltration, dispersion, and some biofiltration BMPs (that use bioretention soil media or compost), or BMPs that provide sedimentation and filtration will capture the particle sizes containing the most readily bioavailable concentrations of 6PPD and 6PPD-q.
- Whether the estimated half-lives of 6PPD and 6PPD-q are reliable and can be used to determine which BMPs are able to hold the contaminants until the concentrations are no longer lethal.
- Effectiveness or role of source control BMPs in preventing 6PPD or 6PPD-q transport to or on the roadways or in the stormwater system and ultimately to receiving waters.

Chapter 5. Research Prioritization

This chapter summarizes the research needs identified in each chapter into a one page table. Research needs are also prioritized as having a high, medium, or low need for the research to be conducted with the highest need focusing on understanding what BMPs would capture/contain/treat the contaminants and the potential impact on surface waters if current knowledge is inaccurate or incomplete. The categories were developed using best professional judgement guided by input from the project advisory committee. The next section provides a summary of the future research recommendations that were identified.

Recommendations for Future Research

- Additional testing is needed to determine if leaching of 6PPD and 6PPD-q will occur (and under what conditions) while adhered to soil, engineered materials, and organic matter. This property has a large impact on the fate and transport of the contaminants within the built environment including whether BMPs would permanently remove the contaminants or whether groundwater could be impacted by the contaminants.
- Study the chemical properties of 6PPD and 6PPD-q to better determine the half-life in different sectors of the environment (soil, water, sediments), within stormwater BMPs, and the toxicity/bioavailability in those forms. Fate of these chemicals in the environment will highlight where to focus our efforts to reduce their impacts on salmon and potentially other aquatic life.
- Whether transport in the dissolved phase, adhered to particles (or both) produces loadings of environmental concern and what phase or range of particle sizes containing or attached to 6PPD and 6PPD-q need to be removed by BMPs to reduce the lethality of stormwater effluent. This will help to understand loading of 6PPD and 6PPD-q from roadways and parking lots and which BMPs will be the most effective at filtering solids with 6PPD-q attached.
- Study the location and concentration of TWP throughout the roadway infrastructure system (driving surfaces, gutters, roadsides, snow or ice piles from winter plowing operations, catch basins and pipe sediments) to determine which operation and maintenance activities or changes will most effectively reduce loading.
- Determine what land uses (e.g., road traffic counts, industrial or commercial areas, various residential types, etc.) and specific locations near roads and parking areas might trigger the greatest need for treatment BMPs. Also assess if there is a traffic count (average daily traffic or ADT) threshold where 6PPD and 6PPD-q concentrations are no longer present in lethal amounts. This information will help to prioritize locations for BMPs.

- Study the relationship of time or seasons on 6PPD and 6PPD-q concentrations in wet weather events to better characterize these discharges. This could lead to BMPs that target the part of the storm that has the highest concentrations of these chemicals.
- Other tire-derived sources of 6PPD and 6PPD-q such as runoff from athletic fields with artificial turf, junk yards, auto repair shops, and tire stores should be investigated to see if they are sources for 6PPD and 6PPD-q to receiving waters. Other 6PPD-containing products beyond tires will likely be discovered.
- Perform field testing on BMPs that provide infiltration, dispersion, and biofiltration or sedimentation and filtration BMPs to assess whether these BMPs will capture the particle sizes associated with the most readily available concentrations of 6PPD and 6PPD-q, thereby reducing the lethality of the effluent.
- Determine loading from construction sites, particularly sites located on or adjacent to highways, to assess the priority of treating runoff from the sites as well as determine the most effective construction source control and flow and treatment BMPs. Construction sites can be active for years, during which time permanent stormwater BMPs in the construction area may be either offline or removed. As such, construction BMPs may be the only stormwater controls in place, and it is important to know whether 6PPD and 6PPD-q are present in runoff from a construction site in lethal amounts and whether the construction BMPs are able to reduce the lethality of the stormwater.
- Test various sorption media to understand whether this treatment process how best to utilize this treatment process in flow and treatment BMPs to remove 6PPD and 6PPD-q.
- Determine how long particles containing or with 6PPD attached will generate 6PPD-q at different stages of transport. The time the chemicals persist in the built environment will highlight where to focus efforts to reduce impacts on salmon and potentially other aquatic life.
- Perform field testing to understand fate and transport of 6PPD-q under environmental conditions other than wet weather events. Specifically, how long does 6PPD-q remain bioavailable and toxic in dry conditions and how is it transported outside of wet weather events. Fate and transport outside of wet weather events will be particularly important during dry seasons, dry periods, or in areas with semi-arid climates.
- Quantify reduction of 6PPD and 6PPD-q from pollutant generating surfaces (roadway or parking surfaces) to stormwater infrastructure by source control BMPs. This will help to prioritize efforts by municipalities and other organizations to reduce impacts to salmon and potentially other aquatic life.

CHAPTER 2: KEY PHYSICOCHEMICAL PROPERTIES FOR STORMWATER MANAGEMENT

2.1 Chapter Purpose

The intent of this chapter is to synthesize the current knowledge and understanding of the physicochemical properties of 6PPD and 6PPD-q. Specifically, how information was developed (i.e., laboratory testing, modeling, etc.), and where gaps in understanding exist. What is known about these pollutants' properties is used in Chapter 3 to evaluate human activities that may be sources, land uses, and potential reservoirs, which are locations where contaminants can be held before mobilizing to or within the MS4, for urban, urbanizing, or rural environments. Chapter 4 evaluates BMPs for their ability to capture, contain, and treat 6PPD and 6PPD-q based on these same physicochemical properties.

2.2 Overview of Chapter Contents and Work Completed

The work completed as part of this chapter included a compilation of 14 different sources of information for physicochemical properties of 6PPD and 6PPD-q and synthesis summarized in Tables 2.1 and 2.2. The sources reviewed were identified by the project advisory committee, and primarily consisted of model data or a combination of information from models and lab or field testing *(Chemaxon, n.d.; ECHA, 2021; National Center for Biotechnology Information, 2021; OECD, 2004; U.S. EPA, 2021a)*. The following is a breakdown of what was found:

- Seven of the 14 sources referenced modeled properties or a combination of model and lab or field data.
- One peer-reviewed journal article was also identified that summarized model data, as well as one unpublished Screening Information Data Set (SIDS) Initial Assessment Report, which was developed using data from the SIDS database[1].
- Three peer-reviewed journal articles provided data from studies performed in laboratories.
- One published report providing a synthesis of literature and a peer-reviewed journal article regarding data collected in the field were also synthesized.

Of the sources synthesized, most (9 of 14 sources) included physicochemical properties for 6PPD but not 6PPD-q. These nine sources represent a mix of lab, field-collected, and model-derived information. Three sources, including data from two models and a peer-reviewed journal article which referenced model data, reported physicochemical properties of both 6PPD and 6PPD-q. Two recent peer-reviewed journal articles summarizing studies performed in laboratories reported physicochemical properties of only 6PPD-q. It is important to note that the contaminant 6PPD-q was recently identified (in 2020), whereas 6PPD has been studied for decades for its use in tires. The higher number of sources for 6PPD resulted in a larger amount of reported physicochemical properties for 6PPD compared to 6PPD-q, as discussed in the following section.

2.3 Findings Summary

This section summarizes what is known about the physicochemical properties of 6PPD and 6PPD-q. The sources for this information along with the reported values are summarized in Tables 2.1 and 2.2. Appendix

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[1] The Screening Information Data Sets (SIDS) Program involves the Organization for Economic Cooperation and Development (OECD) OECD countries collecting existing information and conducting tests on the allocated high production volume (HPV) chemicals following the protocol agreed upon by OECD.

Table A2.1 contains the physicochemical properties of common chemicals found in stormwater along with the properties of 6PPD and 6PPD-q defined in this section to provide a reference.

2.3.1 Density, Solubility, and Polarity

Physicochemical properties reported for 6PPD indicate the contaminant has a density similar to water, a relatively low solubility in water, and a tendency to adhere to soil or organic matter particles. Densities reported for 6PPD range from 0.995 to 1 g/mL (Table 2.1). The maximum solubility reported for 6PPD in the synthesized sources was 2.84 mg/L, with most sources reporting a solubility closer to 1 mg/L. The densities and solubilities reported suggest that 6PPD is likely to remain undissolved for an unspecified amount of time and will float if it is not attached to another particle. Klöckner et al. (2020) reported the concentration of 6PPD adhered to fine particle sizes in roadway sediment. The study sieved all runoff sediments to focus on smaller particle sizes (<500 µm) and found that 6PPD concentrations were highest in the less than 20µm and 50 to100µm particle size ranges. It is important to note that the study excluded larger particles potentially common in roadway sediments, and that larger particle sizes may contribute 6PPD and 6PPD-q to stormwater infrastructure. The density of the roadway sediment was also reported, with almost all of the samples having a density of 1.3 g/mL or higher, and most of the samples having a density above 2.3 g/mL. The higher density may suggest that 6PPD, when attached to roadway sediment particles, may be denser than water, and as such is likely to settle in laminar or less turbulent flow environments where the samples were collected (street sweeper material, underground vaults, settling ponds and lakes).

As mentioned previously, physicochemical properties were less frequently reported for 6PPD-q in field studies. The density was not reported in the sources synthesized in Table 2.2. The solubility of 6PPD-q appears to be higher than 6PPD in water, with reported values of 51 to 67 mg/L. This suggests 6PPD-q may be more likely to travel in the dissolved phase than 6PPD.

2.3.2 Volatility and Bioconcentration

Volatility of the contaminants was assessed through Henry's law constant and the vapor pressure. The estimated Henry's law constant for 6PPD is 7.43×10^{-4} at 25 °C suggesting that it has a moderate potential to volatilize from surface waters (OSPAR Commission, 2006). The vapor pressure for 6PPD and 6PPD-q are reported to be low, 6.85×10^{-3} Pa at 25°C and 6.57×10^{-6} Pa at 25°C, respectively, suggesting they are not likely evaporate at 25°C (77°F). However, due to the tendency for 6PPD to sorb to soil, sediments, and suspended particulates (see Section 2.3.3), 6PPD can be present on suspended particles in the air (OSPAR Commission, 2006).

The bioconcentration factor of a contaminant provides an estimate of the potential for bioaccumulation from exposure in water. 6PPD has a calculated bioconcentration factor range of approximately 349 (Arnot-Gobas Method; US EPA, 2021b) to 801 (BCFWIN v2.15; OSPAR Commission 2006); this range suggests it has a low to moderate potential for bioaccumulation in aquatic organisms (OSPAR Commission, 2006). At the time of this report, additional data was in the process of being published for the bioconcentration factor of 6PPD (U.S. EPA, 2021a). . 6PPD-q has a calculated (Arnot-Gobas Method) bioconcentration factor of 131.9 (US EPA, 2021b), which suggests it has a low potential for bioaccumulation in aquatic organisms.

2.3.3 Melting Point, Water Partition Coefficient (K_{ow}), Organic Carbon Water Partition Co-Efficient (K_{oc})

6PPD and 6PPD-q share some similar physicochemical properties which may inform how long the contaminants persist and how they move through the built environment. High melting points (up to 121.5°C for 6PPD, 169.18°C for 6PPD-q) were reported for both contaminants, which indicates they will likely not melt in the built environment. Additionally, both contaminants have a relatively high log K_{ow} (4.68 to 5.6 for 6PPD and 3.25 to 5.5 for 6PPD-q) and log K_{oc} (4.04 to 4.84 for 6PPD and 3.94 for 6PPD-q) which suggests affinity for soil and organic matter. This would also suggest that 6PPD and 6PPD-q adhered to soil would not leach from the soil particles and enter groundwater, however, additional research is needed to confirm the tendency to adhere and stay adhered to particles under environmental conditions (Sections 2.4 and 2.5).

While 6PPD and 6PPD-q appear to have an affinity to soil or organic matter, both contaminants are moderately non-polar compounds which indicates that transport of the contaminants in the dissolved phase is possible, but not anticipated to be probable. This is supported by Fugacity Model[2] results: a higher percentage in the environment is predicted to adhere to soil and sediment (approximately 90% for both 6PPD and 6PPD-q), though approximately 10% is anticipated to not adhere to soil and remain in the water column (U.S. EPA, 2021b). No lab or field data were reviewed to indicate the prevalence of contaminants in either phase, which is discussed further in Section 2.4.

2.3.4 Degradation

From within a tire rubber matrix (including a tire wear particle), 6PPD will continue to bloom to the surface until there is no more 6PPD remaining in the rubber matrix. Additionally, as long as 6PPD is in the presence of ozone or oxygen, it will form a variety of transformation products, including 6PPD-q. The following paragraphs discuss the half-lives of both contaminants in different media and potential methods of degradation in the environment.

The degradation of 6PPD and 6PPD-q will likely vary based on the medium and environmental and physical conditions (e.g., temperature, pH, presence of metals, etc.). The estimated half-lives of 6PPD and 6PPD-q are 75 days in soil and 337 days, in sediment (meaning soils below water) are based on Fugacity Model results (U.S. EPA, 2021b). No other sources reported on the half-lives in sediment or soil.

Many more sources (model, lab, and field data) reported on the half-lives of 6PPD and 6PPD-q in the water column. In water, reported half-lives for 6PPD range from around 3 hours to less than a day (OSPAR Commission, 2006; ECHA, 2021), with shorter half-lives noted in warmer waters and those containing heavy metals (OSPAR Commission, 2006). However, long-term stability up to four weeks has been noted in cold conditions at a pH of 2 (OSPAR Commission, 2006). The half-life of 6PPD-q in water is less certain: results from the Fugacity Model indicate the half-life is 900 hours (U.S. EPA, 2021b), whereas other sources report the half-life as longer than 6PPD or more specifically at least one day (Tian, 2021). Additional research is needed to better understand the half-lives of both 6PPD and 6PPDq in Washington’s environments. More discussion about this is included in Sections 2.4 and 2.5.

Degradation of 6PPD and 6PPD-q is expected to result from a combination of abiotic and biotic processes (OSPAR Commission, 2006; ECHA, 2021). When on a surface, such as a tire, 6PPD absorbs UV-B

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[2] Fugacity Models are utilized to study and predict the behavior of chemicals in different environmental media,

radiation and is also expected to undergo rapid direct photolysis (OSPAR Commission, 2006) in direct sunlight (OECD, 2004). Moreover, 6PPD is used in tires for its reactivity, to neutralize ozone, and to a lesser extent oxygen (Seiwert B. , Nihemaiti, Troussier, Weyrauch, & Reemtsma, 2022). It is therefore expected that 6PPD on a tire or other surface would degrade in the presence of ozone or oxygen. In the atmosphere, 6PPD undergoes indirect photodegradation via rapid reaction with hydroxyl radicals. Photodegradation is also likely a predominant mechanism for 6PPD loss in surficial soils (OSPAR Commission, 2006).

Environmental degradation is presumed to be largely abiotic for 6PPD, as it is highly reactive and not reported to be readily biodegradable. In an OECD TG 301C test on ready biodegradability, based on biochemical oxygen demand, only approximately 2% of 6PPD was biodegraded; however, based on high-performance liquid chromatography, approximately 92% of 6PPD was removed within 28 days indicating that 6PPD was transformed (OECD, 2004). Moreover, 6PPD degradation was tested in an algae nutrient medium containing traces of ions of heavy metals such as manganese, cobalt, copper, molybdenum, and zinc to represent environmental conditions, and reported results indicated the half-life was decreased compared to tests on 6PPD in a buffered aerobic solution. Aside from the expectation that 6PPD-q is also expected to be degraded by a combination of abiotic and biotic processes (OSPAR Commission, 2006; ECHA, 2021), no lab or field data were reported which indicated methods of degradation of 6PPD-q.

Table 2.1. 6PPD Physicochemical Properties

Physico-Chemical Properties	**(National Center for Biotechnology Information, 2021)**	**(U.S. EPA, 2021a)**	**(U.S. EPA, 2021b)**	**(Klöckner P. , et al., 2020)**	**(OSPAR Commission, 2006)**	**(ECHA, 2021)**	**(Chemaxon, n.d.)**	**(Cheng, et al., 2007)**	**(Williams, et al., 2017)**	**(Tian Z. , et al., 2020)**	**(OECD, 2004)**	**(Hiki, et al., 2021)**	**(BUA, 1998)**	**(Bayer AG, 1997)**
Density	1.02 g/ml (8.51 lb/gal)				0.995 g/cm^3 (62.1 lb/ft^3) at 50ºC (122ºF)									0.995 g/cm^3 (62.1 lb/ft3) at 50ºC (122ºF)
Molecular Weight	268.4 g/mol (0.5917 lb/mol)				268.5 g/mol (.5919 lb/mol)									
Water Solubility	<1 mg/ml (<8.35 X 10^{-3} lb/gal) at 15.6ºC (60°F)		2.84 mg/l (2.37 X 10^{-5} lb/gal) at 25°C (77ºF)		1 X 10^{-3} g/l (8.35 X 10^{-6} lb/gal) at 20°C (68ºF)	0.001 mg/ml (8.35 X 10^{-6} lb/gal) at 50°C (122ºF)					1 mg/l (8.35 X 10^{-3} lb/gal) at 20°C (68ºF)			
Log K_{ow}			4.68	4.68	4.68		4.91	5.6					5.4	
Log K_{oc}	4.84		4.36		4.84				4.04					
Boiling Point	260ºC (500ºF) at 760 mm Hg (14.7 Psi), calculated 370°C (698ºF)	260ºC (500ºF) at 760 mm Hg (14.7 Psi), calculated 354-412°C (669-774ºF)	369.67°C (697.41ºF)		230ºC (446ºF) at 1013 hPa (14.7 Psi)								230°C (446ºF) at 13.33 hPa (0.1933 Psi)	
Henry's Law Constant					7.43 X 10^{-4} at 25ºC (77ºF)									
Bioconcentration Factor					801									
Half-Life			75 days in soil & 337 days in sediments[1]		Less than a day in water; 3 hrs in warmer water containing heavy metals; up to 4 weeks in cold water pH=2									
Melting Point	45-50°C (113-122ºF)		121.5°C (250.7 ºF)		45-48°C (113-118.4ºF)								45-48°C (113-118.4ºF)	
Vapor Pressure	Negligible at 25°C (77°F)		6.85 X 10^{-3} Pa (9.94 X 10^{-7} Psi); 6.129 X 10-7 atm-m^3/ mole (using VP of 4.93 X 10^{-6} mm Hg (9.53 X 10^{-8} Psi) WS of 2.84 mg/l (2.37 X 10^{-5} lb/gal))		6.85 X 10^{-3} Pa (9.94 X 10^{-7} Psi) at 25°C (77°F)						6.85 X 10^{-5}hPa (9.94 X 10^{-7} Psi)			

1. Fugacity Model Results

Table 2.2. 6PPD-q Physicochemical Properties

Physicochemical Properties	(National Center for Biotechnology Information, 2021)	(U.S. EPA, 2021a)	(U.S. EPA, 2021b)	(Klöckner P. , et al., 2020)	(OSPAR Commission, 2006)	(ECHA, 2021)	(Chemaxon, n.d.)	(Cheng, et al., 2007)	(Williams, et al., 2017)	(Tian Z. , et al., 2020)	(OECD, 2004)	(Hiki, et al., 2021)
Density												
Molecular Weight			298.39 g/mol (0.6578 lb/mol)									
Water Solubility			51.34 mg/l (4.28 X 10^{-4} lb/gal) at 25°C (77ºF)									67 +/- 5 ug/l (5.59 X 10^{-7} lb/gal) at pH 8 and 23°C; 73.4ºF) (dechlorinated water)
Log K_{ow}			3.98				3.24	4.1		5-5.5		
Log K_{oc}			3.94									
Boiling Point			430.19°C (806.34ºF)									
Henry's Law Constant												
Bioconcentration Factor												
Half-Life			75 days in soil & 337 days in sediments[1]; 900 hrs in water[1]							At least 1 day in water		
Melting Point			169.18°C (336.52ºF)									
Vapor Pressure			6.57 X 10^{-6} Pa (9.53 X 10^{-10} Psi); 3.77 X 10^{-10} atm-m3/mole (using VP of 4.93 X 10^{-8} mm Hg (9.53 X 10^{-10} Psi) and WS of 51.3 mg/l (4.28 X 10^{-4} Psi))									

1. Fugacity Model Results

2.4 Research Gaps and Assumptions Made

Data obtained from studies conducted in the laboratory or in the field (no model data) composed a smaller fraction of sources synthesized. While modeled physicochemical properties provide information about the contaminants, the lack of lab and field testing is limiting because it does not account for all interactions in a natural environment. The model data is presented in Tables 2.1 and 2.2 as it was the only information available for some of the properties of 6PPD and 6PPD-q. The assumption made for this project is that the specific values for modeled half-lives are accurate and are needed for the following Chapters estimations for fate and transport.

Specific research gaps identified during the review of sources included:

- While the log K_{ow} and log K_{oc} for 6PPD and 6PPD-q (OSPAR Commission, 2006) suggest a tendency for the contaminants to adhere to soil or organic matter, no studies were identified that tested in the laboratory or field whether the contaminants would remain adhered to soil or organic matter. It was assumed for the study that both contaminants would remain adhered and not leach.
- The half-lives of 6PPD and 6PPD-q in sediment in water and soil included in this report are based on Fugacity Model results (U.S. EPA, 2021b).
- Klöckner et al. (2020; 2021) studied concentration and density of road and tunnel sediment with limited particle size ranges of <20 to 500um, virtually no information on 6PPD concentrations was found for larger road dirt or tire wear particulates. 6PPD-q was not evaluated in the report and no additional information was found in other sources regarding the particle size or density of 6PPD-q attached to particles. More information is needed to characterize tire wear particles sizes found in the roadway environment, what is typically transported during storm events, and the lethality of different particle sizes to aquatic species.
- Although 6PPD reactivity is high, it is not presumed to all become 6PPD-q (Hu X. , et al., 2022), even though many of the reaction dynamics are unknown.
- Fugacity model results indicate transport of 6PPD and 6PPD-q is likely in both the dissolved phase as well as adhered to particles. No lab or field data was available on the prevalence of contaminants in either phase. Additionally, no information on how quickly 6PPD or 6PPD-q would adhere to soil or organic matter particles if released into the environment as an individual particle or dissolved particle. Work in the following chapters presume the contaminants are travelling in both phases (dissolved and attached to particles).

2.5 Recommendations for Next Steps and/or Additional Research

Recommendations for next steps and additional research are based on the goals of the project as well as the research gaps described in Section 2.4. The recommendation includes some of the physicochemical properties that will be important to verify through lab and field testing, to better understand the fate and transport of the contaminants as well as what treatment mechanisms will capture, contain, or treat 6PPD and 6PPD-q. The following bullets describe each recommendation for next steps and additional research:

- *Confirm preference to adhere to soil and organic matter* – Additional lab and field testing is needed to confirm leaching of 6PPD and 6PPD-q from soil and organic matter is not likely, and to understand any conditions where it could occur. This property has a large impact on the fate and transport of the contaminants within the built environment and would indicate whether groundwater could be impacted by the contaminants

- *Confirm the half-life of 6PPD and 6PPD-q in soil, water, and sediment in water* – Additional lab and field testing is needed to confirm the values produced by the Fugacity Model and the half-life of 6PPD-q, as these values impact the persistence of 6PPD and 6PPD-q in the environment. The lab and field testing may also inform the methods of how 6PPD and 6PPD-q are degraded in the built environment.
- *Understand the density of 6PPD and 6PPD-q in different phases* – Additional lab and field testing is needed to understand the density of both contaminants when dissolved, adhered to a soil or organic matter particle, or attached to a tire wear particle near the source. This data is needed to understand which BMP treatment mechanisms will be most effective.
- *Understand in which phase (dissolved or adhered to particles) 6PPD and 6PPD-q are typically transported* – Lab or field testing is needed to understand in which phase the contaminants are typically transported. Additionally, information regarding the rate that 6PPD or 6PPD-q would adhere to soil or organic matter particles is needed to understand which BMP treatment mechanisms will be most effective.
- *Characterize the amount of 6PPD in fugitive tire particles (all sizes) in the roadway environment*. It will also be important to understand the sizes of particles that are commonly transported to the storm system or to water bodies.
- *Understand the particle size distribution of roadway particles* – This data is needed to understand what particle sizes are captured by flow and treatment BMPs and the potential to remove 6PPD-q from stormwater. It will also be important to understand the lethality of different particle sizes, to ensure BMPs target particles which would be lethal to aquatic species.

Appendix 2-1

Table A2.1. Physicochemical Properties of Common Chemicals Found in Stormwater

Chemical	**Mass (g/mol)**	**Log Kow**	**Koc (ml/g)**	**Water Solubility (mg/L) at 25oC**	**Henry's Law Constant (atm-m3/mole)**	**Vapor Pressure (mmHg)**
Acetone	58.08	-0.24[b]	6.69[a]	miscible[b]	3.50E-05[a]	232[a]
Methyl Ethyl Ketone	72.11	0.2[b]	17.5[a]	256,000[b]	5.69E-05[a]	90.6[a]
Phenol	94.11	1.47[b]	26.9[a]	77,900[b]	3.33E-07[a]	0.35[a]
Dimethyl phthalate	194.19	1.70[b]	39.8[a]	4,160[b]	*7.60E-08*[a]	3.08E-03[a]
Benzene	78.11	2.05[b]	83[b]	1,770[b]	5.55E-03[a]	94.8[a]
Toluene	92.14	2.58[b]	117[a]	546[b]	6.64E-03[a]	28.4[a]
Ethylbenzene	106.17	3.11[b]	170[a]	181[b]	7.88E-03[a]	9.6[a]
o-Xylene	106.17	3.11[b]	178[a]	221[b]	5.18E-03[a]	6.61[a]
2,4,5-T	255.48	3.40[b]	97.7[a]	273[b]	*2.99E-09*[a]	3.75E-05[a]
Parathion	291.26	3.43[b]	7,751[b]	24.0[b]	2.98E-07[a]	6.68E-06[a]
Cyclohexane	84.16	3.44[b]	*531*[a]	59.3[b]	0.150[a]	96.9[a]
Naphthalene	128.17	3.51[b]	1,300[b]	31.9[b]	4.40E-04[a]	8.50E-02[a]
Lindane	290.81	3.76[b]	1,480[a]	7.30[b]	3.18E-06[a]	4.20E-05[a]
6PPD-Q	298.39	3.98[c]	8,589[c]	51.3[c]	3.77E-10[c]	4.93E-08[c]
Pentachlorophenol	266.32	4.41[b]	20,000[a]	14.0 (at 20^{o}C)[b]	2.45E-08[a]	1.10E-04[a]
Phenanthrene	178.23	4.52[b]	22,400[a]	1.09[b]	4.23E-05[a]	1.21E-04[a]
6PPD	268.40	4.68[c]	*11,000*[a]	1.9[c]	*7.69E-08*[a]	*1.88E-07*[a]
Aldrin	364.90	5.17[b]	410[b]	0.011[b]	4.40E-05[a]	1.20E-04[a]
Pyrene	202.26	5.32[b]	73,350[b]	0.134[b]	1.19E-05[a]	4.50E-06[a]
Chrysene	228.29	5.71[b]	*157,000*[a]	0.0033[b]	5.23E-06[a]	6.23E-09[a]
PCB 1254	326.40	6.31[b]	42,500[d]	0.011[b]	2.83E-04[d]	6.86E-05[d]

a. Values are from CompTox Chemicals Dashboard (Experimental Average where possible; italicized if a Predicted Average).
b. Values are from *Hazardous Wastes: Sources Pathways Receptors*, by Richard J. Watts (1998).
c. Values are from EPA EPI Suite (average of values if multiple given).
d. Values are from Pubchem (average of values if multiple given).

CHAPTER 3: ANTICIPATED FATE AND UN-MITIGATED TRANSPORT

3.1 Chapter Purpose

The intent of this chapter is to synthesize the current knowledge and understanding about 6PPD and 6PPD-q sources and their anticipated fate and un-mitigated transport to determine how they get into and move through the MS4 system. This information was used to prioritize where flow and treatment BMPs should be located. For this study, only tire wear sources were considered and discussed in this chapter. Discussion is also provided regarding research gaps, proposed next steps and additional research needed to close the gaps.

3.2 Overview of Chapter Contents and Work Completed

A literature search was conducted to identify articles and studies that mentioned 6PPD and/or 6PPD-q on several databases and search engines that included Web of Science, PubChem, Science Direct, European Chemicals Agency (ECHA), and Google Scholar. Ecology provided a compilation of articles, memos, and reports that covered these topics as well. For this chapter, we reviewed the articles and reports on the origins, fate, and transport of 6PPD and 6PPD-q in the environment. 18 studies had relevant information for this section and are listed in the references. Of the 18 studies, 13 focus on transport in the environment and are summarized in Table 3.1. The results of this review are highlighted in Appendix 3-1 and further discussed in this document.

3.3 Findings Summary

3.3.1 Sources

Tire particles on roadways come in all sizes from full tires, large parts of tires when delamination or blowouts occur, down to very small particles, between 5 µm to 300 µm with an abundance reported between 70-80 µm (Kreider, Panko, McAtee, Sweet, & Finley, 2010; Wagner, et al., 2018), caused by wear between the tire and road surface. During typical tire wear, small (<10 µm; clay to fine silt size) tire wear particles (TWPs) are emitted into the air and larger TWPs (>10 µm), which make up the majority of TWPs, are deposited onto road surfaces (Wagner, et al., 2018). The smallest of the deposited TWPs may become trapped in asphalt pavement or transported by stormwater runoff into soils, storm sewers, and surface waters, where they can continue to leach their chemical constituents into the surrounding environment (Kole, Löhr, Van Belleghem, & Ragas, 2017; Saifur & Gardner, 2021). Larger particles can remain on the roadside for long periods until they are picked up by litter crews or sweeping operations. All these particles will likely keep exuding 6PPD and 6PPD-q until they are removed from the environment or the 6PPD in the rubber compound is exhausted.

TWPs contain many chemicals and several researchers have reported highest concentrations in tire leachate and in field studies of roadway runoff for HMMM 1,3-DPG, 2-OHBT (a byproduct of the vulcanization accelerator 2-mercaptobenzothiazole) and the cyclic amines 1-cyclohexyl-3-phenylurea (CPU) and 1,3-dicyclohexylurea (DCU) (Saifur & Gardner, 2021). These are commonly used additives in tire manufacturing, with up to 14% of the initial tire mass attributable to these compounds, accounting for up to 2.8 lbs released into the environment per tire (Unice, Bare, Kreider, & Panko, 2015) based on an average passenger tire mass of 20 lbs (Lee, Ju, & Kim, 2020). In Europe, new vehicle tires contain up to 1 to 2% (10,000-20,000 µg/g) of 6PPD (OSPAR Commission, 2006). Thus, while 6PPD-q is now known to be a toxicant to aquatic life at low concentrations, the effects of mixtures of chemicals in roadway runoff from tires, including 6PPD and 6PPD-q, are not known.

Several studies have demonstrated that 6PPD-q, and other chemicals associated with TWPs, are present in roadway runoff and in surface waters near highways, particularly in urbanized areas (Peter, et al., 2018; Tian, et al., 2022; Challis, et al., 2021; Johannessen C. P., Helm, Lashuk, Yargeau, & Metcalfe, 2021). While the parent chemical 6PPD (from which 6PPD-q is formed) is used in many types of applications to help rubber products (e.g., transmission belts, hoses, automotive mounts and bushings, and other mechanical products) resist degradation and cracking (Wagner, et al., 2018; Krüger, Boissiere, Klein-Hartwig, & Kretzschmar, 2005), current research suggests that the primary source of 6PPD-q is from tire wear on roadways (Seiwert B. , Nihemaiti, Troussier, Weyrauch, & Thorsten, 2022; Saifur & Gardner, 2021; Challis, et al., 2021). To the extent that TWP concentrations are indicative of relative concentrations of 6PPD, Wagner, et al. (2018) in their review show that far higher concentrations of TWPs have been found on road surfaces and roadsides than in either the water column or stream sediments. This may indicate that stormwater BMPs located adjacent to road surfaces or just the roadside soils and vegetation are filtering out TWPs and preventing them from reaching surface waters. Additional discussion on this topic is included in Section 3.5.

3.3.2 Fate

Information regarding fate and transport of 6PPD-q in aquatic systems has been primarily derived from laboratory studies examining leaching of TWPs using various methods that are intended to simulate potential environmental fate in the field. Knowing the properties that influence chemical fate water solubility, octanol water partition coefficient (log K_{ow}), and organic carbon partitioning coefficient (log K_{oc}) as discussed in Chapter 2, and how 6PPD-q interacts with the terrestrial and aquatic environment, indirectly provides useful information regarding potential transport mechanisms of 6PPD-q and other TWP chemicals. The degree to which bound 6PPD or 6PPD-q in sediments (below water) can become bioavailable to aquatic biota via biotic and/or abiotic transformation processes is not known.

3.3.3 Transport

Much of our knowledge regarding transport of 6PPD-q has been derived from recent field studies in which street dust, and stream or stormwater samples were collected and analyzed over different seasons, multiple years, and/or different precipitation and hydrologic conditions. The literature review in support of this chapter identified several journal articles and reports that examined stream sites in the Toronto metro area (e.g., (Johannessen C. P., Helm, Lashuk, Yargeau, & Metcalfe, 2021)), Saskatoon, Canada (Challis, et al., 2021), Washington State (Peter, et al., 2020), Germany (Seiwert B. , Nihemaiti, Troussier, Weyrauch, & Thorsten, 2022), China (Huang, et al., 2021), and Australia (Rauert, et al., 2022); Table 3.1). The following summarizes information derived from these studies regarding the fate and transport of 6PPD-q. We also highlight critical data gaps identified by various researchers.

Currently, the believed primary pathway of 6PPD-q transport is via runoff from roads and parking areas with tire wear to surface waters. Limited research suggests that treated wastewater discharges are a minor source of either 6PPD or 6PPD-q (Seiwert B. , Nihemaiti, Troussier, Weyrauch, & Thorsten, 2022). Urbanized or urbanizing areas are particularly prone to wet weather runoff of TWPs and associated chemicals due to the relatively high percentage of untreated impervious surface area and high vehicle traffic and associated TWPs (Wagner, et al., 2018; Challis, et al., 2021; Baensch-Baltruschat, Kocher, Stock, & Reifferscheid, 2020). At the time this report was written, a limited number of studies comparing concentrations of 6PPD-q in streams with different types of surrounding land uses indicate lower concentrations of 6PPD-q in less urbanized areas (Challis, et al., 2021).

Studies have demonstrated the occurrence of many potential contaminants in leachate from tires in addition to 6PPD-q and it appears likely that 6PPD-q is not the only potential hazard to aquatic life (Challis, et al., 2021; Rauert, et al., 2022). However, thus far, it appears that 6PPD-q is the most toxic chemical in TWP leachate to Coho salmon adults (McIntyre & Kolodjiez, 2021) and juveniles (Tian Z. , et al., 2020) but not some other species of aquatic life (Hiki, et al., 2021; Varshney, Gora, Siriyappagouder, Kiron, & Olsvik, 2022). The few comparative aquatic toxicity studies examining different commonly reported TWP contaminants (e.g., DPG) suggest that they may be less toxic to aquatic life than 6PPD-q (Hiki, et al., 2021). Brinkmann et al (2022) investigated the acute toxicity of 6PPD-q to rainbow trout, brook trout, arctic char, and white sturgeon and reported 96-hr acute toxicity thresholds (LC50) of 1.0 ug/L or less for the two trout species. Tian et al (2022) reported a revised juvenile Coho salmon LC50 < 0.1 ug/L, indicating substantial sensitivity to 6PPD-q.

3.3.4 Sampling Methods and Stormwater Timing

Few studies have examined fate and transport of 6PPD-q under environmental conditions other than wet weather events. Until recently, analyses of 6PPD-q had not been reported in studies of TWP (Tian Z. , et al., 2021 ; Tian, et al., 2022; Johannessen & Parnis, 2021). While some differences in analytical methods are being used by different researchers to study 6PPD-q in samples, it appears that quality control in these studies (e.g., precision, percent recoveries, blanks) is satisfactory and detection limits are low enough to reliably compare results across studies. However, there needs to be better harmonization of the source of 6PPD-q used in toxicological studies and as standards for characterizing performance of analytical methods used to quantitate 6PPD-q in stormwater studies.

A study by Challis et al (2021) examined concentrations of 6PPD-q and other tire wear associated chemicals at stormwater outfalls and stream sites along the South Saskatchewan River, Canada that are influenced to varying degrees by road runoff. They sampled several of these sites under different storm events and seasons. The highest concentration of 6PPD-q was recorded during a June wet weather event that had more precipitation than other sampling events in that study (24mm or 0.95in) and a longer dry period preceding the wet weather event. In that study, sampling locations nearest to residential areas and roadways had higher concentrations of 6PPD-q than sites associated with less urbanized and rural land uses. Other studies have been concerned with potential accumulation of 6PPD-q on roadsides during dry weather which may then result in higher concentrations of 6PPD-q during runoff events (Peter, et al., 2020; Department of Toxic Substance Control, Safer Consumer Products, & California EPA, 2021). Although these authors did not examine specific toxicants such as 6PPD or other tire wear chemicals, they noted that more urbanized basins may accumulate sufficient toxicants on roadways over relatively short periods of time, thereby minimizing the influence of antecedent dry intervals. As noted previously, chemical properties of 6PPD-q (e.g., half-life on surface roads and partitioning to soils) are still uncertain (Unice, Bare, Kreider, & Panko, 2015; Tian Z. , et al., 2020). Better quantitative information would help inform the influence of air deposition of TWP dust and dry weather deposits of 6PPD-q on fate and transport to surface waters.

Though unclear currently, 6PPD-q and other TWP contaminants may be deposited on roadways where they may accumulate during dry weather until the next runoff event (Huang, et al., 2021). However, a study by Feist et al (2017), comparing the relationship between stormwater runoff and observed Coho salmon mortality in urbanized versus less developed basins in the Puget Sound region, noted that cumulative precipitation appears to be a factor only in less urbanized basins and not related to Coho mortality in the most urbanized areas (Feist, et al., 2017). This is an active area of research. Another mechanism by which 6PPD-q and other TWP contaminants may be stored temporarily is in snow or ice that is plowed from roadways (Seiwert B. , Nihemaiti, Troussier, Weyrauch, & Thorsten, 2022; Challis, et al., 2021). These studies reported that snowmelt contained relatively high concentrations of these contaminants. This is consistent with other pollutants such as hydrocarbons, metals, solids, nutrients, and chlorides that accumulate in snow piles and are subsequently released in high concentrations during snowmelt (Oberts, 1994).

Several researchers have examined the temporal distribution of 6PPD-q and other TWP contaminants during a wet weather event. Some studies indicate evidence of a first flush phenomenon, whereby the peak concentration of 6PPD-q occurs soon after the onset of wet weather runoff (Johannessen, Helm, & Metcalfe, 2021). For some other tire wear chemicals in roadway runoff, such as the corrosion inhibitor (benzotriazole, 5-methylbenzotriazole, OH-BTH) and the vulcanization accelerator (1,3-diphenylguanidine, DPG), a local study in an urban creek showed that the peak concentration may occur several hours after the wet weather event started (Peter, et al., 2020). Peter et al (2020) suggested that in urban creeks, many of the roadway runoff chemicals examined may be transport-limited rather than mass-limited. Meaning that there is ample contaminant to mobilize and that the limiting factor is the runoff flow to transport it. As a result, the peak concentration of some tire wear chemicals may be delayed due to factors such as distance to the source(s), the type of source and its hydraulic behavior (e.g., stormwater outfall, drains from retention basins, drains from bridges) and or the extent of road traffic from which the chemical originates. Few studies are available thus far that have examined transport dynamics of 6PPD-q in particular, and how factors such as watershed size, time of concentration, traffic behaviors, land cover, and sources affect transport observed concentrations of 6PPD-q in stormwater discharges and to particular stream reaches.

3.4 Research Gaps; Triggers for Treatment BMPs, and Prioritization of Treatment

3.4.1 Research Gaps

Several research gaps were identified in the fate and transport of 6PPD and 6PPD-q which include:

- Some key chemical properties of 6PPD-q (e.g., half-life on surface roads and partitioning to soils) are still uncertain.
- Better information is needed to determine the deposition of TWP dust particles through air deposition and larger particles thrown from tires onto the roadside. What is the distribution of these particles and what are their effects on fate and transport of the particles and 6PPD and 6PPD-q to surface waters?
- The temporal distribution of 6PPD-q and other TWP contaminants in the MS4 and in receiving waters during wet weather events are poorly understood currently. While a few research studies suggest that 6PPD-q transport exhibits a first flush phenomenon, other studies indicate tire wear chemical concentrations peak several hours after the wet weather event starts, suggesting that all these chemicals are transport-limited rather than mass-limited. Studies are needed that examine 6PPD-q; transport dynamics using sites at different distances from roadway sources, time of concentration, concentrations during the entire hydrograph in different storm events and different preceding precipitation histories (e.g., extent of dry period prior to the storm event).
- Few studies have examined fate and transport of 6PPD-q under environmental conditions other than a handful of wet weather events internationally. Research is needed to determine 6PPD-q deposition, how long it remains bioavailable and toxic, and how it’s transported outside of wet weather events. This is particularly important in Washington State with a long dry summer season on the west side and semi-arid environments on the east side of the mountains.

3.4.2 Figure 3.1 an Illustration of Fate and Transport: Unknown and Knowns

The flow chart in Figure 3.1 illustrates what is known and unknown about the fate and transport of 6PPD and 6PPD-q. The chart shows three potential pathways that these contaminants might travel through the MS4 starting with the source and ending with discharges via infiltration or to surface waters. The symbols on the chart represent the following items:

- Source (oval): Roadway runoff is the only source considered in this report
- Pathway (rectangles): The contaminants are carried by three common stormwater pathways: soil/biofiltration BMPs, roads and hard surfaces, and stormwater conveyance such as pipes and ditches.
- Unanswered questions (diamonds): are inserted in the flow chart in the appropriate spots.
- The "known" properties of 6PPD and 6PPD-q from studies and models (polygons): The properties identified by models are identified with an asterisk.

3.4.3 Assessing Available 6PPD and 6PPDq Information with Existing Triggers for Runoff Treatment

What is known about 6PPD and 6PPDq sources and its anticipated fate and unmitigated transport through the MS4 system were reviewed for comparability with the triggers for identifying when and where runoff treatment is needed based on guidance in the Ecology and WSDOT stormwater manuals. The goal was to assess potentials triggers for providing 6PPD and 6PPD-q treatment and consider how that information aligns with the current triggers for providing treatment in the stormwater manuals. Figure 3.2 shows the runoff treatment targets and applications for roadway projects from the WSDOT Highway Runoff Manual (WSDOT, 2019). The requirements shown in this table are the same as the requirements in the Ecology Stormwater manuals; however, the Ecology Stormwater manuals have additional requirements for Enhance Treatment[3].

The literature suggests that highly urbanized areas are the most likely areas to generate TWP and thus 6PPD and 6PPD-q toxic concentrations; however, it is unknown what land uses and level of Average Daily Traffic (ADT) it takes to reach that concentration. Both Enhanced Treatment and Oil Control Treatment requirements shown in Figure 3.2 depend on ADT, vehicle size, and traffic patterns. It is assumed that similar parameters could be used to determine when treatment BMPs for 6PPD and 6PPD-q would be required. For instance, low speed turning movements, like those in parking lots, likely produce more TWP residue than higher speed movements around curves. Similarly, intersections controlled by stop lights might have more TWP residue than similar intersections where the main route is free moving and the side routes are controlled by stop signs. The roadway speeds and ADT likely play a role at intersections as well. A roadway with a high ADT likely has higher concentrations of TWP, 6PPD, and 6PPD-q than roads with lower ADTs. Further, research and monitoring are needed to determine which land uses and ADT levels cause 6PPD and 6PPD-q levels to reach levels of concern in roadway runoff.

3.4.4 Prioritize Treatment

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[3] The SWMMWW and Municipal Permit also include the following sites as requiring Enhanced Treatment.
a. discharge directly to fresh waters designated for aquatic life use or that have an existing aquatic life use; or
b. discharge to conveyance systems that are tributary to fresh waters designated for aquatic life use or that have an existing aquatic life use; or
c. infiltrate stormwater within ¼ mile of a fresh water designated for aquatic life use or that has an existing aquatic life use.

Based on what we know about roadways and TWP production and concentrations, consideration for prioritizing placement of treatment BMPs is shown in Figure 3.3 which illustrates several pathways to receiving waters. Based on what is known about 6PPD and 6PPD-q and stormwater management, BMPs should be located as close to sources as possible. Given the unknowns related to dry periods, and possible atmospheric transport and deposition during those periods, fate and transport of those particles further from their source may call for other locations of BMPs.

3.5 Recommendations for Next Steps and/or Additional Research

The recommendations for next steps and additional research are as follows.

- *Study the chemical properties of 6PPD-q to better determine half-life in different sectors of the environment (soil, water, sediments) and the toxicity/bioavailability in those forms*. Fate of these chemicals in the environment will highlight where to focus our efforts to reduce their impacts on salmon and potentially other aquatic life.
- *Study the location and concentration of TWP in the environment* (e.g., roadway surfaces, gutters, roadsides, snow or ice piles from winter plowing operations, catch basin and pipe sediments) to determine which operation and maintenance activities or changes will most effectively reduce loading.
- *Study the relationship of time or seasons on 6PPD and 6PPD-q concentrations in wet weather events to better characterize these discharges*. This could lead to BMPs that target the part of the storm that has the highest concentrations of these chemicals.
- *Study the location and loading of 6PPD and 6PPD-q to determine what land uses*, e.g., ADT, industrial or commercial, residential density, etc, *will trigger the need for treatment BMPs*.
- *It is anticipated that other product sources beyond tires will be discovered*. Other sources such as runoff from athletic fields with artificial turf, junk yards, and auto repair shops and tire stores should be investigated to see if they are sources for 6PPD and 6PPD-q.

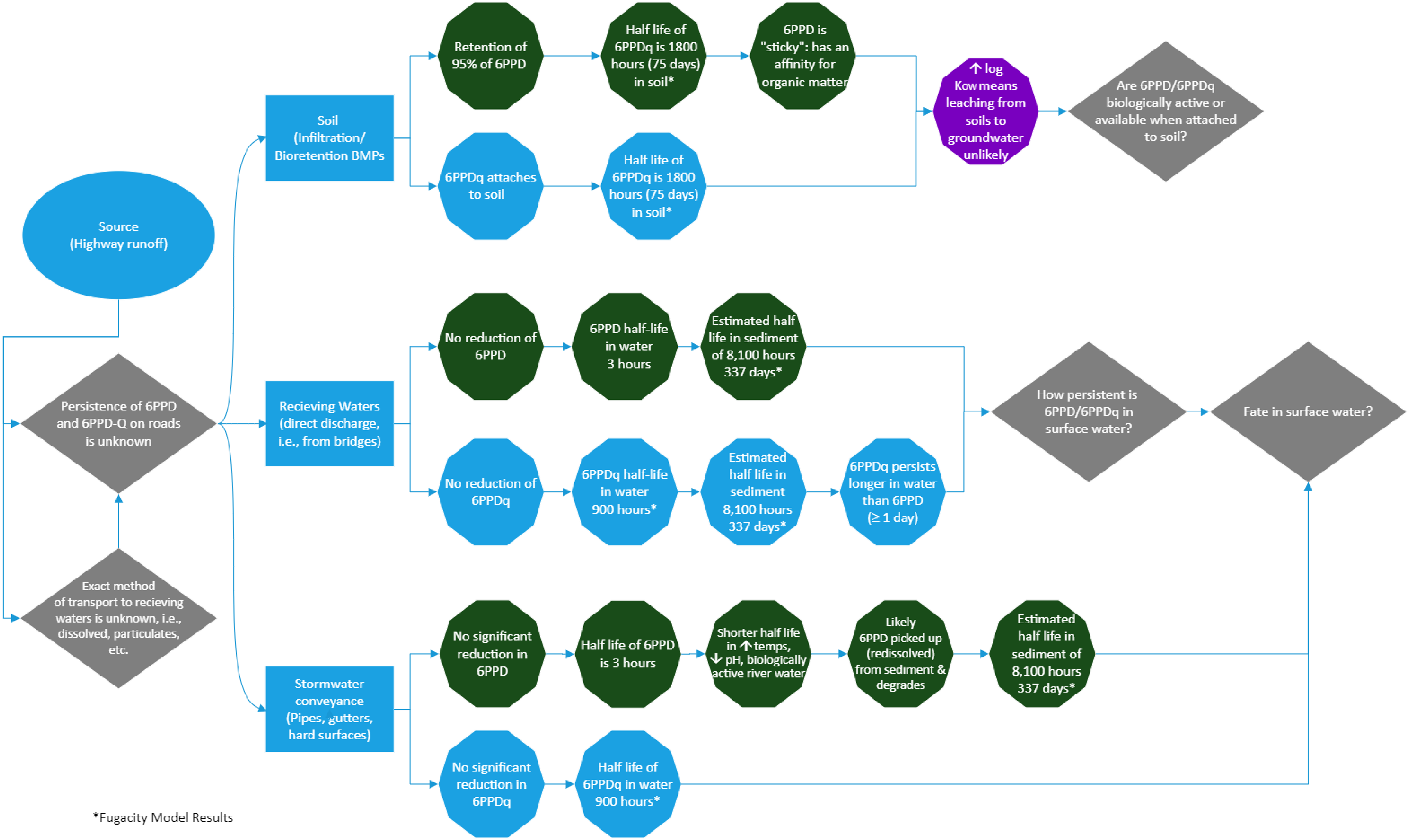


Figure 3.1. **Visualization about what is known and unknown regarding the fate and transport of 6PPD and 6PPD-q**

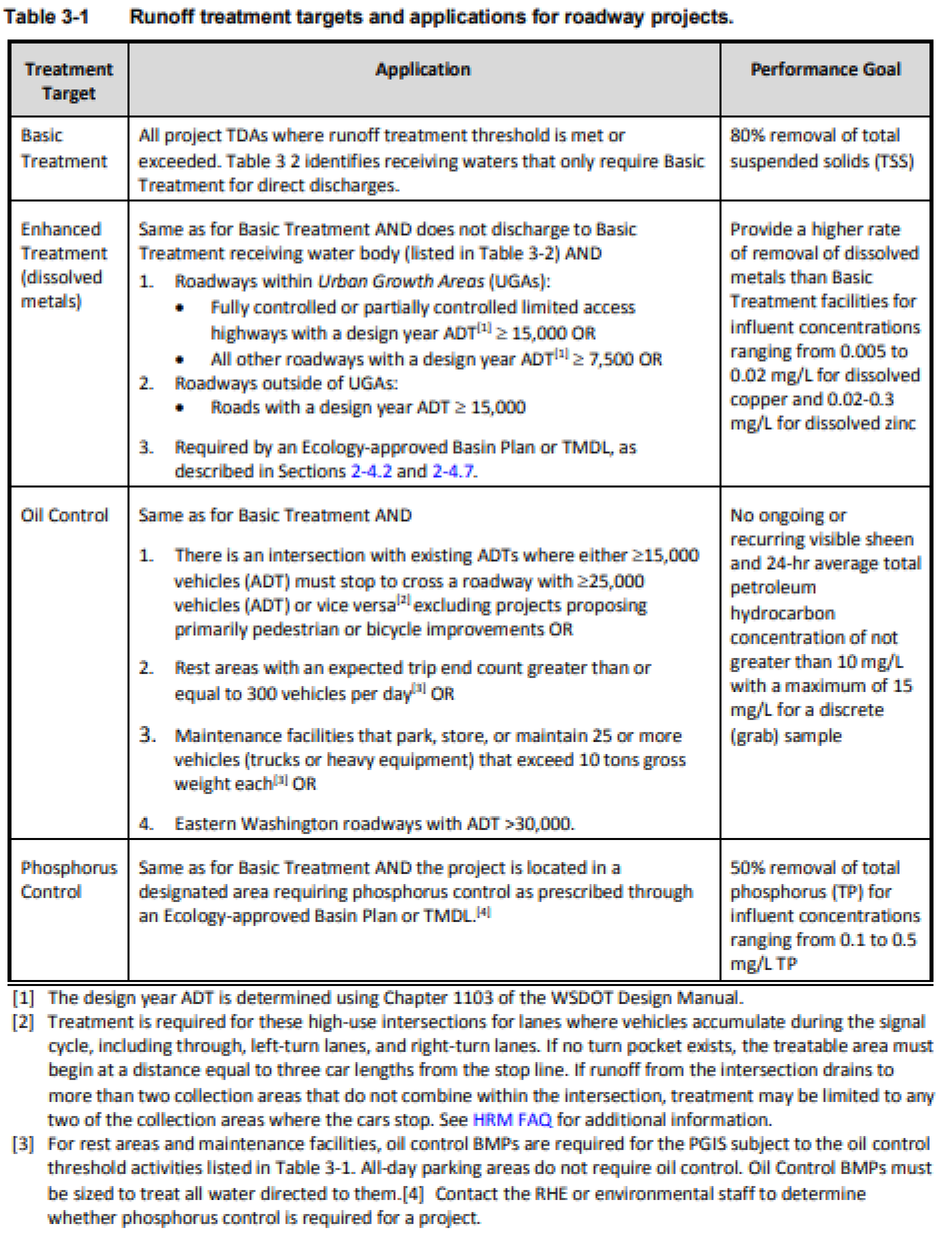


Table 3-1 Runoff treatment targets and applications for roadway projects.

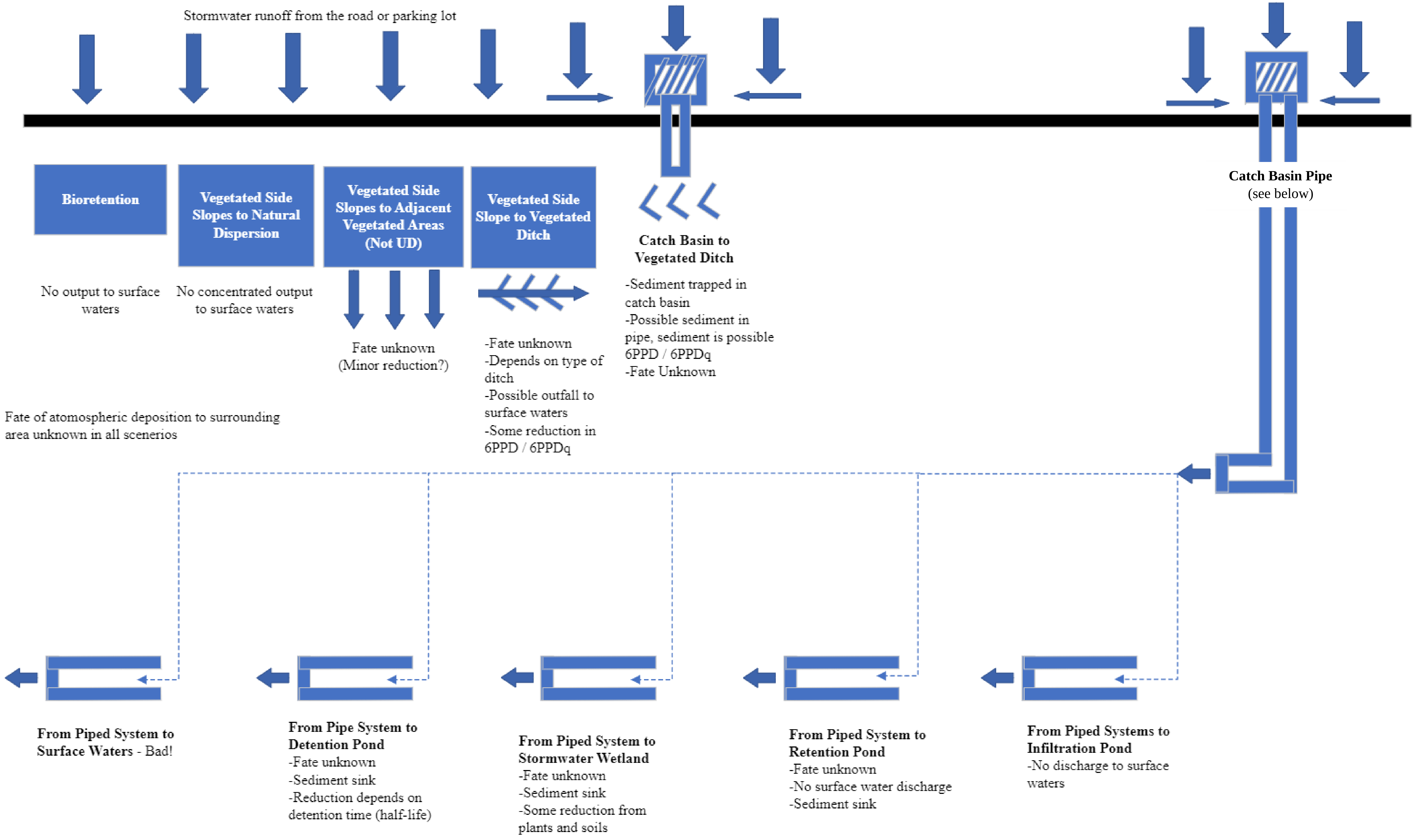
Treatment Target	Application	Performance Goal
Basic Treatment	All project TDAs where runoff treatment threshold is met or exceeded. Table 3 2 identifies receiving waters that only require Basic Treatment for direct discharges.	80% removal of total suspended solids (TSS)
Enhanced Treatment (dissolved metals)	Same as for Basic Treatment AND does not discharge to Basic Treatment receiving water body (listed in Table 3-2) AND 1. Roadways within *Urban Growth Areas* (UGAs): • Fully controlled or partially controlled limited access highways with a design year ADT[1] ≥ 15,000 OR • All other roadways with a design year ADT[1] ≥ 7,500 OR 2. Roadways outside of UGAs: • Roads with a design year ADT ≥ 15,000 3. Required by an Ecology-approved Basin Plan or TMDL, as described in Sections 2-4.2 and 2-4.7.	Provide a higher rate of removal of dissolved metals than Basic Treatment facilities for influent concentrations ranging from 0.005 to 0.02 mg/L for dissolved copper and 0.02-0.3 mg/L for dissolved zinc
Oil Control	Same as for Basic Treatment AND 1. There is an intersection with existing ADTs where either ≥15,000 vehicles (ADT) must stop to cross a roadway with ≥25,000 vehicles (ADT) or vice versa[2] excluding projects proposing primarily pedestrian or bicycle improvements OR 2. Rest areas with an expected trip end count greater than or equal to 300 vehicles per day[3] OR 3. Maintenance facilities that park, store, or maintain 25 or more vehicles (trucks or heavy equipment) that exceed 10 tons gross weight each[3] OR 4. Eastern Washington roadways with ADT >30,000.	No ongoing or recurring visible sheen and 24-hr average total petroleum hydrocarbon concentration of not greater than 10 mg/L with a maximum of 15 mg/L for a discrete (grab) sample
Phosphorus Control	Same as for Basic Treatment AND the project is located in a designated area requiring phosphorus control as prescribed through an Ecology-approved Basin Plan or TMDL.[4]	50% removal of total phosphorus (TP) for influent concentrations ranging from 0.1 to 0.5 mg/L TP

[1] The design year ADT is determined using Chapter 1103 of the WSDOT Design Manual.

[2] Treatment is required for these high-use intersections for lanes where vehicles accumulate during the signal cycle, including through, left-turn lanes, and right-turn lanes. If no turn pocket exists, the treatable area must begin at a distance equal to three car lengths from the stop line. If runoff from the intersection drains to more than two collection areas that do not combine within the intersection, treatment may be limited to any two of the collection areas where the cars stop. See HRM FAQ for additional information.

[3] For rest areas and maintenance facilities, oil control BMPs are required for the PGIS subject to the oil control threshold activities listed in Table 3-1. All-day parking areas do not require oil control. Oil Control BMPs must be sized to treat all water directed to them.[4] Contact the RHE or environmental staff to determine whether phosphorus control is required for a project.

Figure 3.2. Runoff Treatment Targets, Source: WSDOT 2019 Highway Runoff Manual



No output to surface waters

No concentrated output to surface waters

Fate unknown
(Minor reduction?)

-Fate unknown
-Depends on type of ditch
-Possible outfall to surface waters
-Some reduction in 6PPD / 6PPDq

-Sediment trapped in catch basin
-Possible sediment in pipe, sediment is possible 6PPD / 6PPDq
-Fate Unknown

Fate of atomospheric deposition to surrounding area unknown in all scenerios

From Piped System to Surface Waters - Bad!

From Pipe System to Detention Pond
-Fate unknown
-Sediment sink
-Reduction depends on detention time (half-life)

From Piped System to Stormwater Wetland
-Fate unknown
-Sediment sink
-Some reduction from plants and soils

From Piped System to Retention Pond
-Fate unknown
-No surface water discharge
-Sediment sink

From Piped Systems to Infiltration Pond
-No discharge to surface waters

Figure 3.3. Fate and Transport of 6PPD through MS4

Appendix 3-1

Table A3.1 Summary of Fate and Un-Mitigated Transport Key Information

Reference	City/Locale	Type of Sites Sampled (Stormwater Outfalls, Streams, etc.)	Timing of Samples (Seasons, Months)	Tire Wear Chemicals Measured (6PPD-q, others if appropriate)	Range of Concentrations Reported for Each Chemical	Notes
(Johannessen, Helm, & Metcalfe, 2021)	Greater Toronto Area in Ontario, Canada	samples were collected from two rivers adjacent to high traffic highways.	October 2019 - March 2020 (Fall and Winter)	HMMM	0.4 ug/L - 2.08 ug/L	Raw data were not presented in this study, however separate data tables were reference. The max concentration value was specifically mentioned in text, but the min value in this table was estimated from a bar graph presented in the paper. Samples were collected hourly in 300-mL aliquots over a 42-h period, with three aliquots included in each bottle, representing a 3-h composite sample.
(Peter, et al., 2020)	Puget Sound, Washington, USA	Miller Creek, a representative small, urban watershed in the Puget Sound region.	07/26/2018 - 12/12/2018 (Summer/Fall/Winter)	HMMM	0.005 Mass Load (g/day at baseflow) - 0.160 Mass Load (g/day at baseflow)	To assess water quality during summer/early fall baseflow conditions, on July 26, August 15, and September 18, 2018, 12 h time-weighted composite samples were collected via ISCO sampler. Further compositing enabled replicate extractions. Storm hydrograph sampling used composite and grab samples before, during, and after (~48 h/ event) storm events on October 26, November 2, and December 11, 2018. Complementary grab samples during November and December provided coverage during composite sampling gaps due to equipment malfunctions. Grab samples were collected in October because high flows washed away the ISCO sampler.
(Johannessen C. P., Helm, Lashuk, Yargeau, & Metcalfe, 2021)	Greater Toronto Area, Canada	Both sites are within land-use areas with a high degree of urbanization (≥85%) and both rivers discharge into the nearshore zone of western Lake Ontario	July and August 2020 and August 2021	DPG	Mean Values = 0.76 +/- 0.05 ug/L (grab sample, Highland Creek, July 2020) and 0.16 +/- 0.03 ug/L (composite sample, August 2020)	Investigated contaminant contributions of both highways and WWTPs (Don River only during dry period to ensure no interference from highway runoff)
(Johannessen C. P., Helm, Lashuk, Yargeau, & Metcalfe, 2021)	Greater Toronto Area, Canada	Both sites are within land-use areas with a high degree of urbanization (≥85%) and both rivers discharge into the nearshore zone of western Lake Ontario	July and August 2020 and August 2021	HMMM	Mean Values = 10 ug/L (includes HMMM and its TPs and a precursor compound, Highland Creek and Don River, July 2020, grab sample), 2.3 ug/L (Highland Creek, grab sample, one significant pulse), 6.8 ug/L (Don River, composite sample, July 2020), and 18 ug/L (Highland Creek, composite sample, July 2020)	Investigated contaminant contributions of both highways and WWTPs (Don River only during dry period to ensure no interference from highway runoff)
(Johannessen C. P., Helm, Lashuk, Yargeau, & Metcalfe, 2021)	Greater Toronto Area, Canada	Both sites are within land-use areas with a high degree of urbanization (≥85%) and both rivers discharge into the nearshore zone of western Lake Ontario	July and August 2020 and August 2021	6PPD-q	Mean Value = 0.72 +/- 0.26 ug/L (grab sample, Highland Creek, July 2020), 0.54 +/- 0.04 ug/L (grab sample, Don River, July 2020), and 0.21 +/- 0.02 ug/L (composite sample, August 2020)	Investigated contaminant contributions of both highways and WWTPs (Don River only during dry period to ensure no interference from highway runoff)
(Department of Toxic Substance Control, Safer Consumer Products, & California EPA, 2021)	California, USA	NA	NA	6PPD	< 23 ng/g - 1.9 ug/g in road dust and up to a max of 0.11 ug/L in stormwater	This was a draft chemical profile for the California Department of Toxic Substances Control to consider identifying the product chemical 6PPD as a Priority Product. It summarizes available literature and discusses the applicability to the state of California. Report includes a detailed summary of a 2011 Swedish Summary applicable to fate and transport.

Reference	City/Locale	Type of Sites Sampled (Stormwater Outfalls, Streams, etc.)	Timing of Samples (Seasons, Months)	Tire Wear Chemicals Measured (6PPD-q, others if appropriate)	Range of Concentrations Reported for Each Chemical	Notes
(Department of Toxic Substance Control, Safer Consumer Products, & California EPA, 2021)	California, USA	NA	NA	6PPD-q	1 ug/L - 6.1 ug/L in stormwater runoff and surface water	This was a draft chemical profile for the California Department of Toxic Substances Control to consider identifying the product chemical 6PPD as a Priority Product. It summarizes available literature and discusses the applicability to the state of California. Report includes a detailed summary of a 2011 Swedish Summary applicable to fate and transport.
(Challis, et al., 2021)	Saskatoon, Canada	South Saskatchewan River stormwater outfalls, snow dumps, and river water samples with different mixes of residential, industrial, and retail development	June, July, August (summer) 2019; June, August October 2020	6PPD-qu; DPG, DCA, DCU, CPU	6PPD-q: 0 - 1400 ng/L in stormwater samples; snowmelt concentration 2-8-fold greater	Concentration highest in association with the highest precipitation event which was preceded by a long dry period. DPG concentrations > DCU > CPU > 6PPD-Q > DCA
(Seiwert B. , Nihemaiti, Troussier, Weyrauch, & Thorsten, 2022)	Leipzig, Germany	Snow from urban streets and influent and effluent from a WWTP connected to a combined sewer system during snow melting event	February (winter)	6PPD ozonation products including the quinone	WWTP influent: 0.105±0.037 ug/L WWTP effluent: < 25 ng/L dry weather: < 25 ng/L	Snow samples used to identify different degradation products of 6PPD and 6PPD-q; many degradation products identified; half-life of 6PPD-q in drinking water reported to be 33h at room temp (Hiki et al 2021); 6PPD-q subject to additional degradation in the presence of oxidants
(Rauert, et al., 2022)	Brisbane Australia	stormwater near Freeway and other roads	June and October	6-PPD-Q, HMMM, DPG, several benzothiazoles, benzotriazoles, aromatic amines	6-PPD-Q: 0.39 - 88 ng/L	higher concentrations of all TWP chemicals in October sampling; DPG highest6 in concentration> HMMM > 2-OHBT > CPU > DCU More frequent and larger precipitation events in October; concentrations peaked at the beginning or during the storm event but remained elevated at the end of the storm compared to baseflow concentrations. Settled TWPs may be a continuing source of chemicals into the urban creek post storm
(Johannessen & Parnis, 2021)	Greater Toronto Area, Canada	A highly urbanized watershed in close proximity to several major multi-lane highways	NA	6PPD-q	0.30 ± 0.01 ug/L - 2.30 ± 0.05 ug/L	Target compounds were analyzed using ultra-high pressure liquid chromatography with high resolution mass spectrometric detection with parallel reaction monitoring.
(Johannessen & Parnis, 2021)	Greater Toronto Area, Canada	A highly urbanized watershed in close proximity to several major multi-lane highways	NA	DPG	Max = 0.22 ± 0.07 ug/L	Target compounds were analyzed using ultra-high pressure liquid chromatography with high resolution mass spectrometric detection with parallel reaction monitoring.
(Wagner, et al., 2018)	NA	NA	NA	TWP	400-2200 mg/g in river sediments, acute effects of 25 - 100000 mgP/L, chronic effects of 10 - 3600 mg TWP/L, and sublethal effects of 500 - 500000 mg TWP/L	This is a review paper; thus, no actual data were collected and no samples were taken.

CHAPTER 4: BMP EVALUATION PROCESS

4.1 Chapter Purpose

The intent of this chapter is to characterize the likely efficacy of existing BMPs to reduce concentrations of 6PPD and 6PPD-q in stormwater runoff. Gaps in available information from Chapters 2 and 3 are described along with how the gaps influenced the BMP evaluation process. The chapter concludes with recommendations for additional research specific to gaps in understanding the efficacy of BMPs and prioritization of where to locate BMPs.

4.2 Overview of Chapter Contents and Work Complete

An evaluation process was developed to rank flow, treatment, and source control BMPs in terms of their potential ability to reduce 6PPD and 6PPD-q. The evaluation process is a qualitative system that uses defined high, medium, and low categories to rate the BMPs treatment potential. For each category, an evaluation criterion was defined using information collected from literature regarding the physicochemical properties of the contaminants and results from lab or field testing of BMPs (Chapter 2). The evaluation criterion focuses on the capture or treatment processes that would likely reduce (flow and treatment BMPs) or prevent (source control) 6PPD and 6PPD-q from entering stormwater. As part of the category definition, assumptions and unknown information were also identified.

The evaluation process focuses on the full range of particle sizes in which 6PPD and 6PPD-q may be present in the built environment from full tires to TWP down to 10µm as discussed in Chapter 3. For all sizes of TWP, 6PPD is expected to bloom to the surface until there is no more 6PPD remaining in the rubber matrix. As such, the BMP evaluation process was developed to consider the differences in particle sizes received or encountered by source control BMPs and flow and treatment BMPs. For example, smaller particle sizes (less than 500 µm[4]; medium sand size and smaller) include suspended (<25 µm) and settleable solids (>25 µm), which can be transported by most storm events and most likely to reach stormwater infrastructure and receiving waters or flow and treatment BMPs. Particles between 500µm to 4750µm (coarse sand to fine pebbles) typically settle in catch basins, pretreatment BMPs, or may be too dense to be transported by smaller storm events. Particles larger than 4750 µm (medium pebbles to cobbles, floatables, debris, larger TWP) may remain on or along the roadway surfaces, move down embankments, or if they are transported with stormwater, can clog storm drain inlets, build up in storm infrastructure, or over time can reduce the infiltration capacity of flow and treatment BMPs (by clogging the surface layer). Large material is not typically transported by stormwater except for infrequent, larger storm events. Preventing the pebble or cobble sized particles (4750µm or larger) from entering MS4 infrastructure may be addressed more effectively by source control BMPs. Figure 4.1 illustrates the different particle sizes present on roadways.

An inventory of BMPs was compiled which included flow, treatment, and source control BMPs identified from the Table 4.1 stormwater design manuals as well as BMPs approved through the TAPE program. Each BMP was assigned a potential treatment category that indicates whether the BMP appears to have a high, medium, or low potential to reduce 6PPD or 6PPD-q. The following sections describe the basis for the evaluation criteria and the findings of the evaluation process.

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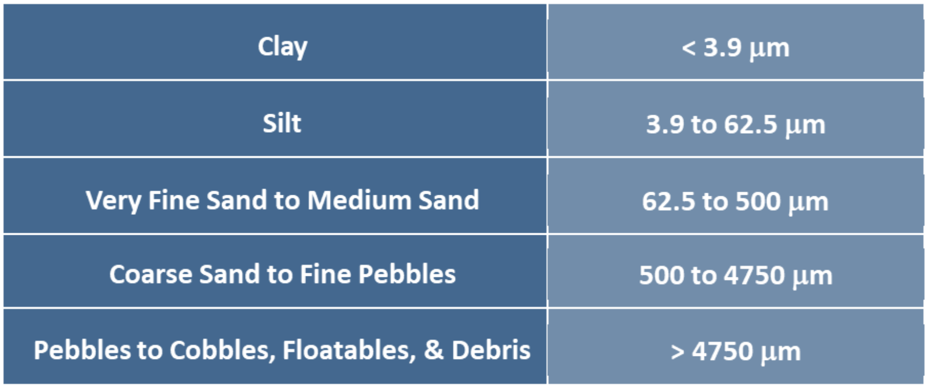
[4] 500 µm is considered the largest size for TSS as part of the TAPE Program (Washington State Department of Ecology, September 2018).



Clay	< 3.9 µm
Silt	3.9 to 62.5 µm
Very Fine Sand to Medium Sand	62.5 to 500 µm
Coarse Sand to Fine Pebbles	500 to 4750 µm
Pebbles to Cobbles, Floatables, & Debris	> 4750 µm

Figure 4.1 Common Stormwater Particle Sizes

Table 4.1 Stormwater Design Manuals Reviewed

Jurisdiction	Year	Title
Caltrans	2019	Stormwater Quality Handbook: Project Planning and Design Guide
District of Columbia	2020	Stormwater Management Guidebook
State of Minnesota	2021	Minnesota Stormwater Manual
New York City	2015	New York City Stormwater Manual
Prince George's County, Maryland	2014	Stormwater Management Design Manual
State of Washington	2019	Stormwater Management Manual for Western Washington (SWMMWW)
State of Washington	2019	Washington State Department of Transportation (WSDOT) Highway Runoff Manual (HRM)
State of Indiana	2007	Indiana Storm Water Quality Manual

4.3 Findings Summary

This section describes the development of the evaluation criteria and findings of the BMP evaluation. The BMP evaluation criteria for high, medium, and low treatment potential categories are summarized in Tables 4.2 for flow and treatment BMPs and Table 4.3 for source control BMPs. Development of the criteria along with the assumptions and unknowns are discussed further in Sections 4.3.1 and 4.3.2. Results of the BMP evaluation, which included BMPs from 8 stormwater design manuals, are included in Section 4.3.3. In the context of this work, flow, treatment, and source control BMPs are defined as follows.

- **Flow and Treatment BMPs** are defined as physical, structural, or mechanical devices intended to limit pollutants from entering stormwater infrastructure by providing water quality or hydrologic benefit, using specific treatment process (WSDOT, 2019; Ecology, 2019). This includes both permanent structural BMPs as well as temporary construction runoff BMPs that are intended to remove particles/solids and other pollutants from stormwater. Examples of permanent structural BMPs include bioretention cells, infiltration ponds, and proprietary treatment devices approved by TAPE. Examples of construction runoff BMPs are silt fences, temporary sedimentation basins, and straw wattles. Construction BMPs are not anticipated to achieve the treatment performance goals of permanent structural BMPs; however, they are designed to reduce TSS and as a result were included with permanent flow and treatment BMPs.

- **Source Control BMPs** are practices meant to prevent the interaction of stormwater with pollutants through physical separation or management of activities that are sources of pollutants (WSDOT, 2019; Ecology, 2019). Examples of source control BMPs include education and outreach programs, operation and maintenance activities such as street sweeping or line cleaning, as well as construction source control BMPs, such as temporary stabilization or proper materials handling.

The number of unknowns and assumptions discussed in Chapters 2 and 3 as well as in this chapter resulted in an evaluation criterion that is similar between 6PPD and 6PPD-q whether bound or unbound to a particle. The only physicochemical property information available for both contaminants was log K_{ow} and K_{oc} data. While other physicochemical properties are available for 6PPD and 6PPD-q that are relevant to this work, no other properties were defined in the literature for both contaminants. To compensate for the missing information, it was assumed that the properties of the other contaminant were the same "ballpark" in order to develop the evaluation criteria. These unknowns and assumptions are described in Section 4.4.

Table 4.2 Flow and Treatment BMP Evaluation Criteria for 6PPD and 6PPD-q

Treatment Potential Category	BMP Evaluation Criteria Definition of Category
High	Dispersion, Infiltration, or some Biofiltration BMPs (that use bioretention soil media or compost) where the underlying soils meet the soil suitability criteria[5], or BMPs that provide the treatment process sorption.
Medium	BMPs that provide sedimentation (removal depending on size/detention time) or filtration (removal depending on size of particles). May need a polishing layer/treatment train including sorption, i.e., sand filter with zero valent iron in layers.
Low	BMP does not provide infiltration, sorption, filtration, or sedimentation.

Table 4.3 Source Control BMP Evaluation Criteria for 6PPD and 6PPD-q

Prevention Potential Category	Definition of Category
High	BMP separates a source (i.e., roadway, parking, etc.) from stormwater.
Medium	BMP partially separates 6PPD and 6PPD-q from stormwater (i.e., E&O efforts); prevents 6PPD and 6PPD-q from entering stormwater from a minor source (i.e., traffic at a construction site)
Low	Unlikely to provide any measurable separation between 6PPD and stormwater.

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[5] The site suitability criteria (SSC) are set of requirements used to assess whether an infiltration BMP can be located at a site. SSC-6 identifies the physical and chemical properties needed in the native soils underlying a BMP to achieve treatment goals: cation exchange capacity ≥ 5 meq/100g dry soil, minimum 18-inch soil depth, 1% organic content, and the soil must not contain waste fill materials.

4.3.1 Flow and Treatment BMPs Categories

Flow and treatment BMPs were described by the primary treatment processes provided by BMP. These processes were identified based primarily on the physicochemical properties of 6PPD and 6PPD-q identified in Chapter 2. In addition, there are only two BMP studies that evaluated 6PPD and 6PPD-q removal and both were conducted in a lab as opposed to field testing (McIntyre, et al., 2015; McIntyre & Kolodjiez, 2021). Using treatment processes allowed for a high-level, direct comparison between BMPs. Since BMPs are included in this evaluation from outside of Washington, BMPs were grouped together by the same treatment processes, not necessarily by their names or design standard. The basis for each category is described in this section. A list of the BMPs evaluated along with the anticipated treatment processes and results of the evaluation are included in Appendix 4-1.

High Treatment Potential

BMPs and BMP processes identified with the highest potential to reduce 6PPD and 6PPD-q are infiltration, dispersion, and some biofiltration BMPs combined with sorption (particularly BMPs that contain bioretention soil media or compost). Reasons for selecting these BMPs and BMP process are as follows:

- Infiltration BMPs and Biofiltration BMPs that infiltrate reduce the volume of runoff and thereby the contaminant load carried to surface water. For both types of BMPs to be classified in the high category, the soil suitability criteria for physical and chemical properties (SSC-6) previously described, must be met.
- Research by McIntyre showed that stormwater passing through the Ecology 60:40 bioretention soil mix prevented pre-spawn mortality in coho salmon that was observed when coho salmon were exposed to untreated stormwater (McIntyre, et al., 2015).
- Initial lab testing conducted by McIntyre and Kolodjiez, indicates that bioretention media appears to remove 6PPD-q to below detection levels (McIntyre & Kolodjiez, 2021).
- Research conducted on Compost-Amended Biofiltration Swales (CABS) in the lab and at a field site off State Route 518 indicates that the BMP has a non-polar compound removal rate above 90% (Tian, et al., 2019). As 6PPD and 6PPD-q are moderately non-polar compounds (Chapter 2), similar removal rates are possible for the contaminants by CABS.
- The log K_{ow} and K_{oc} identified in the literature (Chapter 2) suggest that 6PPD and 6PPD-q tend to adhere to organic particles or organic matter. Because infiltration and bioretention BMPs are designed for stormwater to flow through soil or media, the contaminants are expected to remain fixed in the soil or media as stormwater infiltrates.

Assumptions and unknowns regarding the high potential category relating to the physicochemical properties of 6PPD and 6PPD-q (also discussed in Chapter 2) are as follows:

- No field testing has been performed to confirm that the contaminants will remain adhered when water from later storms flows through soil or organic matter.
- Removal of 6PPD and 6PPD-q by bioretention and infiltration BMPs were assumed to be the same, as the log K_{ow} and K_{oc} are similar for both contaminants and lab testing results were not available for removal of 6PPD and 6PPD-q by infiltration BMPs.

Assumptions and unknowns regarding the high potential category relating to the BMPs which provide the treatment process sorption to reduce 6PPD and 6PPD-q are as follows.

- The previously mentioned research on the effectiveness of bioretention indicates that sorption may be an effective removal method.
- There are contradictory findings regarding the type of sorption responsible for removal. The City of Tacoma was preparing samples for analysis and observed that when a solution of copper was added to samples with sulfur and 6PPD-q, that 6PPD-q was reduced to below detection levels. The city hypothesized that sorption may be responsible for removal of 6PPD-q or that 6PPD-q may be changing form (Bozlee, 2022). Whereas Tian et al. (2020) conducted column testing using a myriad of materials and chemicals that provide different treatment processes (i.e., filtration, cation/anion exchange, etc.) to remove 6PPD and 6PPD-q and no significant removal was measured. The results suggest that both contaminants were in a dissolved form and that neither cation nor anion exchange (forms of sorption) were responsible for removal.

Assumptions regarding the BMP design for high potential category involve whether particles can be suspended during a storm event, and whether the BMP is able to filter the size of particles necessary to remove 6PPD and 6PPD-q when adhered to soil or organic matter or contained in TWP. Specifically:

- In Ecology's Stormwater Management Manuals (SWMM), BMP design guidance has been developed to limit re-suspension of particles and anoxic zones in BMPs during storm events (Howie, 2022). The assumption made for the BMP evaluation was that manuals developed by other organizations developed BMPs in their manuals similarly, and that particles already in the BMP would not be re-suspended and discharge from the BMP.
- Because of the contaminants affinity for soil and organic matter as well as the assumption that particles would not resuspend, it was assumed that dispersion, Infiltration, or biofiltration BMPs where the underlying soils meet soil suitability criteria (SSC6), or BMPs that provide the treatment process sorption would contain 6PPD and 6PPD-q for the duration of their half-lives. However, sedimentation or filtration BMPs are not designed to have a residence time equal or greater than the contaminants half-life and are not expected to provide sufficient time for the contaminant in the dissolved phase to decay. The half-life data identified in Chapter 2 was primarily from Fugacity Model Results which estimates the half-life in water to be 3 hours for 6PPD and 900 hours for 6PPD-q. The half-life for 6PPD and 6PPD-q in soils and sediment (soils in water) was estimated to at 75 days and 337 days respectively. Except for 6PPD in water, there are no BMPs which have a residence time equivalent to the half-life of 6PPD and 6PPD-q. Developing a better understanding of the half-lives are a research gap that is identified in each chapter.
- It was also assumed that infiltration captures the most tire particle sizes (that could fit through the typical catch basin grate) in the upper inches of the soil surface, and that unbound 6PPD and 6PPD-q are immediately sorbed onto nearby soil particles. It is assumed that a given tire will in the end eventually deliver the same amount of 6PPD, but that availability of 6PPD-q to be washed off is higher for smaller particle sizes if they haven't already lost their 6PPD load from the tire matrix.
- At the time this report was written, it was assumed that infiltration, dispersion, and some biofiltration BMPs could remove particles from stormwater (<500um) including those with bound 6PPD and 6PPD-q. These assumptions also applied to BMPs with a medium potential to reduce the contaminants, as is described in the following paragraph.

Medium Potential

The BMPs identified with a medium potential to reduce 6PPD and 6PPD-q include BMPs which provide sedimentation and filtration treatment processes. Both processes provide treatment by capturing particles and for this assessment capturing particles refers to both TWP as well as other solids in stormwater runoff that may have bound 6PPD or 6PPD-q. With sedimentation, solids are removed from stormwater by settling whereas filtration removes solids by physically trapping or capturing them. For both treatment processes the particle size and density can affect removal with heavier and larger particles being more likely to be removed. Tire particles larger than fine silt (25 to 62.5 μm) are expected to be removed through sedimentation and filtration (up to 500 μm or medium sand size). Smaller tire wear or other stormwater solid particles (fine silts and clays) are not expected to be captured through filtration and sedimentation. However, these contaminants have a tendency to sorb to soil or organic matter which will increase the particle size and density. As such it was assumed that a portion of the smaller particles will be removed. For these BMPs, a polishing layer may be needed to fully remove 6PPD and 6PPD-q, as some 6PPD or 6PPD-q may exist in the dissolved fraction (McIntyre & Kolodjiez, 2021).

Low Potential

Any BMP processes (infiltration, sorption, or settling/sedimentation) which did not fall under the criteria defined for high or medium potential to reduce 6PPD or 6PPD-q were defined as BMPs or processes with a low potential to reduce these contaminants. BMPs that fall under this category may also include BMPs which cannot be located near a roadway or other source of 6PPD or 6PPD-q. No information was found during the review of sources on physiochemical properties indicating other stormwater treatment processes could reduce the contaminants.

Flow and Treatment BMP Examples

Examples of BMPs in the high, medium, and low treatment potential categories are summarized in Table 4.4 followed by an illustration of the BMP evaluation process in Figure 4.2. Proprietary and non-proprietary BMPs approved through the TAPE process also fall into these categories. BMPs approved by TAPE which function similar to infiltration or dispersion BMPs or biofiltration BMPs (that use bioretention soil media or compost) that infiltrate into underlying soils and meet SSC-6, as well as BMPs which provide sorption are expected to have a high treatment potential. TAPE BMPs which provide filtration or sedimentation without sorption are expected to provide a medium treatment potential. Information presented in the TAPE documents was used to determine which treatment mechanisms each of these BMP uses which are summarized in Appendix 4-1.

Table 4.4 Examples of Flow and Treatment BMPs by Treatment Potential Category

Treatment Potential Category	Examples of Flow and Treatment BMPs
High	Bioretention, Infiltration Basins, Media Filter Drain, Dispersion
Medium	Sand Filter, Detention Ponds, Permeable Pavements
Low	Perforated Stub-Out Connection, Vegetated Roofs, Tree Retention and Tree Planting

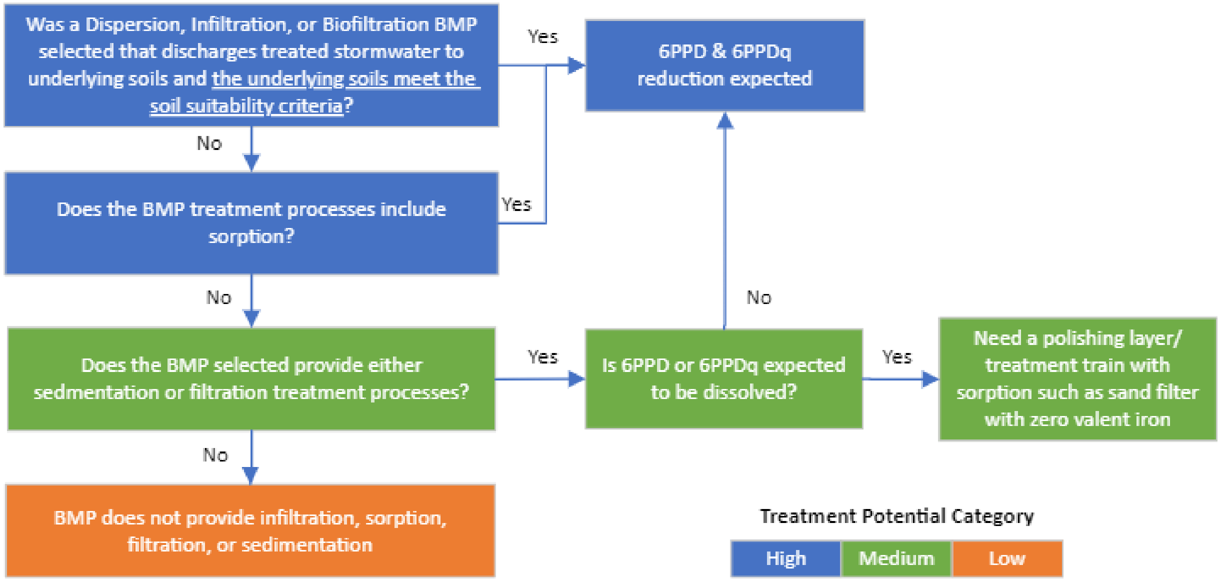

Figure 4.2 Flow and Treatment BMP Evaluation Process

4.3.2 Source Control BMP Categories

The criteria for source control BMPs was developed based upon preventing TWP from entering stormwater infrastructure or the physicochemical properties of 6PPD and 6PPD-q, particularly the tendency to adhere to soil particles or organic matter. No literature was identified which evaluated source control BMPs efficacy for preventing 6PPD or 6PPD-q from mixing with precipitation or stormwater. As a result, the evaluation criteria were assumed to be the same for 6PPD and 6PPD-q and do not incorporate basin-specific conditions. Typically, source control is basin-specific, meaning different results may be achieved depending on the number and type of roadways, land use, urban or rural, topographic, and other characteristics of the basin. Because no literature was identified which evaluated source control BMPs, the criteria was not able to incorporate basin-specific conditions.

Additionally, it is important to note that practices likely exist that are not currently listed as source control BMPs in stormwater design manuals which would prevent 6PPD and 6PPD-q from coming into contact with stormwater. For example, roadway clean-up crews which remove tires or strips of tire treads would remove a potential source of 6PPD and 6PPD-q from roadways. These practices may be performed by other departments (i.e., road maintenance) or organizations than an environmental or stormwater organization. The criteria developed for this report focuses on the BMPs that are included in stormwater design manuals. A list of the BMPs evaluated and results of the evaluation are included in Appendix 4-1.

High Potential

The source control BMPs identified as having the highest potential were BMPs which could prevent precipitation or runoff from contacting tires, tire particles, other 6PPD and 6PPD-q sources, or prevent these contaminants from entering stormwater infrastructure. Once drained from a road or parking lot the SWMMWW, SWMMEW, and WSDOT HRM list road, roadside ditch, and parking lot source control BMPs, which can involve removal of roadway sediment from roads or parking surfaces, as well as sediment transported to roadside ditches. Examples of these BMPs include street sweeping, cleaning roadside ditches, and cleaning catch basins and storm drainpipes (line cleaning). As mentioned previously in this chapter, 6PPD and 6PPD-q are likely to adhere to soil and organic matter as such, removal of these particles from roadways, parking surfaces, and roadside ditches is therefore anticipated to provide the best reduction. Assumptions in the high treatment potential category include that the BMPs can remove 6PPD and 6PPD-q particle sizes that are likely to be washed off roadways and enter stormwater infrastructure (see Section 4.3.1, Chapter 2).

Medium Potential

Source control BMPs with a medium potential to prevent 6PPD and 6PPD-q from mixing with stormwater runoff included BMPs which provide either partial separation of the contaminants from stormwater or separate a potential minor source of contamination to stormwater, like traffic at a construction site. Source control BMPs which provide a partial separation include education and outreach (E&O) programs. It was assumed for the criteria that a successful E&O program which informed the target audience about the impacts of 6PPD and 6PPD-q (and alternative products in the future) would provide some source control. Construction sites, particularly sites located on or adjacent to highways, were assumed to be a minor source that produce a lower loading of 6PPD and 6PPD-q than a roadway due to the lower number of vehicles at a construction site. As such, construction source control BMPs were assumed to only provide a medium treatment potential.

Low Potential

Source control BMPs with a low potential to prevent 6PPD and 6PPD-q from mixing with stormwater runoff included BMPs which were unlikely to provide a separation between the contaminant source and stormwater, as they are not typically located near a major or minor source of 6PPD or 6PPD-q or appropriate for providing separation of roadway particles. It is unknown if other major sources of 6PPD or 6PPD-q exist aside from the presence in tires or other car parts. As previously noted, this report has been developed focusing primarily on roadway sources.

Source Control BMP Examples

Examples of BMPs with categorized with a high, medium, or low prevention potential to separate stormwater runoff from the contaminants are included in Table 4.5.

Table 4.5 Examples of Source Control BMPs with Different Treatment Potential Categories

Prevention Potential Category	Examples of Source Control BMPs
High	BMPs for Streets and Highways, BMPs for Maintenance of Roadside Ditches
Medium	E&O Programs Related to 6PPD or 6PPD-q, Construction Wheel Wash
Low	BMPs for Temporary Fruit Storage, BMPs for Railroad Yards

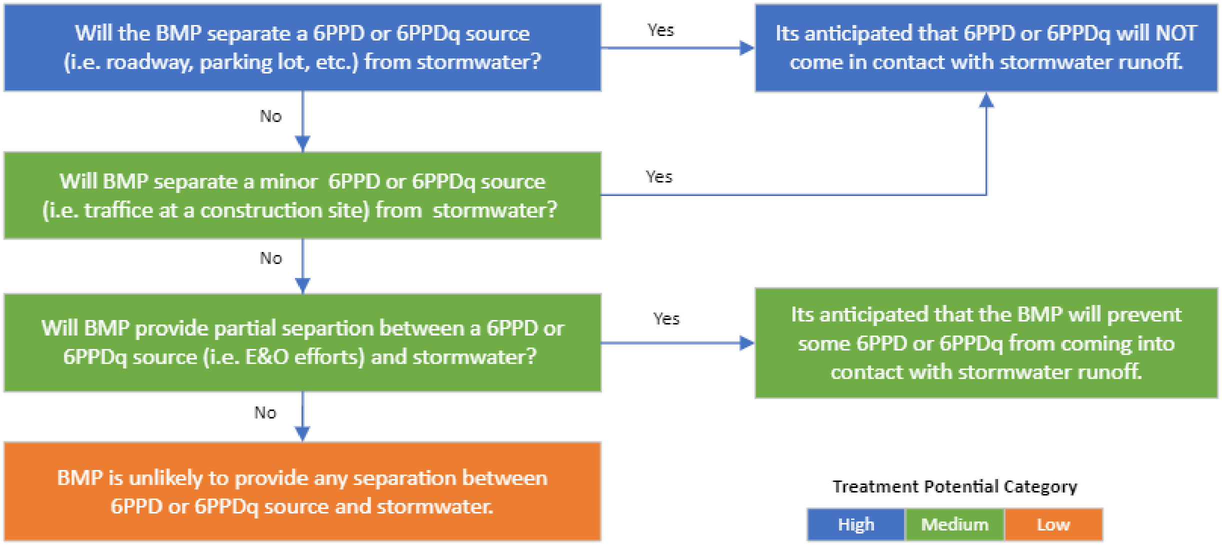

Figure 4.3 Source Control BMP Evaluation Criteria

4.3.3 Results of BMP Evaluation

The BMP evaluation criteria was applied to each flow and treatment BMP and source control BMP in the stormwater design manuals identified in Section 4.2. Table 4.6 summarizes the number of unique BMPs in each treatment and prevent potential category from the SWMMWW, the WSDOT HRM, and BMPs from other states if the BMP was not in the Washington stormwater manuals. All the BMPs identified along with the results from the evaluation are summarized in Appendix 4-1.

Table 4.6 All Unique BMPs (Includes SWMMWW & WSDOT HRM) by Potential Category

Treatment Potential	**Flow and Treatment BMPs**		**Source Control BMPs**	
	Number of BMPs for 6PPD	**Number of BMPs for 6PPD-q**	**Number of BMPs for 6PPD**	**Number of BMPs for 6PPD-q**
High	28	28	9	9
Medium	51	51	3	3
Low	14	14	72	72
Total	**93**	**93**	**84**	**84**

4.4 Research Gaps

During the development of the evaluation criteria, gaps in literature were identified, as such assumptions were made to develop the evaluation criteria (Tables 4.2 and 4.3). In addition, general gaps in understanding were identified (not part of the evaluation criteria) which could impact or prevent BMP treatment and the location of BMPs related to the actual loading of 6PPD and 6PPD-q from sources (i.e., roadway and parking lot surfaces). Specifically, loading can inform the life cycle of BMPs, meaning how long the BMP is expected to provide treatment before it needs to be replaced. Additionally, loading can be used to prioritize locations to install BMPs, as locations with higher loading would result in a higher water quality benefit if a BMP were installed downstream of the 6PPD and 6PPD-q source. Further, no relationship between land use, traffic count (ADT), or other indicators was identified in the literature, and no sampling data to characterize the loading from roadways to BMPs or other stormwater infrastructure was found. However, studies did show that other chemicals used in tires are present in higher concentrations in highly urbanized settings (Seiwert B. , Nihemaiti, Troussier, Weyrauch, & Thorsten, 2022; Hu X. , et al., 2022). Additional discussion about prioritizing BMPs locations is included in Section 3.4.

4.4.1 Flow and Treatment BMP Research Gaps

The following gaps were identified during development of the flow and treatment BMP evaluation criteria.

- *Whether and what type of sorption removes contaminants* – contradictory research exists about the efficiency of sorption to remove 6PPD or 6PPD-q (see discussion of High Treatment Potential in Section 4.3.1). More research is needed to understand which media and soil in existing BMPs can remove these contaminants using this treatment process and identify the process responsible for removal.
- *Whether 6PPD and 6PPD-q will remain adhered to soil* – the log K_{ow} and log K_{oc} for 6PPD and 6PPD-q suggest that the contaminants will adhere to soil or organic matter and not be exported to groundwater, however, no field research was found to confirm this. This research gap was also identified in Chapter 2 and is particularly important in knowing if toxicity reduction can be achieved simply by capturing suspended particles of tire wear and bound 6PPD and 6PPD-q.
- *Lethality of the different forms (dissolved, attached to particles, in soil, etc.) and particle sizes containing or adhered to 6PPD and 6PPD-q* – it was unknown what forms or particle sizes BMPs should target to reduce the toxicity of the effluent. Information on the toxicity of the different forms and particle sizes to reduce lethality of stormwater effluent is needed.
- *Residence Time* – The BMP residence time was discussed in the flow and treatment BMP evaluation criteria; specifically, BMPs are not designed to have a residence time equal or greater than the contaminants half-life and are not expected to provide sufficient time for the contaminant in the dissolved phase to decay. However, the majority of the 6PPD and 6PPD-q half-life data was determined from fugacity model results and more research is needed to understand the half-life in stormwater environments and how it will influence BMP treatment.
- *Design guidance to limit re-suspension of sediment in BMPs with permanent pools* – Wet pool BMPs in Ecology’s SWMMWW and SWMMEW are designed to limit re-suspension of particles and anoxic conditions. It is unknown whether BMPs were developed similarly for other States’ manuals.

4.4.2 Source Control BMP Research Gaps

The following gaps were identified during development of the source control BMP evaluation criteria.

- *Efficacy of source control BMPs* – no research was located on the effectiveness of source control BMPs for preventing 6PPD or 6PPD-q from mixing with stormwater or whether source control BMPs that focus on sediment removal could capture 6PPD and 6PPD-q (based on particle size).
- *Efficacy of E&O programs in reducing 6PPD or 6PPD-q in the environment* – no research on the effectiveness of E&O BMPs in reducing the presence of 6PPD or 6PPD-q in the environment or on roadways was identified.
- *Loading of 6PPD or 6PPD-q from construction site* – no data was identified which described the loading of 6PPD or 6PPD-q from a construction site. It was assumed that the loading of 6PPD or 6PPDq from construction site would be less than a highway, based on the number of vehicles using the site compared to a roadway.

4.5 Recommendations for Next Steps and/or Additional Research

Recommendations for next steps or additional research were identified from the research gaps listed in Section 4.4. The following bullets summarize the recommendations for additional research.

4.5.1 General Recommendations

- *Perform testing of roadway particles to characterize the most common sizes and toxicity of the different forms of 6PPD and 6PPD-q* – understanding the particle size distribution and toxicity of different forms of 6PPD and 6PPDq will help to understand loading from roadways/parking areas and prioritize where BMPs should be located.
- *Perform additional testing to determine if there is an ADT threshold where 6PPD and 6PPD-q concentrations are no longer present in lethal amounts* – understanding where the loading is problematic will allow prioritization to locate BMPs at sites with higher loading.
- *Perform testing to determine loading from construction sites* – an understanding of loading from construction sites (especially highway construction) will help to determine the priority of treating runoff from the sites as well as determine the most effective construction source control and flow and treatment BMPs.

4.5.2 Flow and Treatment BMP Recommendations

- *Perform additional testing to understand the efficacy of sorption* – additional testing is needed to understand whether this treatment process can be used in BMPs to remove 6PPD and 6PPD-q.
- *Perform leach testing of 6PPD and 6PPD-q adhered to soil* – the leach testing will help confirm whether the contaminants will remain adhered to soil and not be exported to groundwater if water flows across the soil and contaminants.
- *Perform field testing to determine what forms (dissolved, adhered to particles, in soil, etc.) and what particle sizes containing or attached to 6PPD and 6PPD-q need to be removed by BMPs to reduce lethality of stormwater effluent* – at the time of this report, no information was available regarding which forms or particle sizes containing or attached to 6PPD and 6PPD-q were toxic, which is needed to determine which forms or particle sizes BMPs should to remove to limit lethality. Additional literature review or lab or field testing may be needed to confirm whether the BMPs can remove these particle sizes.

4.5.3 Source Control BMP Recommendations

- *Perform testing to determine whether solid/TWP removal methods from roadways, parking, and stormwater infrastructure can remove 6PPD and 6PPD-q* – characterizing the solid sizes collected by removal methods may help to understand whether the source control BMPs for roadways, parking, and stormwater infrastructure can reduce 6PPD and 6PPD-q.
- *Conduct a study to assess the potential efficacy of E&O programs* – Conduct an assessment of 6PPD and 6PPD-q sources along with the respective behavior change needed to reduce concentrations of these contaminants and the potential impact of these programs will help determine if an E&O program could provide a measurable reduction of these contaminants. The assessment should also include recommendation for specific E&O campaigns that could be successful. Understanding the potential effectiveness of E&O programs in reducing 6PPD and 6PPD-q in the environment will help to inform the rating for these BMPs.

Appendix 4-1

BMP Name	Density Separation or Sedimentation	Filtration	Sorption	Microbial Activity	Uptake/ Storage	Chemical Treatment	Not Applicable (Source Control/ E&O)	BMP contains Bioretention Media (Compost)	Infiltration	Potential Treatment Rating of Flow and Treatment BMP	Potential Prevention Rating of Source Control BMP	Can the BMP be implemented near sources?
Site Design BMPs												
Preserving Natural Vegetation							X			N/A	Low	N/A
Better Site Design							X			N/A	Low	N/A
Impervious Surface Disconnect (D.C., 2020)							X			N/A	Low	N/A
Dispersion BMPs												
Concentrated Flow Dispersion		X							X	High	N/A	Yes
Sheet Flow Dispersion		X							X	High	N/A	Yes
Full Dispersion (natural or engineered)		X							X	High	N/A	Yes
Roof Downspout BMPs												
Downspout Full Infiltration		X							X	High	N/A	Yes
Downspout Dispersion System		X							X	High	N/A	Yes
Perforated Stub-Out Connection							X			Low	N/A	Yes
Infiltration BMPs												
Permeable Pavements		X								Medium	N/A	Yes
Stone storage under permeable pavement or other BMPs (D.C., 2020)									X	High	N/A	Yes
Infiltration Basins/Ponds		X			X				X	High	N/A	Yes
Infiltration Vault (WSDOT, 2019)									X	High		

BMP Name	Density Separation or Sedimentation	Filtration	Sorption	Microbial Activity	Uptake/ Storage	Chemical Treatment	Not Applicable (Source Control/ E&O)	BMP contains Bioretention Media (Compost)	Infiltration	Potential Treatment Rating of Flow and Treatment BMP	Potential Prevention Rating of Source Control BMP	Can the BMP be implemented near sources?
Infiltration Trenches		X							X	High	N/A	Yes
Bioretention		X	X		X			X	X	High	N/A	Yes
Bioinfiltration (WSDOT, 2019)		X							x	High	N/A	Yes
Underground Attenuation Facilities										Low	N/A	Yes
Drywells		X								Medium	N/A	Yes
Filtration BMPs												
Basic Sand Filter Basin		X								Medium	N/A	Yes
Large Sand Filter Basin		X								Medium	N/A	Yes
Sand Filter Vault		X								Medium	N/A	Yes
Sand Filter Iron Enhanced (Minnesota, 2021)		X	X							High	N/A	Yes
Linear Sand Filter		X								Medium	N/A	Yes
Media Filter Drain	X	X	X			X			X	High	N/A	Yes
Biofiltration BMPs												
Compost-Amended Vegetated Filter Strips (CAVFS)		X	X						X	High	N/A	Yes
Basic Biofiltration Swale		X						X	X	High	N/A	Yes
Wet Biofiltration Swale		X			X			X	X	High	N/A	Yes

BMP Name	Density Separation or Sedimentation	Filtration	Sorption	Microbial Activity	Uptake/ Storage	Chemical Treatment	Not Applicable (Source Control/ E&O)	BMP contains Bioretention Media (Compost)	Infiltration	Potential Treatment Rating of Flow and Treatment BMP	Potential Prevention Rating of Source Control BMP	Can the BMP be implemented near sources?
Continuous Inflow Biofiltration Swale		X								Medium	N/A	Yes
High Gradient Stormwater Step Pool Swale (Minnesota, 2021)	X	X								Medium	N/A	Yes
Vegetated Filter Strip		X								Medium	N/A	Yes
Wetpool BMPs												
Wetponds - Basic and Large	X				X					Medium	N/A	Yes
Wetvaults	X									Medium	N/A	Yes
Stormwater Treatment Wetlands	X	X		X						Medium	N/A	Yes
Submerged Gravel Wetlands (Prince George, 2014)		X	X	X	X					High	N/A	Yes
Combined Detention and Wetpool facilities	X				X					Medium	N/A	Yes
Pretreatment BMPs												
Presettling Basin	X									Medium	N/A	Yes
Pretreatment - Screening and straining devices, including forebays (Minnesota, 2021)	X									Medium	N/A	Yes
Pretreatment - Above ground and below grade storage and settling devices (Minnesota, 2021)	X									Medium	N/A	Yes
Pretreatment - Filtration devices and practices (Minnesota, 2021)	X	X								Medium	N/A	Yes
Misc LID BMPs												
Post-Construction Soil Quality and Depth										Low	N/A	Yes

BMP Name	Density Separation or Sedimentation	Filtration	Sorption	Microbial Activity	Uptake/ Storage	Chemical Treatment	Not Applicable (Source Control/ E&O)	BMP contains Bioretention Media (Compost)	Infiltration	Potential Treatment Rating of Flow and Treatment BMP	Potential Prevention Rating of Source Control BMP	Can the BMP be implemented near sources?
Rain Gardens										Low	N/A	Yes
Tree Retention and Tree Planting					X		X			Low	N/A	Yes
Vegetated Roofs							X			Low	N/A	Yes
Reverse Slope Sidewalks							X			Low	N/A	Yes
Minimal Excavation Foundations							X			N/A	Low	N/A
Rainwater Harvesting							X			Low	N/A	Yes
Detention BMPs												
Detention Ponds	X				X					Medium	N/A	Yes
Detention Vaults or Tanks	X									Medium	N/A	Yes
Oil and Water Separator BMPs												
API (Baffle Type) Separator	X									Medium	N/A	Yes
Coalescing Plate (CP) Separator	X									Medium	N/A	Yes
Multi-Chamber Treatment Train (CalTrans, 2019)	X	X								Medium	N/A	Yes
Gross Solids Removal												
Gross Solids Removal Devices (GSRDs): Linear Radial and Inclined Screen (CalTrans, 2019)		X								Medium	N/A	Yes
Traction Sand Traps (CalTrans, 2019)	X	X								Medium	N/A	Yes

BMP Name	Density Separation or Sedimentation	Filtration	Sorption	Microbial Activity	Uptake/ Storage	Chemical Treatment	Not Applicable (Source Control/ E&O)	BMP contains Bioretention Media (Compost)	Infiltration	Potential Treatment Rating of Flow and Treatment BMP	Potential Prevention Rating of Source Control BMP	Can the BMP be implemented near sources?
Manufactured Treatment Devices as BMPs[6]												
BayFilter w/ EMC Media	X	X	X							High	N/A	Yes
BaySeparator	X									Medium	N/A	Yes
Aqua-Swirl System	X									Medium	N/A	Yes
BioPod Biofilter	X	X	X	X						High	N/A	Yes
CDS Stormwater Treatment System	X	X								Medium	N/A	Yes
Compost-Amended Biofiltration Swale	X	X	X	X						High	N/A	Yes
Downstream Defender	X									Medium	N/A	Yes
ecoStorm plus	X	X	X			X				High	N/A	Yes
Filterra	X	X	X	X						High	N/A	Yes
FloGard Perk Filter	X	X	X							High	N/A	Yes
Jellyfish	X	X								Medium	N/A	Yes
Media Filtration System							X			Low	N/A	Yes
Modular Wetland System - Linear	X	X		X						Medium	N/A	Yes

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[6] Manufactured treatment device treatment mechanisms were determined from information presented in TAPE documents for the device.

BMP Name	Density Separation or Sedimentation	Filtration	Sorption	Microbial Activity	Uptake/ Storage	Chemical Treatment	Not Applicable (Source Control/ E&O)	BMP contains Bioretention Media (Compost)	Infiltration	Potential Treatment Rating of Flow and Treatment BMP	Potential Prevention Rating of Source Control BMP	Can the BMP be implemented near sources?
Stormceptor	X						X			Medium	N/A	Yes
StormFilter using PhosphoSorb	X	X	X			X				High	N/A	Yes
StormFilter using ZPG	X	X	X				X			High	N/A	Yes
StormGarden	X	X		X						Medium	N/A	Yes
StormTree	X	X	X	X						High	N/A	Yes
The Kraken	X	X								Medium	N/A	Yes
Up-Flo Filter w/ Filter Ribbons	X	X								Medium	N/A	Yes
Vortechs	X						X			Medium	N/A	Yes
Construction Source Control												
Buffer Zones							X			N/A	Low	N/A
High-Visibility Fence							X			N/A	Low	N/A
Stabilized Construction Access							X			N/A	Medium	Potentially
Wheel Wash							X			N/A	Medium	Potentially
Construction Road / Parking Area Stabilization							X			N/A	Medium	Potentially
Temporary and Permanent Seeding							X			N/A	Low	N/A
Mulching							X			N/A	Low	N/A

BMP Name	Density Separation or Sedimentation	Filtration	Sorption	Microbial Activity	Uptake/ Storage	Chemical Treatment	Not Applicable (Source Control/ E&O)	BMP contains Bioretention Media (Compost)	Infiltration	Potential Treatment Rating of Flow and Treatment BMP	Potential Prevention Rating of Source Control BMP	Can the BMP be implemented near sources?
Nets and Blankets							X			N/A	Low	N/A
Plastic Covering							X			N/A	Low	N/A
Sodding							X			N/A	Low	N/A
Topsoiling / Composting							X			N/A	Low	N/A
Polyacrylamide (PAM) for Soil Erosion Protection							X			N/A	Low	N/A
Surface Roughening							X			N/A	Low	N/A
Gradient Terraces							X			N/A	Low	N/A
Dust Control							X			N/A	Low	N/A
Materials on Hand							X			N/A	Low	N/A
Concrete Handling							X			N/A	Low	N/A
Sawcutting and Surfacing							X			N/A	Low	N/A
Material Delivery, Storage, and Containment							X			N/A	Low	N/A
Concrete Washout Area							X			N/A	Low	N/A
Certified Erosion and Sediment Control Lead							X			N/A	Low	N/A
Scheduling							X			N/A	Low	N/A

BMP Name	Density Separation or Sedimentation	Filtration	Sorption	Microbial Activity	Uptake/ Storage	Chemical Treatment	Not Applicable (Source Control/ E&O)	BMP contains Bioretention Media (Compost)	Infiltration	Potential Treatment Rating of Flow and Treatment BMP	Potential Prevention Rating of Source Control BMP	Can the BMP be implemented near sources?
Interceptor Dike and Swale		X								Medium	N/A	Yes
Grass-Lined Channels		X								Medium	N/A	Yes
Riprap Channel Lining		X								Medium	N/A	Yes
Water Bars		X								Medium	N/A	Yes
Pipe Slope Drains							X			Low	N/A	Yes
Subsurface Drains							X			Low	N/A	Yes
Level Spreader							X			Low	N/A	Yes
Check Dams		X								Medium	N/A	Yes
Triangular Silt Dike		X								Medium	N/A	Yes
Outlet Protection		X								Medium	N/A	Yes
Inlet Protection		X								Medium	N/A	Yes
Brush Barrier		X								Medium	N/A	Yes
Gravel Filter Berm		X								Medium	N/A	Yes
Silt Fence		X								Medium	N/A	Yes
Vegetated Strip		X								Medium	N/A	Yes

BMP Name	Density Separation or Sedimentation	Filtration	Sorption	Microbial Activity	Uptake/ Storage	Chemical Treatment	Not Applicable (Source Control/ E&O)	BMP contains Bioretention Media (Compost)	Infiltration	Potential Treatment Rating of Flow and Treatment BMP	Potential Prevention Rating of Source Control BMP	Can the BMP be implemented near sources?
Wattles		X								Medium	N/A	Yes
Vegetative Filtration		X							X	High	N/A	Yes
Sediment Trap	X									Medium	N/A	Yes
Sediment Pond (Temporary)	X									Medium	N/A	Yes
Constructed Stormwater Chemical Treatment						X				Low	N/A	Yes
Construction Stormwater Filtration		X								Medium	N/A	Yes
Treating and Disposing of High pH Water						X				Low	N/A	Yes
Source Control Applicable All Sites												
BMPs for Correcting Illicit Discharges to Storm Drains							X			N/A	Low	N/A
BMPs for Formation of a Pollution Prevention Team							X			N/A	Low	N/A
BMPs for Preventative Maintenance/Good Housekeeping							X			N/A	Low	N/A
BMPs for Inspections							X			N/A	Low	N/A
BMPs for Recordkeeping							X			N/A	Low	N/A
BMPs for Spill Prevention and Cleanup							X			N/A	Low	N/A
BMPs for Employee Training							X			N/A	Low	N/A
Source Control Cleaning & Washing												

BMP Name	Density Separation or Sedimentation	Filtration	Sorption	Microbial Activity	Uptake/ Storage	Chemical Treatment	Not Applicable (Source Control/ E&O)	BMP contains Bioretention Media (Compost)	Infiltration	Potential Treatment Rating of Flow and Treatment BMP	Potential Prevention Rating of Source Control BMP	Can the BMP be implemented near sources?
BMPs for Washing and Steam Cleaning Vehicles/Equipment							X			N/A	Low	N/A
BMps for Dock Washing							X			N/A	Low	N/A
BMPs for Portable Water Line Flushing, Water Tank Maintenance, Hydrant Testing							X			N/A	Low	N/A
BMPs for Deicing and Anti-Icing Operations for Airports							X			N/A	High	Yes
Source Control Roads, Ditches, & Parking Lots												
Street Sweeping (Minnesota, 2021)										N/A	Low	N/A
Stormdrain Line Cleaning (Minnesota, 2021)										N/A	Low	N/A
BMPs for Streets and Highways							X			N/A	High	Yes
BMPs for Maintenance of Public and Private Utility Corridors							X			N/A	High	Yes
BMPs for Maintenance of Roadside Ditches							X			N/A	High	Yes
BMPs for Maintenance of Stormwater Drainage and Treatment							X			N/A	High	Yes
BMPs for Parking and Storage of Vehicles and Equipment							X			N/A	High	Yes
BMPs for Urban Streets							X			N/A	High	Yes
Source Control Soil Erosion, Sediment Control, & Landscaping												
BMPs for Dust Control at Disturbed Land Areas and Unpaved Roadways and Parking Lots							X			N/A	High	Yes

BMP Name	Density Separation or Sedimentation	Filtration	Sorption	Microbial Activity	Uptake/ Storage	Chemical Treatment	Not Applicable (Source Control/ E&O)	BMP contains Bioretention Media (Compost)	Infiltration	Potential Treatment Rating of Flow and Treatment BMP	Potential Prevention Rating of Source Control BMP	Can the BMP be implemented near sources?
BMPs for Dust Control at Manufacturing Areas							X			N/A	Low	N/A
BMPs for Lanscaping and Lawn/Vegetation Management							X			N/A	Low	N/A
BMPs for Soil Erosion and Sediment Control at Industrial Sites							X			N/A	Low	N/A
Source Control Storage & Stockpilling												
BMPs for the Storage of Dry Pesticides and Fertilizers							X			N/A	Low	N/A
BMPs for Storage of Liquid, Food Waste, or Dangerous Waste							X			N/A	Low	N/A
BMPs for Storage of Liquids in Permanent Aboveground Tanks							X			N/A	Low	N/A
BMPs for Storage or Transfer (Outside) of Solid Raw Materials							X			N/A	Low	N/A
BMPs for Temporary Fruit Storage							X			N/A	Low	N/A
Source Control Transfer of Liquids & Solid Materials												
BMPs for Fueling at Dedicated Stations							X			N/A	Low	N/A
BMPs for Loading or Unloading Areas for Liquid or Solid Materials							X			N/A	Low	N/A
BMPs for Mobile Fuleing of Vehicles and Heavy Equipment							X			N/A	Low	N/A
BMPs for Spills and Oil and Hazardous Substances							X			N/A	Low	N/A
BMPs for In-Water and Over-Water Fueling							X			N/A	Low	N/A
Source Control Other												

BMP Name	Density Separation or Sedimentation	Filtration	Sorption	Microbial Activity	Uptake/ Storage	Chemical Treatment	Not Applicable (Source Control/ E&O)	BMP contains Bioretention Media (Compost)	Infiltration	Potential Treatment Rating of Flow and Treatment BMP	Potential Prevention Rating of Source Control BMP	Can the BMP be implemented near sources?
BMPs for Nurseries and Greenhouses							X			N/A	Low	N/A
BMPs for Irrigation							X			N/A	Low	N/A
BMPs for Pesticides and an Integrated Pest Management Program							X			N/A	Low	N/A
BMPs for the Building, Repair, and Maintenance of Boats and Ships							X			N/A	Low	N/A
BMPs for Commercial Animal Handling areas							X			N/A	Low	N/A
BMPs for Commercial Composting							X			N/A	Low	N/A
BMPs for Commercial Printing Operations							X			N/A	Low	N/A
BMPs for Log Sorting and Handling							X			N/A	Low	N/A
BMPs for Maintenance and Repair of Vehicles and Equipment							X			N/A	High	Yes
BMPs for Manufacturing Activities - Outside							X			N/A	Low	N/A
BMPs for Painting/Finishing/Coating of Vehicles/Boats/Buildings/Equipment							X			N/A	Low	N/A
BMPs for Railroad Yards							X			N/A	Low	N/A
BMPs for Recyclers and Scrap Yards							X			N/A	Low	N/A
BMPs for Roof/Building Drains at Manufacturing and Commercial Buildings							X			N/A	Low	N/A
BMPs for Wood Treatment Areas							X			N/A	Low	N/A

BMP Name	**Density Separation or Sedimentation**	**Filtration**	**Sorption**	**Microbial Activity**	**Uptake/ Storage**	**Chemical Treatment**	**Not Applicable (Source Control/ E&O)**	**BMP contains Bioretention Media (Compost)**	**Infiltration**	**Potential Treatment Rating of Flow and Treatment BMP**	**Potential Prevention Rating of Source Control BMP**	**Can the BMP be implemented near sources?**
BMPs for Pools, Spas, Hot Tubs, and Fountains							X			N/A	Low	N/A
BMPs for Color Events							X			N/A	Low	N/A
BMPs for Construction Demolition							X			N/A	Low	N/A
BMPs for Pet Waste							X			N/A	Low	N/A
BMPs for Labeling Storm Drain Inlets on your Property							X			N/A	Low	N/A
BMPs for Fertilizer Application							X			N/A	Low	N/A
BMPs for Well, Utility, Directional, and Geotechnical Drilling							X			N/A	Low	N/A
BMPS for Roof Vents							X			N/A	Low	N/A
BMPs for Building, Repair, Remodeling, Painting, and Construction							X			N/A	Low	N/A
BMPs for Goose Waste							X			N/A	Low	N/A

CHAPTER 5: RESEARCH PRIORITIZATION

5.1 Chapter Purpose

The intent of this chapter is to summarize and prioritize the knowledge gaps and next steps identified during the project.

5.2 Overview of Chapter Contents and Work Complete

This chapter contains a prioritized list of the research gaps and next steps that were identified in Chapters 2-4 of this report. Each research gap and associated next step or approach was prioritized into one of three categories: High, Medium, or Low. The categories were developed using best professional judgement guided by input from experts and assuming the highest need is to understand how to capture/contain/treat 6PPD and 6PPD-q generated on roadways and prioritization of where treatment needs to occur first to protect receiving waters. As such, the categories are defined based on the need for the research to understand what BMPs would capture/contain/treat the contaminants and the potential impact on surface waters if current knowledge is inaccurate or incomplete (see Chapter 2 for discussion of modeled parameters).

5.3 Key Findings Summary

Table 5.1 contains a summary of the research needed from each of the chapters. It is important to note that these research needs reflect the current state of knowledge, and that research is ongoing. A topic that is considered low priority at this time may become a high priority as knowledge of 6PPD and 6PPD-q advances. Additionally, research gaps categorized as a low priority are still topics that need to be studied; the low categorization is a ranking, meaning that it is considered low priority only in relation to the remaining research gaps.

The following bullets define the research priority categories.

- **High:** This category includes research that is necessary to determine what treatment processes or BMPs can treat/capture/contain 6PPD or 6PPD-q, and may be limiting the current ability to confidently select or locate BMPs to treat the contaminants The research may help answer multiple questions or informs multiple unknowns regarding 6PPD or 6PPD-q. It also includes research that is necessary to confirm assumptions or hypotheses which, if incorrect, would cause a detrimental environmental impact. For example, testing to confirm that 6PPD and 6PPD-q does not leach from soil, engineered materials, or organic matter under various environmental conditions could confirm several categories of BMPs (infiltration, biofiltration, etc.) could capture/contain/treat the contaminants. If the contaminants do leach in certain conditions, it will be important to know those conditions to limit potential transport and impacts to groundwater and surface waters.
- **Medium:** This category includes research that is not as urgently needed to be able to capture/contain/treat 6PPD and 6PPD-q, but still needs to be answered following the research gaps ranked as high. It also includes research to confirm hypotheses or assumptions regarding the contaminants that would not have as detrimental of an impact to surface waters if the current understanding is inaccurate or incomplete. For example, research gaps related confirming the half-lives of 6PPD and 6PPD-q could potentially impact the ability of filtration BMPs (BMPs with a medium treatment potential) to treat the contaminants, as these BMPs may not contain the contaminants long enough for the contaminants to fully degrade before leaving the BMP. However, the research gap is not expected to impact the ability of infiltration or other BMPs considered to have a high treatment potential, as the contaminants are expected to be captured within the BMP

soil or engineered material and not re-suspended during a storm event. Because this research gap only impacts a category of BMPs or a category of BMPs with a medium or low treatment potential, the research gap is ranked as medium. Research gaps that are necessary to determine prioritization of BMP locations are also included in this category.

- **Low:** This category includes research which informs unknowns regarding the contaminants and prioritization but is not urgently needed to understand how to treat/capture/contain 6PPD or 6PPD-q or only informs one unknown regarding the contaminants. Research gaps that are less necessary to determine prioritization of BMP locations are also included in this category. An example of a low priority research gap includes identification of other sources other than roadways and an understanding of the loading from those sources. As this research gap is not immediately necessary to understand how to capture/contain/treat the contaminants, and addresses prioritization of likely minor sources of 6PPD and 6PPD-q compared to roadways.

Table 5.1 6PPD and 6PPD-q Research Prioritization

Priority/ Urgency	Research Gap	Approach	Chapter
High	Additional testing is needed to confirm leaching of 6PPD and 6PPD-q from soil, engineered materials, and organic matter is not likely, and to understand any conditions where it could occur. This property has a large impact on the fate and transport of the contaminants within the built environment, determines whether existing BMPs would permanently remove the contaminants, and would indicate whether groundwater could be impacted by the contaminants.	Conduct lab or field testing to confirm whether the contaminants remain adhered to soil and organic matter for different environmental conditions.	2, 4
High	Additional testing is needed to confirm the values produced by the Fugacity Model and the half-life of 6PPD-q, as these values impact the persistence of 6PPD and 6PPD-q in the environment and inform the BMP hydraulic residence time needed for certain BMPs (i.e., flow through BMPs). The lab and field testing may also inform the methods of how 6PPD and 6PPD-q are degraded in the built environment.	Conduct lab or field testing to confirm the half-life of both contaminants in different materials and under different environmental conditions.	2, 4
High	Uncertain what land uses, ADT, etc. will trigger the need for treatment BMPs at sites. Also, unknown whether there is an ADT threshold where 6PPD and 6PPD-q concentrations are no longer present in lethal amounts. Understanding where the loading is problematic will allow prioritization of sites with higher concentrations.	Study the location and concentration of TWP to determine what land uses, traffic counts, etc. result in toxic concentrations and subsequently what will trigger the need for treatment BMPs as well as determine if there is a traffic count threshold where 6PPD and 6PPD-q are no longer present in lethal amounts.	3,4
High	Additional testing is needed to understand what forms (dissolved, adhered to particles, in soil, etc.) and what range of particle sizes containing or attached to 6PPD and 6PPD-q need to be removed by BMPs to reduce the lethality of stormwater effluent. It will also be helpful to understand which form the contaminants are typically transported.	Perform field testing to understand what forms of 6PPD and 6PPD-q (dissolved, adhered to particles, in soil, etc.) and sizes of particles containing or attached to 6PPD and 6PPD-q need to be removed by BMPs to reduce the lethality of stormwater effluent.	2, 3, 4
High	Unknown whether BMPs that provide infiltration, dispersion, and biofiltration (including BMPs with bioretention soil media or compost) or sedimentation and filtration BMPs will capture the particle sizes associated with the most readily available concentrations of 6PPD and 6PPD-q.	Perform field testing to determine whether infiltration, sedimentation, and filtration BMPs can remove 6PPD and 6PPD-q particle sizes that will reduce the lethality of the effluent.	4
Medium	No information existing regarding whether solids removal (e.g., street sweeping and line cleaning) BMPs for roadways, parking, and stormwater infrastructure could reduce/capture 6PPD and 6PPD-q in the environment.	Perform field testing to determine whether solids removal methods from roadways parking, and stormwater infrastructure can remove 6PPD and 6PPD-q in the environment.	4
Medium	Unknown how long those particles containing or with 6PPD attached will generate 6PPD-q at different stages of transport.	Conduct lab or field testing to understand for how long particles will generate 6PPD-q under different environmental conditions.	2
Medium	Lack of information on fate and transport of 6PPD-q under environmental conditions other than wet weather events; specifically, how long does it remain bioavailable and toxic in dry conditions, how it is transported outside of wet weather events.	Conduct a study to evaluate concentrations and bioavailability/toxicity of 6PPD-q under environmental conditions other than wet weather events.	3
Medium	It is anticipated that other potential sources, such as athletic fields with artificial turf, junk yards, and auto repair shops and tire stores, will be identified in the future.	Investigate runoff from other potential sources such as athletic fields with artificial turf, junk yards, and auto repair shops and tire stores to determine if BMPs would be beneficial.	3
Medium	Additional testing is needed to understand whether sorption as a treatment process can be used in BMPs to remove 6PPD and 6PPD-q.	Perform additional testing to understand the efficacy of sorption for reducing 6PPD and 6PPD-q and determine which type of sorption (ion exchange or adsorption).	4
Medium	There is a lack of information on loading of 6PPD and 6PPD-q from construction sites. An understanding of loading from construction sites (especially highway construction) will help to determine the priority of treating runoff from the sites as well as determine the most effective construction source control and flow and treatment BMPs.	Perform field testing to determine loading from construction sites (especially highway construction).	4
Low	No information on efficacy of source control BMPs in reducing 6PPD or 6PPD-q in the environment.	Perform field testing of source control BMPs to determine whether they can reduce or prevent 6PPD or 6PPD-q from mixing with stormwater in the environment.	4
Low	No information on efficacy of E&O behavior change programs in reducing 6PPD or 6PPD-q in the environment.	Conduct a study to assess the potential efficacy of E&O behavior change programs.	4
Low	There is a lack of information on 6PPD-q transport dynamics using sites at different distances from roadway sources and at various points during the hydrograph. This information could lead to BMPs that target the part of the storm with the highest concentration.	Study relationship of time or seasons on 6PPD and 6PPD-q concentrations in wet weather events to understand when peak concentrations occur.	3
Low	More information is needed to determine deposition of TWP dust particles through air and deposition of larger particles from tires.	Study the location and concentration of TWP in the environment (e.g., roadway surfaces, gutters, pipe sediments, snow piles, etc.) to determine where highest concentrations occur.	3
Low	Unknown whether other stormwater design manuals develop BMP guidance to limit sediment resuspension when flow enters the BMPs, or anoxic zones in permanent pools.	Perform literature review to determine whether other stormwater manuals develop BMP guidance to limit sediment resuspension when flow enters BMPs, or anoxic zones in BMPs with permanent pools.	4

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Appendix D.

University Memos: Researchers’ Documentation of Scientific Knowledge to Date

WASHINGTON STATE UNIVERSITY
Puyallup Research and Extension Center

From: Jenifer McIntyre & Anand Jayakaran (Washington State University, Washington Stormwater Center), Kathy Peter (University of Washington, Center for Urban Waters)

Subject: Technical memorandum on aquatic toxicity of stormwater and role of 6PPD-quinone

Date: July 14, 2022

History of WSU studies on stormwater toxicity, impacts, treatment

In 2011, researchers from several institutions published a 7-year forensics study documenting acute mortality of coho salmon spawners (*Oncorhynchus kisutch*) in Seattle-area streams and exploring the cause (Scholz *et al.* 2011). Based on weight-of-evidence, the authors concluded that stormwater runoff was responsible for the acute mortality phenomenon. That same year, research into the toxicology of stormwater runoff began at Washington State University Puyallup Research & Extension Center (WSU). Most work was in collaboration with researchers at the NOAA Northwest Fisheries Science Center (NOAA) and the U.S. Fish & Wildlife Service. Test organisms were aquatic invertebrates (daphniids from the WSU colony and wild-caught *Baetis* spp. mayfly larvae), zebrafish embryos (*Danio rerio*) from the colony at NOAA (and later WSU), Pacific herring embryos (*Clupea pallasii*) fertilized from wild-caught spawners in Puget Sound, adult coho and chum from the Suquamish Tribe Grovers Creek hatchery, and juvenile salmonids reared at WSU including coho (*O. kisutch*), chum (*O. keta*), steelhead (*O. mykiss*), Chinook (*O. tshawytscha*) and sockeye (*O. nerka*).

Our initial attempts to study the toxicity of stormwater runoff to aquatic organisms used street dirt or mixtures of chemicals known to contaminate stormwater runoff. Pilot work with street dirt from refuse piles of street sweeping by the City of Seattle did not produce acute toxic responses in the daphniid *Ceriodaphia dubia* nor in zebrafish embryos (McIntyre *unpublished data*). Mixtures of metals and hydrocarbons did not elicit acute toxic responses in adult coho salmon (Spromberg *et al.* 2016). Clearly, these simple attempts at a synthetic stormwater were missing contaminant(s) necessary to the toxicity observed when aquatic organisms are exposed to stormwater runoff (Skinner *et al.* 1999, Kayhanian *et al.* 2008, Scholz *et al.* 2011, and others).

In contrast, collected roadway runoff re-created the acute mortality syndrome of coho spawners observed in runoff-impacted streams (Spromberg *et al.* 2016). Behaviors and blood changes associated with the mortality syndrome were observed in coho, but not in co-exposed chum (*O. keta*) salmon (McIntyre *et al.* 2018). Juvenile coho were determined to be a suitable model for studying impacts on adults, based on acute sensitivity as well as changes in behavior and blood prior to mortality (Chow *et al.* 2019). Using juvenile coho, we elucidated the behavioral progression of the mortality syndrome: lethargy -> discrete surfacing -> continuous surface swimming -> loss of equilibrium -> immobility -> mortality (Chow *et al.* 2019). The point-of-no-return occurs before surface swimming, as transfer to clean water at this stage did not prevent or delay mortality (Chow *et al.* 2019). High dilutions and brief exposures of roadway runoff are required to prevent mortality (≥95%, ≤4h) (Prat 2019). A spectrum of sensitivity to runoff exists among tested salmonids; runoff collected from three storm events produced differential lethality in the order of *O. kisutch* > *O. mykiss* > *O. tshawytscha* >> *O. nerka* = *O. keta* (French *et al.* In review). Coho embryos exposed episodically to roadway runoff during development died upon hatching, but prior to hatching showed a variety of sub-lethal effects, including impaired growth (McIntyre *et al.* In Prep) and defects in the mechanosensory system (Young *et al.* 2018). For mode of action, we have ruled out hemoglobin as a target; oxidation does not appear to underlie the various symptoms of hypoxia in coho exposed to runoff (Blair *et al.* 2020). Elevated hematocrit associated with advanced symptoms appears to result from loss of vascular integrity, causing plasma to leak from the blood into cerebral and other tissues (Blair *et al.* 2021).

Additional aquatic species are also sensitive to stormwater runoff. Studies by WSU showed that roadway runoff could be acutely toxic to daphniids, mayfly nymphs, and zebrafish embryos (McIntyre *et al.* 2014, McIntyre *et al.* 2015). Although runoff was rarely lethal to developing fish, cardiac defects are common in developing zebrafish (Wu *et al.* 2014, McIntyre *et al.* 2016) and also in developing herring (Harding *et al.* 2020) exposed to runoff. As with coho embryos, zebrafish embryos showed neurotoxicity to the mechanosensory system when developing in dilutions of runoff (Young *et al.* 2018).

Research into solutions for preventing stormwater toxicity began at WSU in 2014. We showed that lethality to coho juveniles (McIntyre *et al.* 2015), adults (Spromberg *et al.* 2016), and alevin (McIntyre 2016, McIntyre *et al.* In Prep) could be prevented by bioretention filtration, as could sublethal impairments to aquatic invertebrates (McIntyre *et al.* 2015), zebrafish (McIntyre *et al.* 2014, Young *et al.* 2018), and Pacific herring (Harding *et al.* 2020). Compost-amended bioswales (CABS) for treating runoff along roadways were moderately effective at preventing sub-lethal impacts in zebrafish embryos (Tian *et al.* 2019), as were various alternative bioretention blends designed to leach less copper and phosphorus tested at bench-scale (Herrera 2019). Similarly, field-scale bioretention installations receiving real-time inputs of runoff for two years did not always prevent sublethal toxicity (McIntyre *et al.* 2020). An innovation to use rolls of coarse sand and compost to filter incoming water as a retrofit to existing stormwater detention ponds appeared to provide toxicity reduction benefits greater than from CABS and similar or better than from bioretention (McIntyre 2021). As bioretention media ages, it may provide less protection against some types of toxicity. For example, bioretention media used to treat collected roadway runoff protected fish from sublethal impairments during a first year of use, but not during a second (Young *et al.* 2018, McIntyre *et al.* In Prep). Anecdotally, age-related loss of ability to prevent sub-lethal impairment to developing fish was also observed at WSU for experimental bioretention media containing

60% sand, 15% compost, 15% shredded bark and 10% water treatment residuals (McIntyre *unpublished data*).

Identification of 6PPD-quinone as primary causal toxicant of coho mortalities

In 2016, WSU began collaborating with analytical chemists at the University of Washington Tacoma (UWT) to learn more about the chemicals in roadway runoff causing aquatic toxicity. Using liquid chromatography coupled to high resolution mass spectrometry (LC-HRMS), thousands of unique chemicals were observed in roadway runoff, many of which were also detected in the tissue of exposed coho spawners (Du *et al.* 2017). At this time, we began exploring sources of toxic chemicals to roadway runoff, including tire wear particles, windshield wiper fluid, antifreeze, used motor oil, gear oil, and transmission fluid. Sub-lethal impacts to zebrafish embryos were best explained by the presence of tire-related chemicals (McIntyre *unpublished data*), and tires were the vehicle source most similar chemically to waters that killed coho (Peter *et al.* 2018).

To explore whether tire-derived chemicals were the source of acute toxicity to coho salmon, we made a tire particle leachate by recirculating water through particles abraded from tire tread; realistic of how rainwater could interact with tires or particles worn from the tread of tires. Chemicals leached from tire tread particles were sufficient to re-create the mortality syndrome in coho salmon, including changes in blood physiology, behavior, and rapid onset of mortality, while not causing any apparent impacts in chum salmon (McIntyre *et al.* 2021). In 2018, the team began fractionating tire particle leachate to learn about the chemical properties of the toxicant(s) killing coho and support an effects direct analysis approach to toxicant identification. This involved treating the leachate to create fractions containing chemicals with different properties. These fractions were tested for toxicity to coho and analyzed by LC-HRMS. In early testing, leachate was treated by silica sand filtration, cation exchange, and chelation with ethylenediaminetetraacetic acid (EDTA). Toxicity persisted in each case, confirming that the toxicant(s) were not associated with particles, cations, or metals, respectively.

Subsequent fractionation focused on organic contaminants in tire particle leachate. Utilizing techniques including cation exchange, polarity-based separation, reverse phase high performance liquid chromatography (HPLC), and multi-dimensional HPLC in series, the chemical complexity of the toxic fraction was reduced from >2000 chemicals to just four (Tian *et al.* 2021). The most abundant chemical in the final fraction was a previously unknown chemical with molecular formula $C_{18}H_{22}N_2O_2$, which was determined to be a transformation product of 6PPD (N-(1,3- dimethylbutyl)-N′-phenyl-p- phenylenediamine) – the most widely used anti-ozonant in tire rubber. By exposing commercial 6PPD ($C_{18}H_{24}N_2$) to ozone, the team produced $C_{18}H_{22}N_2O_2$ with mass spectral properties identical to those of the $C_{18}H_{22}N_2O_2$ purified from tire wear particle leachate, confirming the origin of this previously unknown transformation product. The structure of the unknown chemical was identified by nuclear magnetic resonance (NMR) to be 6PPD-quinone (Tian *et al.* 2021).

Purified 6PPD-quinone, isolated from 6PPD subjected to ozone, was highly acutely lethal to coho salmon. The median lethal concentration (LC_{50}) was originally estimated as 0.79 µg/L (95% C.I. = 0.63-0.96 µg/L). The LC_{50} of 6PPD-quinone in unfractionated/unpurified tire tread particle leachate and roadway runoff was 0.82 µg/L (95% C.I.: 0.56-1.10 µg/L), supporting that 6PPD-quinone was the primary causal toxicant for coho salmon exposed to roadway runoff (Tian *et al.* 2021). These concentrations were determined using a 6PPD-quinone standard isolated and purified from tire wear particle leachate. Recent availability of a commercial standard and an isotope-labeled standard (D5-6PPD-Q; HPC Standards Inc.) revealed a substantially higher (15-fold) peak area response for the commercial standard relative to the in-house standard. This difference was attributed to less 6PPD-quinone mass in the in-house stocks than previously thought. On-going studies are examining possible causes of the loss of mass (including 6PPD-quinone solubility, sorption to laboratory materials, or possible oxidative polymerization) (Tian *et al.* 2022). Additionally, use of an internal standard revealed that recovery of 6PPD-quinone during sample processing was 60-70%. The net result of the refined methodology in Tian *et al*. 2022 was an 8-fold reduction of reported environmental and effect concentrations.

6PPD-quinone sources

Sources of 6PPD-quinone to the environment are expected to be primarily from tires. The parent compound, 6PPD, from which 6PPD-quinone is derived by reaction with ozone, is recommended for use as an anti-ozonant in the tread, sidewall, and rim strip of tires, as well as the rubber cover of conveyor belts (Sheridan 2010). All tires produced by the 12 member companies of the U.S. Tire Manufacturers Association use 6PPD as the primary antiozonant (https://www.ustires.org/6ppd-and-tire-manufacturing). Tire stored uncovered outdoors and re-uses of tires such as crumb rubber in synthetic turf, playgrounds, and incorporation into materials such as rubberized asphalt may continue to contribute 6PPD-quinone to the environment, but direct investigation is required for confirmation.

Rubbers used as seals may also contain 6PPD, depending on the ozone resistance of the elastomer (Sheridan 2010). For example, whereas ethylene-propylene rubbers (EPM or EPDM) are resistant to ozone, and isobutylene-based elastomers and neoprenes are moderately resistant, natural rubber, styrene-butadiene, polybutadiene, and nitrile elastomers readily degrade in the presence of ozone and require an anti-ozonant such as 6PPD to protect the rubber from cracking as it ages (Sheridan 2010). A recent report has identified dust generated from e-waste recycling (<100 µm) as a potentially important source of 6PPD-quinone, containing concentrations of 87-2,850 ng/g (Liang *et al.* 2022). For comparison, 6PPD-quinone in various other dusts (25-250 µm) was reported at up to 0.4 ng/g for households, 88 ng/g for roads, 146 ng/g for vehicles, 277 ng/g for parking lots (Huang *et al.* 2021), and for roadside soils (<250 µm) was 9.5-936 ng/g (Cao *et al.* 2022).

Lethal/sub-lethal impacts concentrations and species

In the published scientific literature, 6PPD-quinone toxicity has been directly tested on nine species of fish and two aquatic invertebrates (Table 1). As summarized above, Tian *et al.*

(2021) initially reported a 24-h LC_{50} for juvenile coho salmon of 0.8 µg/L. Tian *et al.* (2022) recently revised that estimate to be 8-fold lower (0.95 µg/L, 95% C.I. = 0.80-1.10 ng/L) based on refined analytical chemistry methods (described above). In contrast, Hiki *et al.* (2021) reported no mortality in four aquatic species tested at initial concentrations of 40-94 µg/L. Significant decreases in concentration were measured over the 48-96-hour exposures by Hiki *et al.*, resulting in time-weighted average exposure concentrations of 34-54 µg/L. Additionally, similar to Tian *et al.* (2021), Hiki *et al.* conducted their studies before a commercial standard was available for 6PPD-quinone. As such, they may have similarly over-estimated exposure concentrations. Varshney *et al.* (2021) reported a 24-h LC_{50} for zebrafish embryos of 308.7 µg/L, with sub-lethal impacts described for 96-h exposure at concentrations as low as 10 µg/L (eye size, heart rate, locomotion), based on nominal concentrations of 6PPD-quinone. Pilot studies in our lab have indicated that adsorption to polymers and presence of biota can be sources of significant loss of concentration during an exposure. More recent studies include measurement with a commercial standard, similar to Tian et al. (2022). Concentrations of 6PPD-quinone did not decrease appreciably (i.e., <20%) during an exposure by Brinkmann *et al.* (2022) likely due to high exposure volumes. The study identified two additional salmonids sensitive to 6PPD-quinone (*O. mykiss* and *Salvelinus fontinalis*), with LC50s of 0.6 µg/L and 1.0 µg/L, respectively (Table 1). The sensitivity of *O. mykiss* to 6PPD-quinone was also supported by Di et al. (2022).

6PPD-quinone concentrations in stormwater tested to date

Published studies documenting 6PPD-quinone concentrations in stormwater or surface waters are increasing in number but are still limited. Available data are summarized in Table 2. Likewise, limited evaluations of observed 6PPD-quinone concentrations with respect to land-use data have been performed to date. However, Challis *et al.* (2021) included a linear regression of 6PPD-quinone mass loads observed in Saskatoon, Canada stormwater outfalls as a function of land-use area, finding a strong positive correlation to roads and residential areas, but no correlation with industrial areas or green spaces (Challis *et al.* 2021). This result supports previous modeling efforts by NOAA and USFWS researchers linking increased risk of coho mortality with roads/traffic intensity in Seattle, WA area watersheds (Feist *et al.* 2017).

6PPD-quinone of statewide concern

Based on 6PPD-quinone concentrations observed by our research teams and those available in the literature, we anticipate statewide 6PPD-quinone concentrations in road runoff and surface waters similar to observations elsewhere (see Table 2). However, additional sampling is needed to evaluate 6PPD-quinone variability with respect to different land use and land cover characteristics, distinct watershed hydrology, and roadway types/traffic intensities.

6PPD-quinone toxicity to typical indicator species

There is very limited information on whether typical indicator species are or will be sensitive to 6PPD-quinone. Zebrafish embryos are a commonly used test species for environmental toxicants. This species does not have an acute lethal response to 6PPD-quinone (Table 1), but shows evidence of sublethal impairments. Based on the low sensitivity that we have documented in coho and herring embryos exposed to stormwater (described above), and of zebrafish embryos exposed to 6PPD-quinone (Varshney *et al.* 2021), we suspect that the chorion reduces bioavailability of 6PPD-quinone to fish embryos. All fish species typically used in early life stage testing may therefore show similar protection compared with free swimming life stages.

The relative sensitivity of various indicator species to 6PPD-quinone may be related to their sensitivity to complex mixtures containing 6PPD-quinone, including stormwater and tire leachate, but this association needs to be tested empirically. Species and endpoints shown to be sensitive to stormwater, including reproduction in *Ceriodaphnia dubia* and survival of wild *Baetis* spp (McIntyre et al. 2015) should be explored as potential indicators for detrimental effects from 6PPD-quinone exposure. Notably, species not sensitive to 6PPD-quinone may yet be sensitive to the parent compound 6PPD (Di et al. 2022), or to other chemicals derived from tires. The toxicity of other antiozonants should also be considered, particularly as we move towards identifying a replacement for 6PPD in tires.

Next steps for toxicology research on 6PPD-quinone to limit impacts from stormwater

This section will focus on the toxicology of 6PPD-quinone. The relevant chemistry affecting toxicology of 6PPD-quinone will be described in a separate memo by researchers at UWT. Briefly however, to understand toxicity of 6PPD and 6PPD-quinone, an accurate and reliable method is needed for measurements in water and tissues. Methods have been developed for accurately and reliably measuring 6PPD-quinone in water, but we will need to be able to accurately measure 6PPD-quinone in fish tissues – a more complex matrix than water.

Defining toxicity of 6PPD and 6PPD-quinone to coho salmon and other sensitive species relevant for Washington State requires understanding the toxicokinetics and toxicodynamics of these contaminants. Toxicokinetics are the fate and transport of a chemical within the tissues of an organism, including the pathways of uptake (e.g., gills, skin, gastrointestinal tract), biotransformation (i.e., metabolites), distribution (e.g., concentrations in various tissue compartments), and elimination (e.g. *via* gills, kidney, feces). Toxicodynamics describe the way(s) in which toxicity is manifest in the organism, including target tissues and modes of action (e.g., liver via necrosis). A first step towards understanding toxicokinetics of 6PPD-quinone is underway at WSU by testing toxicity to coho under varying water quality conditions (temperature, pH, ionic strength). We will additionally test toxicity for different life stages (embryo, alevin, juvenile, adult) and under different water flow conditions.

For toxicodynamics, ongoing work at WSU is exploring impacts to the blood brain barrier (BBB) of coho exposed to roadway runoff. We have shown that BBB disruption is concurrent with advanced symptoms of the mortality syndrome (Blair *et al.* 2021). Pilot studies confirm that 6PPD-quinone alone is sufficient to cause the observed impacts. Continued work is needed to confirm that BBB disruption is the proximal cause of death, rather than a co-occurring condition, and much more work is needed to determine the molecular initiating event leading to BBB disruption. Determining safe levels of 6PPD and 6PPD-quinone will also require evaluating sublethal impairments that are likely to impact fitness, including growth, behavior, and reproduction for coho and other species. A potential role for 6PPD-quinone in the toxic response of other aquatic species sensitive to roadway runoff remains to be determined.

Although the discovery of 6PPD-quinone allows us to begin ascribing some toxic impacts from stormwater to 6PPD-quinone specifically, it does not change our need to further understand stormwater toxicity. We must continue to elucidate the ways in which the complex chemical mixture of stormwater affects aquatic communities and develop solutions to reduce those impacts. As we learn more about organisms affected by stormwater contaminants, and the specific contaminants driving those impacts, we can work towards optimizing treatment systems and reducing inputs.

To optimize treatment systems, we first need to understand how they work. For example, bioretention is arguably the best understood of the green stormwater infrastructure (GSI) technologies for reducing stormwater contaminants and preventing toxicity. We know that contaminants are treated in bioretention by a variety of pathways including physical filtration, chemical adsorption, and microbial degradation. However, our lack of knowledge about the relative importance of these pathways, the factors affecting their efficacy, and their long-term effectiveness demonstrate that this research is still in its infancy.

At WSU we are quantifying 6PPD-quinone treatment for three ongoing research studies and one that will begin this fall: 1) a study of bioretention funded by Stormwater Action Monitoring (SAM), 2) a permeable pavement study in collaboration with IDEA School (Tacoma, WA) funded by The Boeing Foundation, 3) VIS system field test in collaboration with Long Live the Kings (LLTK), the Nisqually Tribe, and Cedar Grove Composting, and 4) a study of the role of compost in bioretention. In the SAM study, we are researching the effects on chemistry and toxicology of treatment by bioretention for various media depths aged to 10 years under accelerated conditions with collected stormwater. We preserved influent and effluent water samples for analysis of 6PPD-quinone from the final 3 events. Water samples from an additional 5 events are planned for an assessment of performance at water years 6 to 13. At IDEA School, effluents from permeable pavements to which tire particles have been applied have been analyzed for 6PPD-quinone and several other tire-derived compounds. The transport of applied tire wear particles through porous asphalt and pervious concrete have also been quantified. Two additional synthetic storms spiked with a 6PPD-quinone standard are also planned. In total, three storms will be completed to quantify removal efficiencies of 6PPD-quinone by permeable pavement. Results are expected to be published in early 2023. With LLTK, we are testing toxicity of influent and effluent waters from a VIS system treating roadway runoff over Ohop Creek, a tributary to the Nisqually River. Tire-derived chemicals, including 6PPD-quinone, are being measured by UWT as part of evaluating chemical performance. Finally, a 2022 WA State legislative proviso is funding a 3-year study of the role of compost in treating tire wear particles and tire-derived chemicals in bioretention systems.

Research needs beyond toxicology

Analyses are needed to evaluate the relative inputs of tire-derived chemicals to surface waters from various sources and the merits of various types of source controls. For example, what reductions might be achieved by increased telework to reduce daily commuting by individuals? How much reduced tire wear could be achieved by a program encouraging the purchase of lighter vehicles? What contributions do re-uses of tires make to tire chemicals in receiving waters, e.g., from playgrounds, artificial turf fields, and tire-modified asphalt?

Ultimately, tires need to be re-designed for environmental safety, while maintaining standards for road safety and tire durability. A group of experts should be conferred to define environmental safety for tires. This definition should ultimately include the health of diverse members of aquatic ecosystems, as well as humans, over acute and chronic exposures, during both intended use and end-of-life re-use applications. In the meantime, we should evaluate among currently available tires which are 'best-in-class' that could be recommended for governmental and/or commercial vehicle fleets. Finally, safe disposal options for existing tires should be identified.

Jenifer K. McIntyre, Ph.D.
Assistant Professor | School of the Environment | Washington State University
Puyallup Research & Extension Center | Washington Stormwater Center
2606 W Pioneer Ave | Puyallup, WA 98371
Jen.mcintyre@wsu.edu | 253-445-4650

[Tables and Cited References to Follow]

Table 1. 6PPD-quinone aquatic toxicity in peer-reviewed literature. LC50 = median lethal concentration, C.L. = confidence limits

Species	pH	Conductivity (µS/cm)	Temp. (°C)	Exposure Time	Solution renewal	LC50 (µg/L; 95% C.L.)	Ref.
Oncorhynchus kisutch	7.6-7.8	1250-1300	10-12	24 h	None	0.79 (0.6-1.0)[a,*]	1
Oncorhynchus kisutch	7.6-7.8	1250-1300	10-12	24 h	None	0.10 (0.08-0.11)[a,+]	2
Danio rerio	7.7 ± 0.0	3090 ± 200	25.9 ± 0.1	96 h	48 h	>70[b,^]	3
Danio rerio	7.4 ± 0.1	ISO[c]	27 ± 1	24 h	24 h	308.7 (258.3-368.9)[d]	4
Oryzias latipes	7.9 ± 0.1	3420 ± 1100	24.4 ± 0.2	96 h	48 h	>40[b,^]	3
Daphnia magna	8.0-8.4	6380-6430	21.6-21.9	48 h	None	>60[b,^]	3
Hyallela azteca	8.0 ± 0.1	3100 ± 1100	23.5 ± 0.2	96 h	48 h	>90[b,^]	3
Salvelinus fontinalis	6.7 ± 0.1	131 ± 2.33[e]	10.3 ± 0.7	24 h	24 h	0.59 (0.48-0.63)[b,+]	5
Oncorhynchus mykiss	8.4 ± 0.5	132 ± 6.80[e]	12.8 ± 0.8	72 h	24 h	1.00 (0.95-1.05)[b,+]	5
Oncorhynchus mykiss	6.5 ± 0.0	143 ± 2	16 ± 1	96 h	48 h	2.26 (2.13-2.44)[a]	6
Salvelinus alpinus	8.4 ± 0.5	132 ± 6.80[e]	12.8 ± 0.8	96 h	24 h	>14.2[b,+]	5
Acipenser transmontanus	8.4 ± 0.5	132 ± 6.80[e]	12.8 ± 0.8	96 h	24 h	>12.7[b,+]	5
Gobiocypris rarus	8.0 ± 0.0	149 ± 2	25 ± 1	96 h	48 h	>500[a]	6

1 Tian et al. 2021
2 Tian et al. 2022
3 Hiki et al. 2021
4 Varshney et al. 2022
5 Brinkmann et al. 2022
6 Di et al. 2022

[a] Based on measured concentration at the start of exposure

[b] Time weighted average concentration

[c] ISO (International Standards Organization) Standard Fish Media

[d] Based on nominal concentrations

[e] Hardness as mg/L $CaCO_3$

[*] Concentrations measured using in-house standards without internal standard normalization. Tian et al. (2022) observed that use of a commercial standard yielded ~15-fold higher peak area response for the same 6PPD-quinone concentration in the UWT in-house standard, and 6PPD-Q recovery without internal standard normalization was ~60-70%.

[+] Concentrations measured using a commercial standard.

[^] Hiki et al. (2021) also created their own in-house standard and did not use an internal control when measuring exposure concentrations. Therefore, their reported concentrations may be overestimated, similar to Tian et al. 2021.

Table 2. 6PPD-Q concentrations in stormwater and surface waters

Location	**Water Type**	**Grab/Composite (duration)**	**6PPD-quinone Concentrations [ng/L]**	**Land Use**	**Ref.**
Seattle, WA, USA	Roadway runoff	Grab (24 h)	50-1270 ng/L*	Urban highway	1, 2
Los Angeles, CA, USA	Roadway runoff	Grab (unspecified)	270-400 ng/L *	Urban highway	1, 2
Seattle, WA, USA	Surface water (creeks during storm events)	Grab (unspecified) or composite (4 h)	<20-210 ng/L *	Highly urbanized residential watersheds (Miller Creek, Longfellow Creek, Thornton Creek)	1,2
San Francisco, CA, USA	Surface water (creeks during storm events)	Grab (unspecified)	65-230 ng/L*	Not available	1,2
Saskatoon, SK, Canada	Stormwater runoff (outfall sampling)	Grab (unique)	86-1400 ng/L+	Urban (residential / light industrial)	3
Saskatoon, SK, Canada	Snowmelt	Composite (8-12 locations in pile)	15-756 ng/L+	Urban (residential / light industrial)	3
Toronto, ON, Canada	Surface water (river during storm events)	Composite (42 h)	930-2850 ng/L+	Urban, downstream of high-traffic corridor (Don River)	4
Toronto, ON, Canada	Surface water (river during storm events)	Composite (42 h)	720 ± 260 ng/L (July 2020)+ 210 ± 20 ng/L (Aug 2020)+	Urban, downstream of high-traffic corridor/roadway input (Don River, Highland Creek)	5
Nanaimo, BC, Canada	Surface water (stream, during storm event)	Grab (unspecified)	96-112 ng/L	Not available	6
Nanaimo, BC, Canada	Stormwater	Grab (unspecified)	48-5580 ng/L	Not available	6
Australia	Urban tributary	Grab (unique)	0.44-88 ng/L	Sub-urban (low density residential, open space)	7
Michigan, USA	Road puddles	Grab (unique)	54-660 ng/L	Various	8
Michigan, USA	Surface water (during storm)	Grab (unique)	<9-37 ng/L	Various	8
Hong Kong	Urban runoff	Grab (unspecified)	21-243 ng/L	Dense traffic, urban area	9

1 (Tian *et al.* 2021)
2 (Tian *et al.* 2022)
3 (Challis *et al.* 2021)
4 (Johannessen *et al.* 2021)
5 (Johannessen *et al.* 2022)
6 (Monaghan *et al.* 2021)
7 (Rauert *et al.* 2022)
8 (Nedrich 2022)
9 (Cao *et al.* 2022)

*Concentration adjusted by 15-fold relative to originally reported concentration (Seattle roadway: 800-19000 ng/L; LA roadway: 4100-6100 ng/L; Seattle creeks: <300-3200 ng/L; San Francisco creeks: 1000-3500 ng/L) to account for response-factor difference in commercial vs. In-house analytical standard. Resulting concentrations may be underestimated by 30-40% because an internal standard was not used during sample extraction and quantification.

+Concentrations quantified using potentially impure in-house standard for 6PPD-quinone, and thus may overestimate actual concentration. However, Challis et al. 2021 noted potential underestimation of 50% due to matrix effects evaluated using an internal standard.

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CENTER FOR URBAN WATERS
UNIVERSITY of WASHINGTON | TACOMA

January 13, 2022

From: Katherine T. Peter, Edward P. Kolodziej
Center for Urban Waters
University of Washington-Tacoma

Subject: 6PPD in Stormwater Technical Memo - Characterizing 6PPD and 6PPD-Quinone in Stormwater

In August 2021, Dr. Ed Kolodziej at the Center for Urban Waters (CUW) began discussion with representatives of the Washington State Department of Ecology (Ecology) to produce technical memorandums describing the current state of knowledge and various data gaps around 6PPD-quinone. These memos would summarize current knowledge around the formation, characteristics, and fate of 6PPD-quinone, which is currently believed to be the "primary causal toxicant" for regional observations of coho mortality. The memos also would research gaps with respect to 6PPD-quinone research, management, and impacts. 6PPD-quinone is a newly discovered (by CUW and WSU researchers) environmental transformation product of the industrial antioxidant "6PPD", a compound that is used as an antioxidant and antiozonant in all vehicle tire rubbers globally to the best of our knowledge. Given its high lethality, consideration of the occurrence, fate, and transport of 6PPD-quinone is critical to understanding options for its management and control. This memo is expected to help summarize certain aspects of the current state of knowledge around 6PPD-quinone chemical properties and characteristics.

The Center for Urban Waters subsequently agreed to develop a technical memorandum that would include the following:

"CENTER will produce a technical memorandum or similar white paper on the evaluation of the chemical properties of 6PPD and 6PPD-quinone, known and estimated to date, such as Koc, Kow, Kd, sorption isotherms, solubility, and specific gravity.

Box 358438 | 326 East D St | Tacoma, WA 98421

253.254.7030 | urbanh2o@u.washington.edu | www.urbanwaters.org

Discuss and compare the results provided by EPA's EPI Suite for both compounds and describe verification work of these modeled results through laboratory analysis or other techniques. Discuss or recommend key parameters for Ecology to focus on for an evaluation of capture, containment, and treatment approaches and BMPs for stormwater. Summarize key properties that impact fate and transport of these compounds in surface or stormwater, included the mechanism(s) for capture and removal. If known, describe a surrogate compound with more data available for fate and transport that would have a similar fate and transport in stormwater systems."

We note that as a newly discovered compound, substantial and pervasive data gaps exist around 6PPD-quinone occurrence, chemical properties, environmental fate, transport, and toxicological effects across various endpoints. Additionally, little existing knowledge exists surrounding chemical characteristics and properties of quinones as a class of environmental pollutants. Therefore, at the current time, substantially more unknowns exist relative to knowns for 6PPD-quinone. While certain properties and aspects of fate and transport may be predicted computationally, studies to develop data derived parameters from direct observation have largely not been reported by CUW or any other research group to date. In contrast, 6PPD has been used for decades, so substantially more information is known concerning it. However, despite that long history of usage and the substantial industrial production of this compound, there still exist some considerable data gaps regarding 6PPD characteristics and fate, particularly with respect to its mass balance, formation of oxidative transformation products, and the toxicological relevance of such transformation products against acute and chronic endpoints.

1. Predicted chemical properties of 6PPD and 6PPD-quinone

Select predicted chemical properties of 6PPD and 6PPD-quinone derived from literature reports are summarized in **Table 1** below. We also note that a recent report by the California Department of Toxic Substances Control (DTSC) provides an excellent summary of 6PPD physicochemical properties, environmental fate, and current knowledge regarding fate/transport,[1] as do older OECD and OSPAR Commission reports from the European Union.[2,3] Reports generated by EPA EPI-Suite are provided as Appendices A and B.

Table 1. Predicted or estimated chemical properties of 6PPD and 6PPD-quinone. Note that many of these for 6PPD-quinone are computational predictions derived from software platforms.

Property	6PPD	6PPD-quinone	Reference
Molecular Formula	$C_{18}H_{24}N_2$	$C_{18}H_{22}N_2O_2$	--
logK_{ow}	4.68, 4.91, 5.6	3.98, 3.24, 4.1, (5-5.5*)	EPI-Suite[4], Marvin[5] and XLogP3[6], (Tian et al. 2021)[7]
logK_{oc}	4.36, 4.04	3.94	EPI-Suite[4], EPA CompTox[8]
Solubility in water	2.84 mg/L (25 °C), 1 mg/L (20 °C)	51.34 mg/L (25 °C), 67 ± 5 µg/L (pH 8, 23 °C)	6PPD: EPI-Suite[4], OECD[3] 6PPD-quinone: EPI-Suite[4], Hiki et al. 2021[9]
Vapor pressure	6.85×10^{-3} Pa	6.57×10^{-6} Pa	EPI-Suite[4]

*range of observed LC retention times

Both 6PPD and 6PPD-quinone are moderately non-polar compounds, indicating aspects of both dissolved phase and particle/solid associated behaviors are likely important to their fate. Estimates for logK_{ow} support that 6PPD-quinone is more polar than 6PPD, which is expected for an oxidized transformation product. For 6PPD-quinone, logK_{ow} values estimated by available prediction algorithms are lower than that initially estimated by Tian et al. (2021).[7] The estimate provided by Tian et al. (2021) relied on a previously developed linear regression between liquid chromatography-based retention time and logK_{ow} for a group of 260 chemical standards.[10] This instrument-specific estimate of relative polarity is subject to greater estimation error relative to algorithm-based estimates based upon structural identity. However, both estimate types provide a similar overall comparison, indicating the greater polarity of 6PPD-quinone relative to 6PPD. In general, this would imply more potential for dissolved phase environmental transport for 6PPD-quinone relative to 6PPD.

The estimated logK_{oc} values for 6PPD and 6PPD-quinone indicate a slightly higher likelihood of sorption to organic carbon for 6PPD, which would tend to reduce its mobility and increase treatment system performance for 6PPD in systems where equilibrium sorption dominates removal. A recent study by Huang et al. (2021) reported 6PPD and 6PPD-quinone on roadside dust and in-vehicle dust at 6PPD-quinone:6PPD concentration ratios of 0.1 – 8.5, although the relative contribution of 6PPD transformation to 6PPD-quinone on the dust surface versus separate sorption of the two compounds to dust remains uncertain.[11]

6PPD is poorly soluble in water and is known to be quite unstable in water due to rapid hydrolysis.[2,9] This instability is not surprising: as a redox-sensitive antioxidant, 6PPD has an inherent instability and propensity for reaction, especially when considering the widespread abundance of oxidant species in aqueous (and other) environmental systems. Reported timescales of reaction for 6PPD in aqueous systems can be as low as 1.9 h (the OSPAR-reported half-life of 6PPD in microbially active surface waters), with instability reportedly dependent on pH, ionic strength, heavy metals, and dissolved oxygen concentrations.[2] Acid-base speciation of 6PPD (based on an estimated pK_a of ~6-7 for the most basic amine in 6PPD) will yield both protonated (occurrence as a cation) and neutral species under typical circumneutral environmental conditions. As an ionizable chemical, this characteristic would tend to increase 6PPD solubility at neutral to lower pH values relative to that expected for neutral conditions. Overall, in our experience, accurate and reproducible 6PPD quantification in water is highly uncertain and challenging, and would require development of rapid, specialized methods and expertise. 6PPD is primarily expected to be sorbed to soil/dust, with negligible amounts in air, given its low vapor pressure. Despite its low vapor pressure, recent reports indicate a substantial quantity of both 6PPD and 6PPD-quinone present in house dusts and atmospheric PM2.5 particulates,[11,12] indicating a relatively high potential for human exposures via atmospheric aerosol pathways.

Although 6PPD-quinone is predicted by EPI-Suite to be much more soluble in water than 6PPD (51.34 mg/L),[4] Hiki et al. (2021) recently reported a 6PPD-quinone water solubility of 67 ± 5 µg/L in dechlorinated tap water (pH 8, 23 ºC).[9] Our preliminary observations at CUW laboratories also indicate low values for aqueous solubility and higher than expected propensities for impaired dissolution and formation of solid phases or sorption to various solid surfaces. Although 6PPD-quinone is expected to be neutral across the environmental pH spectrum, the impact of ionic strength, pH, oxidants, and other water chemistry parameters on 6PPD-quinone solubility and related fate/transport behaviors require further investigation. Like 6PPD, negligible amounts of 6PPD-quinone would be expected to volatilize. However, the expected distribution and partitioning rates of 6PPD-quinone between soil/dust, sediment, and water phases under various environmental conditions requires further investigation and is currently unknown.

2. Key properties to evaluate with respect to informing 6PPD-quinone fate, transport, and treatment in stormwater

There are several key parameters that should be evaluated to inform both analytical methods and environmental occurrence, fate, transport, and treatment of 6PPD-quinone. These are summarized in **Table 2** and described further below.

Table 2. Key parameters to evaluate for 6PPD and 6PPD-quinone.

Parameter [unit]	Additional Detail	Utility
Aqueous solubility [ng/L]	Evaluate dependency on environmental variables and constituents (e.g., pH, temperature, ionic strength, oxidants/reductants, dissolved organic carbon, etc.)	Fundamental to accurate detection
Half-life [months]		Informs environmental persistence
Reaction rate constant, k [s^{-1}]	Evaluate with respect to range of environmental and engineered oxidants (e.g., ozone, metals, chlorine, etc.) and possible transformation processes (photolysis, hydrolysis, biotransformation, redox reactions)	Informs environmental persistence, treatment approaches
Formation rate constants (6PPD to 6PPD-quinone), k [s^{-1}]	Evaluate for pure compound in air and water	Provides fundamental understanding of reactivity
Mass load in tire rubber [ng/g]	Evaluate across various tire rubber matrices, such as whole tires, skid marks, tire and road wear particles, recycled rubber products, etc. Many such parameters would be surface area normalized	Informs expected contaminant loads, release rates, and dominant sources
Diffusivity in tire rubber, D [m^2/s]		
Formation rate constant (6PPD to 6PPD-quinone) in tire rubber, k [s^{-1}]		
Leaching rates from tire rubber [ng / (g-h)]		
Partitioning coefficients (e.g., K_{aw}, $K_{w\text{-}sed}$, etc.)	Evaluate partitioning with respect to air, water, soil, sediment, rubber, and biological tissue	Informs environmental transport and fate, important for modeling efforts
Sorption coefficients (K_d, K_{oc})	Evaluate for stormwater treatment media (e.g., soil, compost, high performance BSM, etc.)	Inform BMP design, efficacy, maintenance, and longevity
Sorption rate [min^{-1}]		

In particular, understanding 6PPD-quinone aqueous solubility and stability in water, including the impact of environmental variables (e.g., pH, temperature, ionic strength, oxidants/reductants, and dissolved organic carbon) is critical fundamental knowledge relevant to accurate detection and subsequent environmental persistence. While we do not currently anticipate 6PPD-quinone to be a very long-lived pollutant (half-lives of days to months are probably expected in most environmental systems), little to nothing is known regarding its stability and reactivity with respect to various environmental constituents.

We also note that 6PPD and 6PPD-quinone are redox active and redox-sensitive chemicals (an inherent attribute of antioxidants), a characteristic that likely strongly contributes to their potential to induce toxic adverse effects in organisms and has substantial implications for environmental fate and reactivity. Experiments specifically designed to probe abiotic redox-sensitive behaviors and characteristics will be needed to understand the potential for oxidative polymerization, complexation, and addition type reaction endpoints. We also note that a relatively limited base of knowledge exists for quinone environmental pollutants relative to other pollutant structures, indicating some potential for unexpected or poorly documented fate outcomes relative to expectations for environmental pollutants. Therefore, a more limited series of analogous pollutants is available to fully define or predict aspects of environmental fate and instability related to redox-sensitive behaviors. Evaluating reactivity with respect to environmental oxidants (e.g., in air, in water, and on environmental surfaces) and engineered oxidants (e.g., chlorine, advanced oxidation processes, etc.) is needed as an aspect of understanding 6PPD and 6PPD-quinone environmental fate.

Additionally, limited data are currently available regarding the total load/lifetime of 6PPD within tire rubbers (including recycled rubber products), the diffusivity of 6PPD within tire rubber, transformation rates from 6PPD to 6PPD-quinone within tire rubber matrices or at tire rubber surfaces, and the rates at which 6PPD and 6PPD-quinone leach from tire rubber surfaces and move through phase boundaries. These parameters are relevant across whole tires, rubber embedded in roads (such as in skid marks), crumb rubbers and other recycled rubber materials, and dispersed tire and road wear particles (TRWP, which are heteroaggregates of tire rubbers and road minerals). Determining whether one or multiple of these matrices is a dominant source of 6PPD-quinone mass loads in stormwater or impacted receiving waters will be important for informing on-road and road-adjacent BMPs and source control efforts (e.g., street sweeping). This aspect of fate essentially involves the need to understand the broader mass balance of 6PPD in tires (e.g., formation and yields of key transformation products) and its potential to move (along with 6PPD-quinone) across interfacial boundaries into air, water, soil, and biological tissue. Without such information, leaching rates and time scales of pollution regeneration (for example, how long does it take for roadway runoff to re-pollute itself during or after storm events) cannot be accurately determined. It is also currently unclear if 6PPD and 6PPD-quinone are transporting within the environment and into receiving waters as dissolved chemicals, or whether transport of the residual rubber phases or of dusts/soils/aerosols with sorbed 6PPD and 6PPD-quinone, represent the primary transport vectors for these chemical pollutants.

To inform treatment system performance with respect to 6PPD-quinone removal from the dissolved phase, we anticipate that sorption characteristics and timescales are especially important parameters. In particular, many aspects of passive green stormwater infrastructure (GSI) like bioretention, bioswales, and bioinfiltration systems rely upon sorptive sequestration for initial pollutant removal. Therefore, the sorption capacity and K_d/K_{oc} values (e.g., developing sorption isotherms to understand mass or area normalized maximum mass removals, as well as evaluating possible desorption from treatment media) and sorption kinetics (e.g., partitioning rates) of various matrices that are anticipated to be important within stormwater treatment systems/BMPs (e.g., compost, soil, GAC, biochar, synthetic media) should be evaluated. These parameters are needed to help define treatment system sizes and flowrates (e.g., hydraulic retention times). In addition, evaluating 6PPD-quinone partitioning between aqueous and particulate phases (including tire wear particles and soil/road dust/sediments, of varying size fractions and with varied organic carbon content) will also inform best management practices with respect to management approaches focused on removal of suspended solids (and potentially rubber particulates) from stormwater (e.g., street sweeping, settling, etc.) relative to treatment of the dissolved phase.

BMP efficacy, maintenance needs, and longevity will also be impacted by the fate of captured 6PPD-quinone. For example, research is needed to determine whether 6PPD-quinone sorbed to treatment system media is further transformed and/or may be re-exported as hydrologic conditions vary (including wet/dry cycles) or over time as sorption capacity is exceeded. We might also expect that over the long term, microbial processes are ultimately responsible for mineralization of 6PPD and 6PPD-quinone that are captured in treatment systems and removed from the mobile phase. Rates and mechanisms of microbial biotransformation, including their extension to operating treatment systems and BMPs, would also need characterization. Given previous observations of tire-derived chemical concentrations and mass loads in receiving waters that indicate the existence of semi-infinite sources in urban watersheds, it will be important to understand the relative role of dissolved phase 6PPD-quinone in stormwater runoff vs. 6PPD-quinone that is released from in-place sediments/tire rubber deposits (e.g., on road surfaces, in dusts/sediments adjacent to roads, or in stormwater treatment or conveyance systems). BMPs might need to consider both rubber particulate removal and dissolved phase 6PPD-quinone removal to be fully protective, which may include multiple barrier or dual component conceptual approaches to treatment.

3. Surrogate compounds for 6PPD-quinone in stormwater systems

To date, there is no known or hypothesized surrogate compound that would be reasonably anticipated to accurately represent 6PPD-quinone fate and transport in stormwater systems. We anticipate that identification of surrogate compounds from within existing databases of "standard" stormwater pollutants may be especially difficult and unlikely because few commonly monitored stormwater pollutants have similar chemical characteristics or functional groups. For removal of residual rubber phases and particulates, TSS potentially might be correlated to the transport of bulk rubber microplastics as one source of 6PPD-quinone, although further investigation of the size distribution and densities of tire rubber particles is needed to assess this potential. As another common component of tire rubbers, zinc may also offer some correlative potential for 6PPDS-quinone, although it is uncommon that organic contaminants and metals exhibit similar environmental fate and transport outcomes. Additionally, methods for direct tire rubber particle quantification (i.e., by pyrolysis GC-MS) require further refinement because of inherent uncertainties in tire rubber chemical composition and relative amounts of natural and synthetic rubbers.[13] However, 6PPD-quinone contains nitrogen and oxygen groups that are atypical of stormwater contaminants subject to routine monitoring efforts. There is little reason to believe that metals, nutrients, turbidity, basic water quality parameters, and even other organics like PAHs might serve as accurate surrogates for 6PPD-quinone, given both its redox sensitivity and chemical composition.

Looking at existing data for emerging organic contaminants, Peter et al. (2018) previously developed a chemical fingerprint for the coho salmon urban runoff mortality syndrome (URMS) by isolating co-occurring contaminants in laboratory and field waters that were known to induce acute mortality.[14] This chemical fingerprint contained several tire-derived compounds, including 1,3-diphenylguanidine (DPG), hexa(methoxymethyl)melamine (HMMM) and other related MMM family members, and 1,3-dicyclohexylurea. Accordingly, the presence of these chemicals is generally indicative of tire rubber impacts on water quality. However, relationships between the relative abundance and fate/transport behavior of these contaminants and that of 6PPD-quinone remain largely undefined at the current time.

Johannessen et al. (2021) examined concentrations of DPG and 6PPD-quinone during storm events in a river in Toronto, Canada, finding that larger storm events (more precipitation) correlated to higher observed mass loads in the river.[15] This data reflected trends observed by Peter et al. (2020) for tire-derived chemicals (including DPG, but not 6PPD-quinone) in Miller Creek in Burien, WA, USA.[16] During a single storm event, Johannessen et al. (2021) observed both first-flush and middle-flush dynamics for DPG (i.e., mass loads rapidly entering the receiving water early in the storm event, followed by sustained loading with increasing runoff volumes during the hydrograph peak), but primarily observed middle-flush dynamics for 6PPD-quinone.[15] To date, this is the only available side-by-side data describing fate and transport behavior of 6PPD-quinone with respect to any other tire-derived or vehicle-derived contaminants. Additional sampling is necessary to evaluate whether the observations by Johannessen et al. (2021) are repeatable, and to evaluate the behavior of 6PPD-quinone relative to other tire-derived contaminants or pollutants that are regularly monitored in stormwater.
We here note one additional observation from our unpublished data: One additional detection from the chemical fingerprint reported by Peter et al. (2018) is notable: a compound initially reported as an *m/z* 333.2212 adduct was later determined by CUW to be a compound with a formula of *m/z* 275.1741 ($C_{16}H_{22}N_2O_2$). This compound (currently denoted TP 274) was recently detected as a 6PPD transformation product during laboratory-scale ozonation of both pure 6PPD and TWP, and was observed by retrospective analyses to be relatively abundant within roadway runoff samples (>10-fold higher peak area than 6PPD-quinone).[17] Thus, in retrospect, inclusion of TP 274 in the coho mortality chemical signature provided a direct link to tire rubber and 6PPD transformation products, thus indicating the primary chemical source of the coho mortality syndrome. Notably, detection of TP 274 in the 2019 EPA crumb rubber report[18] and by Klöckner et al.[19] in tire rubbers and road dust suggest its potential value as a chemical indicator for tire rubber and roadway runoff, as it can be both abundant and detectable by mass spectrometry even

in cases where 6PPD-quinone itself is not easily identifiable within bulk data due to matrix suppression. However, its utility as a direct and analytically viable surrogate chemical for the subsequent fate/transport of 6PPD-quinone requires additional investigation.

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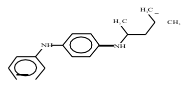
Appendix A. EPA EPI-Suite Report for 6PPD

```
CAS Number: 793-24-8
SMILES : N(c(ccc(Nc(cccc1)c1)c2)c2)C(CC(C)C)C
CHEM   : 1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N -phenyl-
MOL FOR: C18 H24 N2
MOL WT : 268.41
------------------------------ EPI SUMMARY (v4.11) ------------------------------
 Physical Property Inputs:
    Log Kow (octanol-water):   ------
    Boiling Point (deg C)  :   ------
    Melting Point (deg C)  :   ------
    Vapor Pressure (mm Hg) :   ------
    Water Solubility (mg/L):   ------
    Henry LC (atm-m3/mole) :   ------
```



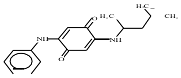
```
 Log Octanol-Water Partition Coef (SRC):
    Log Kow (KOWWIN v1.69 estimate) =  4.68
    Log Kow (Exper. database match) =  4.47
       Exper. Ref:  SAKURATANI,Y ET AL. (2007)

Boiling Pt, Melting Pt, Vapor Pressure Estimations (MPBPVP v1.43):
    Boiling Pt (deg C):  369.67  (Adapted Stein & Brown method)
    Melting Pt (deg C):  121.50  (Mean or Weighted MP)
    VP(mm Hg,25 deg C):  4.93E-006  (Modified Grain method)
    VP (Pa, 25 deg C) :  0.000658  (Modified Grain method)
    Subcooled liquid VP: 4.49E-005 mm Hg (25 deg C, Mod-Grain method)
                       : 0.00598 Pa (25 deg C, Mod-Grain method)

 Water Solubility Estimate from Log Kow (WSKOW v1.42):
    Water Solubility at 25 deg C (mg/L):  2.841
       log Kow used: 4.47 (expkow database)
       no-melting pt equation used

 Water Sol Estimate from Fragments:
    Wat Sol (v1.01 est) =  2.8262 mg/L

 ECOSAR Class Program (ECOSAR v1.11):
    Class(es) found:
       Neutral Organics

 Henrys Law Constant (25 deg C) [HENRYWIN v3.20]:
   Bond Method :   3.36E-009  atm-m3/mole  (3.41E-004 Pa-m3/mole)
   Group Method:   Incomplete
 For Henry LC Comparison Purposes:
   User-Entered Henry LC:  not entered
   Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]:
      HLC:  6.129E-007 atm-m3/mole  (6.210E-002 Pa-m3/mole)
      VP:   4.93E-006 mm Hg (source: MPBPVP)
      WS:   2.84 mg/L (source: WSKOWWIN)

 Log Octanol-Air Partition Coefficient (25 deg C) [KOAWIN v1.10]:
  Log Kow used:  4.47  (exp database)
  Log Kaw used:  -6.862  (HenryWin est)
      Log Koa (KOAWIN v1.10 estimate):  11.332
      Log Koa (experimental database):  None

 Probability of Rapid Biodegradation (BIOWIN v4.10):
   Biowin1 (Linear Model)         :   0.2804
   Biowin2 (Non-Linear Model)     :   0.0564
 Expert Survey Biodegradation Results:
   Biowin3 (Ultimate Survey Model):   2.3581  (weeks-months)
   Biowin4 (Primary Survey Model) :   3.2486  (weeks       )
 MITI Biodegradation Probability:
   Biowin5 (MITI Linear Model)    :  -0.1043
   Biowin6 (MITI Non-Linear Model):   0.0069
 Anaerobic Biodegradation Probability:
   Biowin7 (Anaerobic Linear Model): -0.9047
 Ready Biodegradability Prediction:   NO
```

```
Hydrocarbon Biodegradation (BioHCwin v1.01):
    Structure incompatible with current estimation method!

 Sorption to aerosols (25 Dec C)[AEROWIN v1.00]:
  Vapor pressure (liquid/subcooled):  0.00599 Pa (4.49E-005 mm Hg)
  Log Koa (Koawin est  ): 11.332
   Kp (particle/gas partition coef. (m3/ug)):
       Mackay model           :  0.000501
       Octanol/air (Koa) model:  0.0527
   Fraction sorbed to airborne particulates (phi):
       Junge-Pankow model     :  0.0178
       Mackay model           :  0.0385
       Octanol/air (Koa) model:  0.808

 Atmospheric Oxidation (25 deg C) [AopWin v1.92]:
   Hydroxyl Radicals Reaction:
      OVERALL OH Rate Constant = 226.4928 E-12 cm3/molecule-sec
      Half-Life =     0.047 Days (12-hr day; 1.5E6 OH/cm3)
      Half-Life =     0.567 Hrs
   Ozone Reaction:
      No Ozone Reaction Estimation
   Fraction sorbed to airborne particulates (phi):
      0.0282 (Junge-Pankow, Mackay avg)
      0.808 (Koa method)
    Note: the sorbed fraction may be resistant to atmospheric oxidation

 Soil Adsorption Coefficient (KOCWIN v2.00):
      Koc    :  2.305E+004  L/kg (MCI method)
      Log Koc:  4.363       (MCI method)
      Koc    :  2151  L/kg (Kow method)
      Log Koc:  3.333       (Kow method)

 Aqueous Base/Acid-Catalyzed Hydrolysis (25 deg C) [HYDROWIN v2.00]:
    Rate constants can NOT be estimated for this structure!

 Bioaccumulation Estimates (BCFBAF v3.01):
   Log BCF from regression-based method = 2.616 (BCF = 413.3 L/kg wet-wt)
   Log Biotransformation Half-life (HL) = -0.1137 days (HL = 0.7697 days)
   Log BCF Arnot-Gobas method (upper trophic) = 2.468 (BCF = 293.8)
   Log BAF Arnot-Gobas method (upper trophic) = 2.468 (BAF = 294)
       log Kow used: 4.47 (expkow database)

 Volatilization from Water:
    Henry LC:  3.36E-009 atm-m3/mole  (estimated by Bond SAR Method)
    Half-Life from Model River: 2.855E+005  hours   (1.19E+004 days)
    Half-Life from Model Lake : 3.114E+006  hours   (1.298E+005 days)

 Removal In Wastewater Treatment:
    Total removal:              54.44  percent
    Total  biodegradation:     0.51    percent
    Total  sludge  adsorption:  53.93  percent
    Total to Air:               0.00  percent
      (using 10000 hr Bio P,A,S)

 Level III Fugacity Model: (MCI Method)
          Mass Amount    Half-Life    Emissions
           (percent)        (hr)       (kg/hr)
   Air       0.0146         1.13         1000
   Water     10.8           900          1000
   Soil      75             1.8e+003     1000
   Sediment  14.2           8.1e+003     0
     Persistence Time: 1.71e+003 hr

 Level III Fugacity Model: (MCI Method with Water percents)
          Mass Amount    Half-Life    Emissions
           (percent)        (hr)       (kg/hr)
   Air       0.0146         1.13         1000
   Water     10.8           900          1000
```

```
    water     (10.4)
    biota     (0.0154)
    suspended sediment (0.36)
  Soil      75               1.8e+003     1000
  Sediment  14.2             8.1e+003     0
    Persistence Time: 1.71e+003 hr

Level III Fugacity Model: (EQC Default)
          Mass Amount    Half-Life    Emissions
           (percent)        (hr)       (kg/hr)
  Air       0.0155          1.13         1000
  Water     11.9            900          1000
    water     (11.7)
    biota     (0.0172)
    suspended sediment (0.212)
  Soil      79.7            1.8e+003     1000
  Sediment  8.34            8.1e+003     0
    Persistence Time: 1.61e+003 hr
```

Appendix B. EPA EPI-Suite Report for 6PPD-quinone

```
CAS Number:
SMILES : CC(C)CC(C)NC1=CC(=O)C(=CC1(=O))Nc2ccccc2
CHEM   :
MOL FOR: C18 H22 N2 O2
MOL WT : 298.39
------------------------------ EPI SUMMARY (v4.11) ------------------------------
 Physical Property Inputs:
    Log Kow (octanol-water):   ------
    Boiling Point (deg C)  :   ------
    Melting Point (deg C)  :   ------
    Vapor Pressure (mm Hg) :   ------
    Water Solubility (mg/L):   ------
    Henry LC (atm-m3/mole) :   ------
```



```
 Log Octanol-Water Partition Coef (SRC):
    Log Kow (KOWWIN v1.69 estimate) =  3.98

Boiling Pt, Melting Pt, Vapor Pressure Estimations (MPBPVP v1.43):
    Boiling Pt (deg C):  430.19  (Adapted Stein & Brown method)
    Melting Pt (deg C):  169.18  (Mean or Weighted MP)
    VP(mm Hg,25 deg C):  4.93E-008  (Modified Grain method)
    VP (Pa, 25 deg C) :  6.57E-006  (Modified Grain method)
    Subcooled liquid VP: 1.52E-006 mm Hg (25 deg C, Mod-Grain method)
                       : 0.000202 Pa (25 deg C, Mod-Grain method)

 Water Solubility Estimate from Log Kow (WSKOW v1.42):
    Water Solubility at 25 deg C (mg/L):  51.34
       log Kow used: 3.98 (estimated)
       no-melting pt equation used

 Water Sol Estimate from Fragments:
    Wat Sol (v1.01 est) =  1317.4 mg/L

 ECOSAR Class Program (ECOSAR v1.11):
    Class(es) found:
       Aliphatic Amines
       Quinones

 Henrys Law Constant (25 deg C) [HENRYWIN v3.20]:
   Bond Method :   1.12E-013  atm-m3/mole  (1.14E-008 Pa-m3/mole)
   Group Method:   Incomplete
 For Henry LC Comparison Purposes:
   User-Entered Henry LC:  not entered
   Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]:
      HLC:  3.770E-010 atm-m3/mole  (3.820E-005 Pa-m3/mole)
      VP:   4.93E-008 mm Hg (source: MPBPVP)
      WS:   51.3 mg/L (source: WSKOWWIN)

 Log Octanol-Air Partition Coefficient (25 deg C) [KOAWIN v1.10]:
  Log Kow used:  3.98  (KowWin est)
  Log Kaw used:  -11.339  (HenryWin est)
      Log Koa (KOAWIN v1.10 estimate):  15.319
      Log Koa (experimental database):  None

 Probability of Rapid Biodegradation (BIOWIN v4.10):
   Biowin1 (Linear Model)         :   0.6673
   Biowin2 (Non-Linear Model)     :   0.2437
 Expert Survey Biodegradation Results:
   Biowin3 (Ultimate Survey Model):   2.4063  (weeks-months)
   Biowin4 (Primary Survey Model) :   3.3126  (days-weeks  )
 MITI Biodegradation Probability:
   Biowin5 (MITI Linear Model)    :   0.0470
   Biowin6 (MITI Non-Linear Model):   0.0117
 Anaerobic Biodegradation Probability:
   Biowin7 (Anaerobic Linear Model): -0.9987
 Ready Biodegradability Prediction:   NO

Hydrocarbon Biodegradation (BioHCwin v1.01):
```

```
   Structure incompatible with current estimation method!

Sorption to aerosols (25 Dec C)[AEROWIN v1.00]:
 Vapor pressure (liquid/subcooled):  0.000203 Pa (1.52E-006 mm Hg)
 Log Koa (Koawin est  ): 15.319
  Kp (particle/gas partition coef. (m3/ug)):
      Mackay model           :  0.0148
      Octanol/air (Koa) model:  512
  Fraction sorbed to airborne particulates (phi):
      Junge-Pankow model     :  0.348
      Mackay model           :  0.542
      Octanol/air (Koa) model:  1

Atmospheric Oxidation (25 deg C) [AopWin v1.92]:
  Hydroxyl Radicals Reaction:
     OVERALL OH Rate Constant = 144.9250 E-12 cm3/molecule-sec
     Half-Life =     0.074 Days (12-hr day; 1.5E6 OH/cm3)
     Half-Life =     0.886 Hrs
  Ozone Reaction:
     OVERALL Ozone Rate Constant =     0.350000 E-17 cm3/molecule-sec
     Half-Life =     3.274 Days (at 7E11 mol/cm3)
     Half-Life =     78.583 Hrs
  Fraction sorbed to airborne particulates (phi):
     0.445 (Junge-Pankow, Mackay avg)
     1 (Koa method)
   Note: the sorbed fraction may be resistant to atmospheric oxidation

Soil Adsorption Coefficient (KOCWIN v2.00):
     Koc    :  8481  L/kg (MCI method)
     Log Koc:  3.928       (MCI method)
     Koc    :  8697  L/kg (Kow method)
     Log Koc:  3.939       (Kow method)

Aqueous Base/Acid-Catalyzed Hydrolysis (25 deg C) [HYDROWIN v2.00]:
   Rate constants can NOT be estimated for this structure!

Bioaccumulation Estimates (BCFBAF v3.01):
  Log BCF from regression-based method = 2.291 (BCF = 195.4 L/kg wet-wt)
  Log Biotransformation Half-life (HL) = -0.4467 days (HL = 0.3575 days)
  Log BCF Arnot-Gobas method (upper trophic) = 2.120 (BCF = 131.9)
  Log BAF Arnot-Gobas method (upper trophic) = 2.120 (BAF = 131.9)
      log Kow used: 3.98 (estimated)

Volatilization from Water:
   Henry LC:  1.12E-013 atm-m3/mole  (estimated by Bond SAR Method)
   Half-Life from Model River:  9.03E+009  hours   (3.763E+008 days)
   Half-Life from Model Lake : 9.851E+010  hours   (4.105E+009 days)

Removal In Wastewater Treatment:
   Total removal:              29.16  percent
   Total  biodegradation:     0.31    percent
   Total  sludge  adsorption:  28.84  percent
   Total to Air:                0.00  percent
     (using 10000 hr Bio P,A,S)

Level III Fugacity Model: (MCI Method)
          Mass Amount    Half-Life    Emissions
           (percent)        (hr)       (kg/hr)
  Air       1.33e-006       1.73         1000
  Water     10.4            900          1000
  Soil      84.4            1.8e+003     1000
  Sediment  5.13            8.1e+003     0
    Persistence Time: 1.94e+003 hr

Level III Fugacity Model: (MCI Method with Water percents)
          Mass Amount    Half-Life    Emissions
           (percent)        (hr)       (kg/hr)
  Air       1.33e-006       1.73         1000
```

```
  Water     10.4            900          1000
    water     (10.3)
    biota     (0.00491)
    suspended sediment (0.131)
  Soil      84.4            1.8e+003     1000
  Sediment  5.13            8.1e+003     0
    Persistence Time: 1.94e+003 hr

Level III Fugacity Model: (EQC Default)
          Mass Amount    Half-Life    Emissions
           (percent)        (hr)       (kg/hr)
  Air       1.36e-006       1.73         1000
  Water     11              900          1000
    water     (10.9)
    biota     (0.0052)
    suspended sediment (0.064)
  Soil      86.6            1.8e+003     1000
  Sediment  2.47            8.1e+003     0
    Persistence Time: 1.89e+003 hr
```

CENTER FOR URBAN WATERS
UNIVERSITY of WASHINGTON | TACOMA

January 13, 2022

From: Katherine T. Peter, Edward P. Kolodziej
Center for Urban Waters
University of Washington-Tacoma

Subject: **6PPD Research Assessment Technical Memo – Status and Next Steps for Research on 6PPD-Quinone to Manage Impacts from Stormwater**

In August 2021, Dr. Ed Kolodziej at the Center for Urban Waters (CUW) began discussion with representatives of the Washington State Department of Ecology (Ecology) (e.g., Brandi Lubliner) to produce technical memorandums describing the current state of knowledge and various data gaps around 6PPD-quinone. These memos would summarize current knowledge around the formation, characteristics, and fate of 6PPD-quinone, which is currently believed to be the "primary causal toxicant" for regional observations of coho mortality. The memos also would research gaps with respect to 6PPD-quinone research, management, and impacts. 6PPD-quinone is a newly discovered (by CUW and Washington State University (WSU) researchers) environmental transformation product of the industrial antioxidant "6PPD", a compound that is used as an antioxidant and antiozonant in all vehicle tire rubbers globally to the best of our knowledge. Given its high lethality, consideration of the occurrence, fate, and transport of 6PPD-quinone is critical to understanding options for management and control. This memo is expected to help summarize knowledge of and short- and long-term research needs regarding 6PPD-quinone.

The Center for Urban Waters subsequently agreed to develop a technical memorandum that would include the following components:

"Provide a brief background and timeline of UW - Tacoma's involvement on stormwater toxicity, impacts, and stormwater toxicity treatment studies. Describe research questions and data needs to control or limit 6PPD and 6PPD-quinone contamination of stormwater and

surface waters from the known sources of these compounds. Describe research needs or questions to characterize different sources, land uses, treatments, or management options for nonpoint and point source stormwater. Briefly describe active university research on stormwater or 6PPD-quinone, such as treatment BMPs and modelling. Data gaps and future information needs are anticipated to be wide and ranging therefore characterization of needs should be done in the next two, five, and ten year timeframes."

1. <u>Background of UW Tacoma Center for Urban Waters stormwater research</u>

In 2014, Ed Kolodziej joined the faculty at University of Washington (Tacoma/Seattle) and began building a research group focused on water quality characterization at the Center for Urban Waters (CUW). Dr. Kolodziej soon became involved in the on-going collaborative research effort by Washington State University Puyallup Research & Extension Center (WSU), the NOAA Northwest Fisheries Science Center (NOAA), and the U.S. Fish & Wildlife Service (USFWS) to better understand ongoing coho salmon (*Oncorhynchus kisutch*) mortality events linked to urban stormwater exposure (i.e., "urban runoff mortality syndrome" or "URMS"). Initial research efforts at CUW focused on development of advanced analytical methods that leveraged liquid chromatography coupled to high resolution mass spectrometry (LC-HRMS) to perform broad-scope screening of organic contaminants in environmental samples, including both water and fish tissues. Relative to targeted analytical methods, LC-HRMS enables non-targeted analyses that do not require *a priori* knowledge of the contaminants of interest, instead allowing researchers to detect as many chemicals as possible (within the limitations of certain sample processing and analytical method choices) and subsequently use advanced data reduction approaches to prioritize chemicals of interest for identification.

These methods were first described in Du et al. (2017), along with optimized water and fish tissue extraction methods.[1] Du et al. (2017) analyzed roadway runoff samples and fish tissue samples collected during controlled exposures of adult coho salmon,[1,2] leading to the identification of several to many contaminants these samples. Notably, acetanilide (a toxic compound used industrially and in rubber vulcanization) was detected in runoff and in runoff-exposed fish gill and liver.[1] Diphenylguanidine, a compound also used in rubber vulcanization, also was widely present, supporting the importance of roadway derived chemicals in affected receiving waters. However, given the limited number of chemical identifications (from the thousands of total detections) achieved during this initial effort, it was evident that substantial further refinement and prioritization was necessary to isolate the URMS causal toxicant(s).

Beginning in fall 2015, CUW researchers began collaborating with local citizen scientists (Miller-Walker Community Salmon Investigation, Puget Soundkeeper) that conduct daily surveys in regional creeks (Miller Creek, Walker Creek, Longfellow Creek) during the fall storm and salmon spawning season to count live and dead coho and chum salmon, document instances of URMS (identified based on egg retention in female coho), and mark/count redds. Citizen scientists were asked to alert CUW researchers if they observed symptomatic salmon in distress (i.e., actively dying) to allow for water and tissue collection during actual mortality events. Through these collaborations, CUW researchers collected and analyzed paired water and fish tissue samples from field observations of URMS across 2016 – 2020 years. These samples provided a valuable link between laboratory observations that roadway runoff replicated the symptomology of the mortality syndrome[2] and water quality during actual field mortality events.

In particular, these data allowed CUW researchers to develop a chemical "signature" or "fingerprint" for the mortality syndrome that consisted of all chemicals that co-occurred in both laboratory and field water samples that were linked to mortality events.[3] In the absence of a known causal toxicant at the time, the coho mortality chemical signature provided a surrogate chemical metric that could be tracked in other waters, through treatment systems, and used to evaluate potential sources of chemicals linked to URMS. The mortality signature contained 57 chemicals in total, of which 32 were ultimately identified: polyethylene glycols (PEGs), polypropylene glycols (PPGs), octylphenol ethoxylates (OPEOs), bicyclic amines (e.g., diphenylguanidine, dicyclohexylurea), and a family of (methoxymethyl)melamine (MMM; e.g., hexa-MMM, tetra-MMM) compounds.[3] Additionally, based on a concurrent effort between Washington State University-Puyallup (WSUP) and CUW to characterize vehicle-derived contaminant sources to roadway runoff, the occurrence and relative abundance of the coho mortality signature in several complex mixture sources such as motor oil, antifreeze, and tire wear particles was evaluated with respect to the mortality signature in waters linked to coho mortality events.[3] Results indicated the closest chemical similarity between mortality-linked waters and tire tread wear particle (TWP) leachates, providing early evidence of the importance of tire wear particles as a dominant source of contaminants in roadway runoff and as a potential toxicant source.[3] The importance of TWP leachates as a source of the toxicant(s) driving URMS was then confirmed by exposures of juvenile coho salmon and subsequently, concurrent exposures of adult coho and chum salmon to TWP leachate, which replicated the symptomology observed during both field mortality events and laboratory exposures to roadway runoff.[4] These exposures clearly indicated that coho salmon were extremely sensitive to unknown toxicant/s present in TWP leachate.

By late 2017, an extensive effort was underway to isolate the causal toxicant(s) from TWP leachates, using fractionation (i.e., physical/chemical manipulations to separate the thousands of chemicals present in TWP leachate into smaller groups, or fractions, based on their physico-chemical properties) and effects-directed analysis (exposures of juvenile coho salmon to determine which fraction(s) were toxic)). This effort, in close collaboration with WSU, required hundreds of fish and thousands of person-hours to develop and apply new methods and fractionation techniques, conduct exposures, analyze samples, and identify candidate chemical toxicants. Ultimately, in late 2019-early 2020, these collaborative efforts allowed CUW researchers to successfully isolate and identify a single chemical as the primary causal toxicant for URMS – 6PPD-quinone, a newly discovered oxidative transformation product of the ubiquitous tire rubber antiozonant 6PPD.[5] CUW researchers have since built on the discovery of 6PPD-quinone, including development of a targeted analytical method for 6PPD-quinone[6] (currently submitted to Ecology for accreditation) and on-going efforts to understand both fundamental properties and environmental occurrence/dynamics of 6PPD-quinone.

In parallel with research efforts specifically focused on URMS toxicant identification, CUW research projects have also sought to address a range of related questions about stormwater quality, impacts, and treatment. These include studies employing both targeted and non-targeted analytical approaches, including extensive retrospective analysis of archived HRMS data and samples, to examine the efficacy and of stormwater treatment systems, such as bioretention barrels, compost-amended bioswales,[7] and engineered hyporheic zones.[8] Additionally, a targeted LC-MS/MS method was developed for a suite of 39 stormwater tracers[9] (also currently submitted to Ecology for accreditation) that includes several tire-derived organic contaminants as an improved metric of urban stormwater composition which includes representative organic contaminants. Both targeted and non-targeted analytical methods have been applied over the past several years to understand contaminant occurrence and dynamics in Puget Sound watersheds, with respect to storm hydrographs and land-use characteristics. For example, CUW researchers evaluated contaminant pollutographs (concentration and mass load profiles as a function of time) with respect to the hydrograph in Miller Creek, a representative small urban watershed.[10] Results indicated that emerging organic contaminants (including many tire-derived chemicals) exhibited both "first flush" and "middle flush" dynamics, where concentrations in the receiving water were rapidly elevated (before the peak of the storm hydrograph) and remained elevated through and after the hydrograph peak.[10] These observations pointed to the potential role of "semi-infinite" stagnant contaminant sources in urban watersheds, such as tire wear particle residuals in stormwater conveyance systems or watershed sediments.[10] Such efforts are currently being extended to include 6PPD-quinone and other roadway tracers to better understand linkages between roadway runoff and water quality composition during baseflow and storm events, including identification of key source zones within watersheds.

2. Research questions and data needs to characterize, control, and manage 6PPD and 6PPD-quinone

Research needs are summarized in **Table 1** below, with respect to 2, 5, and 10+ year timeframes.

Table 1. Research needs regarding 6PPD and 6PPD-quinone over the next 0-10+ years.

Research Category	0-2 years	2-5 years	5-10+ years
Analytical Methods	• Develop sample processing methods for 6PPD-quinone analysis in soils, sediments, dusts, aerosols, and biological tissues	• Develop quantitative 6PPD sample processing and analytical methods, including analysis of similar or alternative antioxidants	• High throughput LC-HRMS screening and identification of stormwater contaminants and linkages to key sources
Sources	• Evaluate 6PPD-quinone mass loads across various tire types (passenger car, light truck, commercial truck) and tire components (tread, sidewall, etc.) • Develop representative tire mixture to support source tracking and ecotoxicological studies • Evaluate aqueous leaching rates of 6PPD-quinone from tire rubber (including impact of liquid/solid ratios, environmental variables/constituents, turbulent vs. static flow, etc.)	• Evaluate 6PPD and 6PPD-quinone mass loads and aqueous leaching rates across various types of environmentally relevant rubber deposits, such as whole tires, skid marks, tire and road wear particles, recycled rubber products (e.g., crumb rubber), etc. • Determine 6PPD and 6PPD-quinone diffusivity in tire rubbers (long-term release rate) • Assess potential for non-tire 6PPD and 6PPD-quinone sources (e.g. crumb rubber playing fields, building materials, etc) based on production/manufacturing data • Characterize and report tire rubber chemical composition and linkages to water quality	• Assess 6PPD-quinone and TWP contaminant releases from recycled and scrap tire products • Evaluate long term trends in TWP chemical composition and link such trends to receiving water quality • Perform regional and national comparisons with respect to management and source control efforts • Identify and promote best in class options for passenger and commercial tires; implement purchase of salmon safe tires
Fate & Transport	• Determine 6PPD-quinone solubility (aqueous, organic solvents; impact of environmental variables/constituents) • Evaluate 6PPD-quinone stability and half-life (aqueous, organic	• Identify additional 6PPD transformation pathways (ozonation, hydrolysis, etc.) and resulting transformation products • Evaluate the role of TWP particles in subsequent environmental transport of TWP-derived chemicals	• Identify transformation products of alternative anti-ozonants • Evaluate long term trends on concentrations and mass loads in relation to management and source control efforts

	solvents; impact of environmental variables/constituents) • Assess whether other PPDs form PPD-quinones • Ozonation kinetics and yields o pure 6PPD to 6PPD-quinone o 6PPD in tire rubber to 6PPD-quinone	• Evaluate reactivity (reaction rates, end-products) of 6PPD-quinone (and other 6PPD transformation products) with respect to a range of environmental and engineered oxidants under varied environmental conditions • Evaluate 6PPD-quinone partitioning with respect to environmental matrices (water, soil, sediment, air, biological tissues), including persistence and potential for (bio)accumulation	• Extend fate and transport knowledge from aqueous systems to soils, sediments, and atmospheric aerosol transport pathways. • Develop mechanistic and predictive insights for fate and reactivity of PPD industrial chemicals
Environmental Occurrence	• Environmental occurrence of 6PPD, 6PPD-quinone, and related transformation products (roadway runoff, surface waters, road dust, soils, sediments) • Evaluate 6PPD-quinone pollutograph behavior to understand contaminant occurrence, transport, and risk profile in receiving waters during stormflow conditions • Initial identification of high risk locations and time periods	• Evaluate relative importance of 6PPD-quinone “transport pathways” (e.g., stormwater outfall pipes vs. overland flow vs. TWP deposits in pipes vs. TWP deposits in road-side soils, detention basins, stagnant waters, freshwater sediments, or stormwater treatment systems) • Evaluate relationship between tire tread wear particle (TWP) concentrations and TSS in stormwater, including 6PPD-quinone loads • Relate occurrence data to land-use parameters (e.g., road types, urbanization levels) to begin predictive modeling and optimize management efforts	• Monitor and evaluate long term trends in receiving water quality, relate to land use and management efforts • Attain predictive capabilities for relative water quality within and across watersheds, and as a function of management and source control efforts
Human & Environmental Health Risk	• Screen 6PPD-quinone as a risk to human health • Evaluate toxicity of 6PPD-quinone to aquatic species other than coho salmon	• Identify pathways for human exposure to 6PPD-quinone and quantify exposures • Validate toxicity mechanism for 6PPD-quinone in coho salmon, translate to in vitro biological screening techniques	• Evaluate potentials for sub-lethal toxicity impacts in other species • Determine whether alternative anti-ozonants are a risk to human and ecological health

	• Identify mechanisms of acute toxicity	• Evaluate potentials for sub-lethal toxicity impacts in coho salmon and other salmonids • Assess toxicity of other PPD-quinones • Evaluate toxicity of alternative anti-ozonants and their transformation products	
Treatment & Management	• Evaluate sorption coefficients, capacities, rates for stormwater treatment media (soil, compost, high performance BSM, etc.) • Develop an approach to prioritize locations (watersheds, land-use types, road types, etc.) and treatment options for 6PPD-quinone management	• Identify and optimize BMPs and treatment systems for 6PPD-quinone removal to protective levels (e.g., < 40-50 ng/L) • Determine hydraulic retention times (i.e., sizing) of stormwater treatment systems needed for 6PPD-quinone removal to protective levels • Evaluate treatment system longevity, including potential for 6PPD-quinone export • Determine treatment system maintenance needs, such as sediment/TWP removal or media replacement • Evaluate efficacy of non-treatment BMPs (e.g., street sweeping) • Develop a method to evaluate and certify BMPs for treatment of 6PPD-quinone (i.e. integrate 6PPD-quinone treatment performance into TAPE program)	• Evaluate long term performance of treatment systems, including effect of various maintenance efforts • Identify and widely implement best in class options for treatment and management efforts

3. Active University Research on Stormwater or 6PPD-Q and alternatives

Researchers at CUW and WSU are currently working to maintain their global leadership on these topics by pursuing several lines of research regarding 6PPD-quinone and the broad role of tire rubber derived chemicals on water quality and impacts on salmonids. First, CUW has developed a targeted LC-MS/MS analytical method based on isotope dilution techniques for 6PPD-quinone quantification in water samples;[6] this analytical method was submitted to Ecology for accreditation in June 2021. This method is currently being applied to quantify 6PPD-quinone concentration in samples collected both by CUW researchers and by other institutions (including from on-going WSU studies examining 6PPD-quinone toxicity). CUW researchers are currently leveraging sample collections occurring for other projects to evaluate 6PPD-quinone occurrence and dynamics in representative regional surface waters and the efficacy of several stormwater treatment systems, although no substantial newly funded projects are currently specifically focused on evaluating environmental occurrence or treatment of 6PPD-quinone in detail. Select samples from previous studies (e.g., compost-amended bioswale influent/effluent samples,[7] roadway runoff,[3,5] regional surface water samples[5,10]) have also been retrospectively analyzed for 6PPD-quinone, although results should be considered semi-quantitative because sample processing methods were not optimized at the time for 6PPD-quinone analysis. Nevertheless, valuable relative comparisons along with reasonably accurate concentration data can typically be derived from these sample types.

Notably, comparisons between a commercial standard for 6PPD-quinone (HPC Standards Inc., available in March 2020) and the CUW in-house standard prepared via purification of tire leachate and/or ozonated 6PPD revealed a substantially higher (~15 fold) peak area response for the commercial standard relative to the in-house standard used for our prior research efforts. This difference was attributed to an unexpected loss of 6PPD-quinone mass in in-house stocks due to previously unobserved instability (e.g. oxidative polymerization) or solubility issues with 6PPD-quinone. To understand possible causes, laboratory studies are on-going to examine 6PPD-quinone solubility in aqueous and solvent systems, stability during sample handling (e.g., stock solution preparation, filtering, storage), sorption to a range of common laboratory materials (e.g., tubing, stoppers, containers), and possible oxidative polymerization or addition reactions typical of similar redox-active compounds. Such efforts are expected to be critical to both analytical accuracy and key aspects of environmental fate for 6PPD-quinone. While all prior relative comparisons of environmental occurrence and toxicity remain accurate, absolute values for both environmental concentrations and LC50 values will decrease by approximately one order of magnitude. Publication of such results is expected shortly.

Researchers at CUW are also investigating the ozonation of both pure 6PPD phases and 6PPD in tire wear particles through controlled laboratory studies. These efforts include evaluating ozonation reaction rates and yields for 6PPD-quinone from 6PPD, examining the 6PPD to 6PPD-quinone transformation pathway, and identification of other 6PPD transformation products, including evaluation of their environmental occurrence. Similar initial observational efforts are being extended to other PPDs, including with respect to discussions led by State of California management agencies focused on potential alternatives to 6PPD within tire rubbers.

Finally, through the "Clean Cars" effort focused on consumer product safety (led by Craig Manahan Ecology), CUW will quantify the concentration of surface-available 6PPD-quinone and screen for other tire-derived chemicals/transformation products in tire wear particles. The concentration/mass load and variability of available 6PPD-quinone in different types of new and used tires (passenger car, light truck, commercial truck) will be evaluated beginning in 2022. Experiments to characterize the leaching dynamics of 6PPD-quinone from TWPs as a function of time and environmental variables will also be conducted. Additionally, samples from studies conducted by WSU researchers to understand changes in 6PPD-quinone toxicity to coho salmon with respect to various environmental variables (e.g., pH, temperature, ionic strength) will be analyzed at CUW.

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Appendix E.

Stormwater Work Group 6PPD Subgroup Recommendations

Stormwater Work Group 6PPD Subgroup

Findings and Recommendations

July 7, 2022

Background

This subgroup convened in April 2021 to discuss what is known about the stormwater management needs and options to address 6PPD-quinone, the chemical now known to originate from 6PPD in motor vehicle tires and to cause coho pre-spawn mortality. The subgroup hosted a series of discussions through July 2022 to learn and discuss what is known about 6PPD-quinone and its impacts to biota, and how that information relates to stormwater best management practices (BMPs).

Overarching Questions

What do natural resource managers need to know about 6PPD-quinone?

- How effectively do current stormwater treatment BMPs (besides bioretention using the 60:40 mix) remove 6PPD and 6PPD-quinone?
- What is the geographic scope of the problem and where should we focus retrofits?
- What are the chemical and physical characteristics of 6PPD-quinone, including fate and transport?
- To what extent can maintenance (such as street sweeping, catch basin cleaning, and line cleaning) or other stormwater source controls reduce transport from roadways to water bodies?

What else will be helpful for us to know about 6PPD-quinone?

- What are the sub-lethal effects on other species and at what concentrations?
- What progress are we making towards approved lab standards and sampling methods?

Key Findings

This is a new chemical discovery and research is needed to gather information to answer our questions, particularly about environmental fate and transport of 6PPD and 6PPD-quinone.

About chemistry and treatment and source control of 6PPD and 6PPD-quinone in stormwater:

- Filtration, sorption, and adsorption are most likely to effectively remove 6PPD and 6PPD-quinone.
- Tire particles are likely a continuous source of 6PPD that can transform to 6PPD-quinone when exposed to ozone or oxygen.
- Stormwater source control alone will not prevent toxicity effects of 6PPD-quinone; treatment is needed.
- As LC50s are revised downward, there may not be a "safe" level of 6PPD-quinone in the environment.

About geographic considerations for stormwater management:

- Focus on high quality coho rearing habitat; update population vulnerability mapping to key in on priorities and inform how best to provide continuity of habitat.

- Focus on high average daily traffic roads, parking areas, and busy intersections.

Additional findings are detailed in following our recommendations to funders.

Recommendations

Here are our recommendations for future study to fill gaps in our knowledge and understanding. Some of these priorities are appropriate for SAM projects and are indicated as such, but any of these could be conducted by other state/federal/private funding sources. Coordination and communication will be essential to avoid duplicative efforts and provide opportunities to leverage efforts.

Findings from all of these studies should be shared with both the SAM Coordinator at Ecology and the SIL Staff at WSU-Puyallup for broad distribution and shared learning. Funders should consider any recommendations that come out of Ecology's report to the legislature and other study findings that continue to be released (see the Washington Stormwater Center's Box site). Develop a plan to communicate findings to stormwater managers, salmon recovery managers, and others. A QAPP, or at a minimum, standard protocols are needed for studies to follow.

Recommendations for future study to improve selection and application of BMPs are detailed in the final technical report at 2022_SWTreatmentOfTireContaminants-BMPEffectiveness.pdf (wa.gov). In particular, the following tables in the report provide specificity to the more general recommendations below:

- Appendix 4-1 includes an exhaustive list of all of the known existing treatment and source control BMPs. Studies should focus on BMPs ranked *high* or *medium*.

- Table 5-1 research recommendations. All three categories (high, medium, low) are of interest.

Recommendations for funders

1. All funders should support research that:
    a. Builds on our knowledge that bioretention removes acute toxicity of 6PPD-quinone.
    b. Identifies which BMPs most effectively remove 6PPD and 6PPD-quinone.
    c. Improves our understanding of impacts of 6PPD-quinone to fish and biota, and in. particular, informs our target for a stormwater treatment effluent concentration of 6PPD-quinone.
    d. Improves our understanding of environmental fate and transport of 6PPD and 6PPD-quinone.
    e. Develops monitoring protocols and methods standardization.
2. The Stormwater Action Monitoring (SAM) program funded by municipal stormwater permittees should solicit projects that:

   a. Focus on identifying additional BMPs that most effectively remove 6PPD and 6PPD-quinone.

   b. Contribute to our understanding of environmental fate and transport of 6PPD and 6PPD-quinone.

   c. Study street sweeping and/or line cleaning to get more information about 6PPD and 6PPD-quinone removal; also look at decant water.

   d. Test other (besides 60:40) approved bioretention soil media to see if they also remove the acute toxicity to coho.

3. The Stormwater Strategic Implementation Lead (SIL) should consider funding the following efforts in addition to (1) above:

   a. Design a stream sampling program to understand the scope of the problem; this monitoring might then be conducted by SAM[1] or another entity, to be determined.

   b. Determine the fate of 6PPD-quinone (i.e., from decant water) discharged to wastewater treatment plants.

   c. Learn about 6PPD and 6PPD-quinone in the marine environment.

4. Other state and federal grant programs, including but not limited to Ecology's Stormwater Financial Assistance Programs, State Revolving Funds, and other US Environmental Protection Agency funding beyond the National Estuary Program, should consider funding these efforts in addition to (1) above:

   a. Add 6PPD-quinone as an optional or required TAPE parameter and focus on evaluation of private domain BMPs with minimal right-of-way space requirements for application in transportation corridors. TAPE is the Washington State Department of Ecology's process for evaluating and approving emerging stormwater treatment BMPs.

5. Private granting agencies should consider funding studies that answer the following questions:

   a. What are additional BMPs that effectively remove 6PPD and 6PPD-quinone?

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[1] SAM's stream status and trends monitoring design does not include "chasing storms" but rather focuses on the stream benthic community and sediment sampling during summer low flows. This design may not lend itself to monitoring 6PPD-q in water. If a sediment method is developed and the half-life of 6PPD-q is long enough to make it relevant, SAM might be able to add the analysis, but it would require additional funding.

Recommendations for targeted researchers

6. The Washington Stormwater Center (inclusive of Washington State University and University of Washington-Tacoma and Center for Urban Waters) should work with above funders and seek additional support to conduct research and studies that answer the following questions:

    a. What additional BMPs remove the acute toxicity to coho?

    b. What are the impacts of 6PPD-quinone on other salmonid, other life stages, and other biota?

    c. Is there a "safe" level of 6PPD-quinone in receiving waters?

    d. What are the environmental fate and transport of 6PPD and 6PPD-quinone?

    e. What is the mechanism(s) by which 6PPD-quinone acts, particularly in a way that fish cannot recover?

    f. What is the fate of 6PPD-quinone (i.e., from decant water) discharged to wastewater treatment plants?

        i. General evaluation of plastic micro-and nanoparticles in treated effluent.

    g. Are bioretention soils toxic to biota?

    h. Does 6PPD-quinone bioaccumulate?

7. The National Marine Fisheries Service should seek funding to conduct research and studies to:

    a. Describe the scope of the 6PPD-quinone problem on a national scale.

    b. Learn about 6PPD and 6PPD-quinone in the marine environment.

    c. Identify the mechanism(s) by which 6PPD-quinone acts, particularly in a way that fish cannot recover.

    d. Develop biological markers to assess treatment BMP effectiveness.

    e. Determine whether and to what extent 6PPD-quinone bioaccumulates.

Thank you

Thank you to our >100 subgroup members who participated in eight subgroup meetings; to our panelists who made presentations and discussed these topics in depth, including:
Ed Kolodziej (UW Tacoma), Kathy Peter (NIST), Craig Manahan (Ecology), Jen McIntyre (WSU Puyallup), Brandi Lubliner (Ecology), Ani Jayakaran (WSU Puyallup), Todd Hunsdorfer (King Co), Don McQuilliams (Bellevue), Michelle Purdue (Kitsap Co), Julie Watson (WDFW), Nat Scholz

(NOAA), Bob McKane (USEPA), Jonathan Halama (OSU), Jana Crawford (WSDOT), Evan Lewis (King Co), David Troutt (Nisqually Tribe), Keith Dublanica (GSRO), Doug Howie (Ecology), Doug Navetski (King Co), Bob Bernhard (King Co), Sarah Amick (USTMA), Julie Panko (ToxStrategies), Christian Nilsen (Geosyntec), Dana de Leon (Tacoma), Bryson Finch (Ecology), Abbey Stockwell (Ecology); and to our co-chairs Eli Mackiewicz (Bellingham) and Abby Barnes (WDNR) and supporting Ecology staff Emma Trewhitt and Karen Dinicola.

Appendix F.

Sources of 6PPD and 6PPD-q

Sources of 6PPD

6PPD is a commercially available product. Presently, motor vehicle tires are the main rubber products known to use 6PPD as an anti-degradant and are therefore assumed to be the primary source of 6PPD-q in the environment. Over 300 million tires are expected to be shipped in 2022 (US Tires). Millions of motor vehicles are registered in Washington State. Until a suitable replacement chemical is identified and less-toxic but equally safe tires replace most of the tires that are currently in use, 6PPD in tires will continue to produce 6PPD-q that may be carried by untreated road runoff into aquatic systems.

Tires

Tire manufacturers incorporate the 6PPD solid, powder, or pellets into tire rubber. Tires all over the world include 0.4-2% 6PPD by mass (Lewis et al. 1986; Hu et al. 2022). The 6PPD migrates to the surface as the tire is worn to create a protective film that protects the rubber polymer from reaction with oxygen (O_2) and ozone (O_3). Without a preservative, oxidation of the rubber causes it to crack and thereby shortens the safe lifespan of the tire.

It is still unclear how long it takes for 6PPD to fully migrate out of the tire rubber, but ultimately all of the 6PPD will react with O_2 or O_3 and be released to the environment in various forms, called transformation products, including 6PPD-q. Recent studies suggest that about 10% of 6PPD in tires becomes 6PPD-q upon oxidation with ozone and the remaining 90% transforms into other chemical byproducts with unknown fates and toxicity (Hu et al. 2022, Seiwert 2022).

Tire Wear Debris and Particles

Motor vehicle tires emit rubber pieces as large as the treads and other visible chunks found along the roadway down to microscopic-size particles (Figure G1) as vehicles turn, stop, start, and drive on the road. Tire wear particles are sometimes called “dust”, “microplastic”, or “microrubber.” Automobile types and weights produce variable amounts of tire and road dust (Figure G1). Road types affect friction and abrasion of tires and result in tire wear particles. Tire wear dust and debris are believed to continually release 6PPD and 6PPD-q to the environment.

Decades of research evaluating tire wear particles in the environment is available; however, little information is available on rates of 6PPD and 6PPD-q release from the particles and the influence of environmental factors, such as temperature, oxygen, and pH. More research is needed to help us understand how releasing rates differ by particle size under variable environmental conditions.

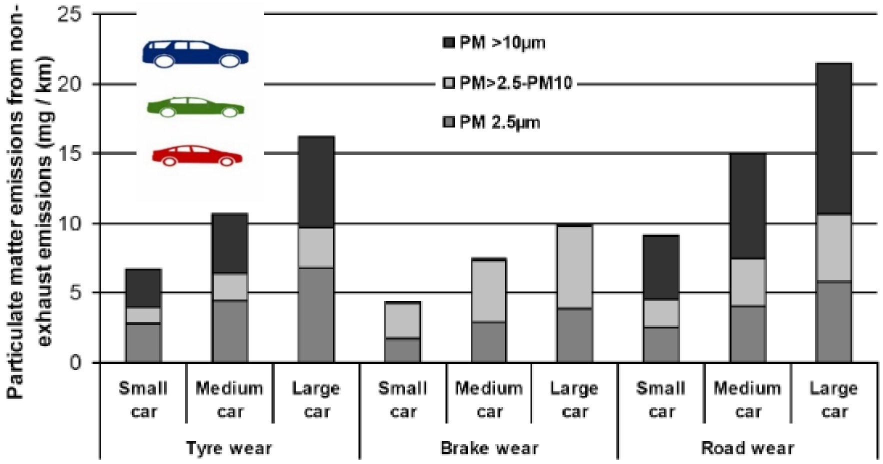

Figure G1. Tire wear particle emissions increase with vehicle size (Kole et al. 2017; Oroumiyeh & Zhu 2021).

Heavier vehicles produce more tire wear particles

Airborne microscopic tire wear particles present a potential air pollution concern and an additional transport mechanism to aquatic systems. As part of a regional air monitoring program, Seattle monitors 2.5 micron (µm) particulate matter (2.5 PM) at 10th avenue and Elliot street. EPA gathers and summarizes 2.5 PM studies to characterize the particles captured by air monitoring stations. Tire wear particles are present at this location and are suspected to be dispersed a few hundred meters on either side of major transportation corridors (personal communication, Ecology Air Quality Program staff, 2022).

Tire wear particles not only release acutely toxic contaminants; the particles themselves are a pollutant. Tons of tire particles end up in the environment each year. These microplastics, like other types of microplastics, pose health risks to aquatic life and accumulate up the food chain, especially in rivers, estuaries, and the ocean.

Tire Waste and Recycled Tire Products

Discarded tires, crumb rubber, and other recycled tire landscaping products are additional potential sources of 6PPD and 6PPD-q to vulnerable aquatic systems. It is difficult to know how much 6PPD is left in the rubber matrix at any given point in tires or tire products of various ages. These recycled tire products are presumed to release 6PPD-q until the 6PPD is fully depleted from the rubber matrix (Hu et al. 2022).

Other Rubber Products

Additional products contain 6PPD, but product identification is an information gap. Ecology is currently coordinating with the state of California and other organizations to understand scope of products containing 6PPD and scale of 6PPD use in consumer, commercial, and industrial products. 6PPD is shipped around the world and is advertised as extending the life of household, office, and industrial rubber products.

Understanding the various sources and delivery pathways of 6PPD-q to vulnerable aquatic habitats will inform future mitigation approaches. Meanwhile, we presume that 6PPD-containing tires, tire pieces, and tire particles will continue to produce 6PPD-q for quite some time and are the dominant source of the problem in the environment.

Tire Wear Chemicals

WA Ecology 6PPD Alternatives Legislative Report 2021[1]

CA DTSC 6PPD Safer Alternative Evaluation and Priority Product Request[2]

EPA Tire Crumb Rubber Characterization[3]

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[1] https://www.ezview.wa.gov/site/alias__1962/37732/research_and_proposed_alternatives_to_6ppd.aspx

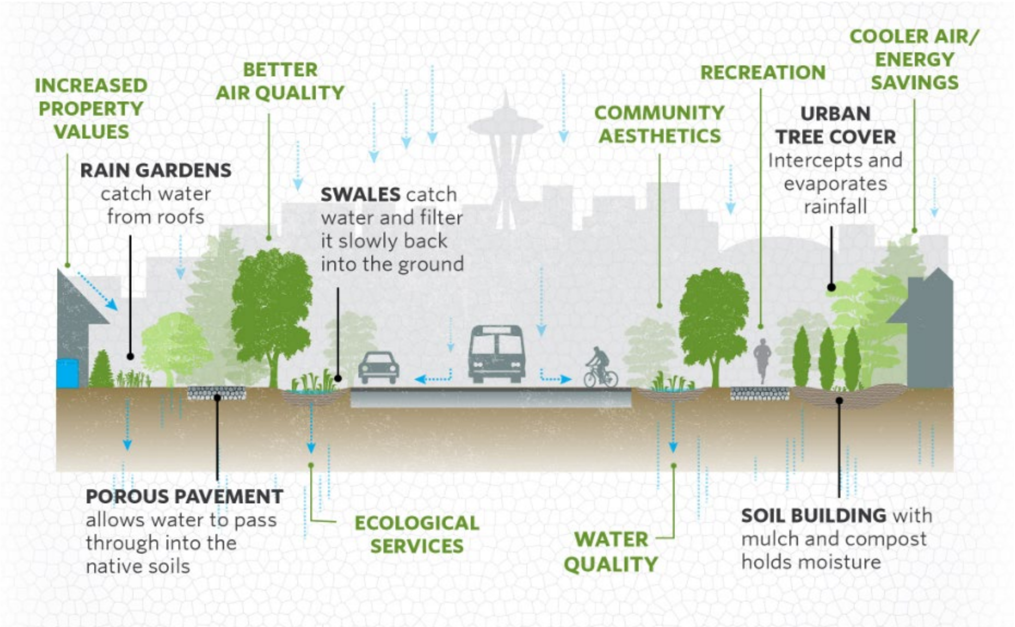
[2] https://dtsc.ca.gov/2022/05/23/news-release_t-07-22/

[3] https://www.epa.gov/chemical-research/public-webinar-part-1-tire-crumb-rubber-characterization

Appendix G.

Green Stormwater Infrastructure Information

Green Infrastructure Resources



GREEN & GRAY STORMWATER INFRASTRUCTURE

A study by the city of Philadelphia has shown a hybrid approach of green and gray infrastructure can get the same freshwater solutions as gray infrastructure, plus additional benefits to the community.

Data Source: City of Philadelphia Water Department
Infographic © TNC\Erica Simek Sloniker

Washington Nature Conservancy: Green Infrastructure
Washington Nature Conservancy: Cities
LID Technical Guidance Manual for Puget Sound
DOC Building Cities in the Rain
City of Seattle On-Site Stormwater Management BMPs
City of Seattle Managing Stormwater on Your Site
EPA Urban Runoff: Low Impact Development
King County Stormwater Pollution Prevention Manual
Low Impact Development (LID) guidance
Portland Sustainable Stormwater
PSRC Building Green Cities
Rain Garden Handbook for Western WA
Soils for Salmon
Stormwater Parks
Washington State University Extension Rain Gardens
Washington Stormwater Center Low Impact Development
Depave
City Habitats

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Appendix H.

Pre-Spawn Mortality in Urban Streams

Pre-Spawn Mortality in Urban Streams

Montlake combined sewer overflow (Photo by Blake Feist).

This section provides a timeline summary of the research efforts to identify the toxic agents in stormwater that kill coho, and the parallel pursuit of stormwater management solutions that reduce the toxicity.

Sporadic reports in the 1980s and 1990s described coho salmon exhibiting symptoms of distress and dying in stream-fed hatcheries and in urban streams before they had a chance to spawn. Symptoms include disorientation, lethargy, gaping, fin splaying, and loss of equilibrium that ultimately progressed to death within hours. Observations of these mortality events in urbanized streams continued to increase over the past two decades with reports of 20-90% of returning adult coho salmon dying before having a chance to reproduce.

Coho tagging efforts supported theories that wild salmon populations had already been declining in urban streams and that many of the salmon found in urban basins are hatchery strays. Small urban streams that were associated with the mortality events comprise important habitat for coho salmon and also provide critical refuge for juvenile salmon transitioning from their home streams into estuaries and the ocean.

Ecotoxicologists from Ecology responded to recurrent coho salmon mortality events at a stream-fed fish hatchery in Bellingham with the first hint of a possible agent driving pre-spawn mortality, concluding after two years of sampling that the *"first flush of urban contaminants may be the source of toxicity"* (Kendra and Wilms 1990). They detected copper, lead and zinc substances in amounts above federal toxicity criteria further supporting the surface runoff theory. Histopathological exams of deceased coho salmon revealed chloride cells in gill tissue, but they lacked the analytical innovations needed to identify the toxic agent. The recurrent coho mortality events stopped after the hatchery switched from drawing water from the urban stream to well water.

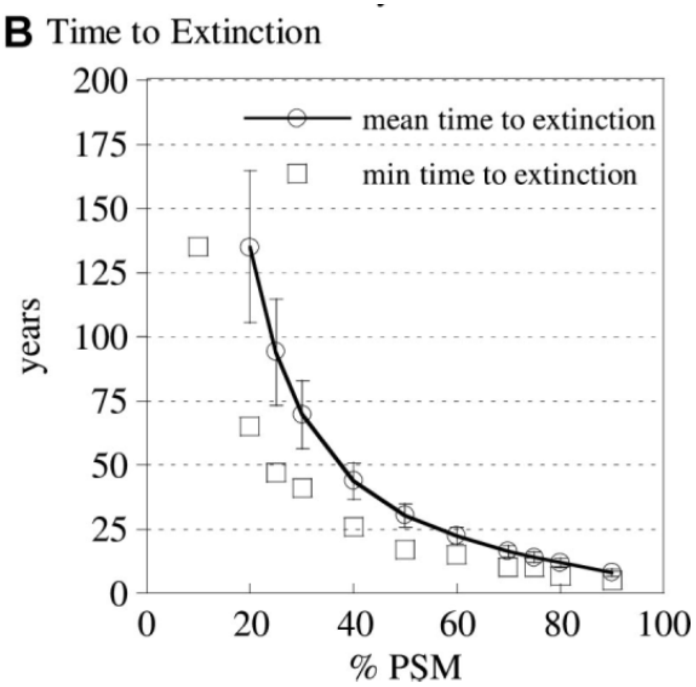
Whatcom creek metal concentrations following storm events resembled stormwater surface samples (Kendra and Wilms 1990). Lastly, they assessed Benthic macroinvertebrate community structure and concluded that fish are more sensitive to stormwater pollutants than invertebrates. This last observation has important implications for urban stream monitoring strategies. Stormwater treatment BMPs that capture sediments, but decant water may help improve invertebrate communities and protect salmonid eggs from being smothered by fine sediments, but other dissolved chemicals including PCP, PAH, PCB, metals and now, 6PPD-quinone are potentially discharged directly into our urban streams. Kendra and Willms (1990) stated "The ultimate solution to this problem lies in stormwater pollution control in the watershed".

A dedicated, multi-disciplinary group of researchers, referred to as the Puget Sound Stormwater Science Team, trained staff and organized pre-spawn salmon mortality surveys within salmon bearing urban streams throughout the Puget Sound area to identify the cause of pre-spawn mortality (Figure H1). The team included students, post-doctoral scholars, university faculty, citizen scientists, non-profit groups, Tribal governments, and state and federal agencies.

Figure H1. Line-up of coho for pre-spawn mortality surveys in WRIA 7,
Wild Fish Conservancy 2003.

Spromberg and Scholz (2011) of the National Marine Fisheries Service at National Oceanic Atmospheric Association documented significant pre-spawn mortality rates across several urban drainages over multiple years and corroborated the theory that pre-spawn mortality events are correlated with urban stormwater run-off. The average time to predicted extinction for these coho runs varies with the extent of urban runoff, from 8-115 years (Figure H2). At the same time, multi-agency research efforts attempted to identify what specifically in stormwater was causing pre-spawn mortality by trying to recreate the toxic effect from piles of street sweepings and custom stormwater mixtures of metals and hydrocarbons. Despite not identifying the chemical agent, these researchers provided the first direct evidence that motor vehicles in urban landscapes were correlated with abnormal rates of pre-spawn coho mortality (Scholz et al. 2011). Longfellow Creek, in West Seattle, experienced 60-100% premature spawner mortality, while a non-urban reference creek, Forston Creek, experienced <1%. More recent studies have inventoried additional creeks along transportation corridors that suggest more complicated risk attributes.

A NOAA led spatial modeling effort using characteristics such as traffic density, land use, land cover, and rainfall across an urban gradient found a correlation between vehicles, road runoff and pre-spawn mortality (Feist et al. 2017). This geographical information system (GIS) modeling effort led the investigative team to focus research efforts on motor vehicles and roads.



Pre-spawn mortality has been occurring for over 20 years, and coho populations in small urban streams have dwindled, presenting challenges to recovery efforts.

Figure H2. Estimated mean time of extinction for coho experiencing pre-spawn mortality for isolated, small urban streams, without hatchery strays (Spromberg and Scholz 2011).

Analytical Innovations Identify the Contaminant

The stormwater science team set up experiments at Washington State University Research and Extension Center in Puyallup to attempt to isolate the specific toxic chemical in stormwater causing pre-spawn salmon mortality by analyzing stormwater collected from downspouts with mixtures of road debris and metals to mimic stormwater chemical cocktails. Using new, advanced analytical technology, thousands of unique chemicals were discovered in roadway runoff, many of which were also detected in the tissue of coho that had succumbed to Urban runoff mortality syndrome (URMS) (Du et al. 2017).

Washington State University in Puyallup (WSU-Puyallup) and University of Washington in Tacoma (UW Tacoma) investigated the suite of chemicals in roadway runoff from specific motor vehicle sources including tires, windshield wiper fluid, antifreeze, motor oil, gear oil, and transmission fluid. The chemicals from tire treads best matched the toxic road runoff and also caused the sudden changes in blood physiology, behavior, and rapid onset of death observed during URMS events (McIntyre et al. 2021).

UW Tacoma researchers successfully isolated the toxicant(s) killing coho, by separating more than 2000 individual chemicals in the tire tread into component parts called fractions (Peter et al. 2018). After further narrowing the search to four chemicals in just two years, the article "*A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon*" identified a previously unknown chemical, 6PPD-quinone (6PPD-q), as the most abundant chemical in this last fraction and the chemical agent responsible for URMS (Tian et al. 2020).

UW Tacoma and WSU-Puyallup have since conducted ecotoxicology experiments on coho with a newly available 6PPD-q commercial standard. They established a lethal concentration at which half of the fish die in 24 hours (LC_{50}) for coho; 95 ng/L, (96 parts per trillion). The extremely low concentration at which mortality occurs highlights the extreme sensitivity of coho to 6PPD-q. Researchers at UW Tacoma, WSU-Puyallup, and NOAA continue to pursue new information on several important fronts including chemical fate and transport, the mechanism of injury in coho, and impacts to other fish and other aquatic species.

The effectiveness of future risk assessment research, similar to Feist et al. 2017 and Ettinger et al. 2021, will depend on the availability of accurate (reconnaissance completed), standardized and accessible stormwater infrastructure geographic information. Source identification and laboratory studies are needed to understand the geographic scope and persistence of tire wear particles and chemicals to strategically place and administer the most appropriate BMPs.

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