

WELCOME!!

6PPD-q Subgroup Meeting October 4, 2024

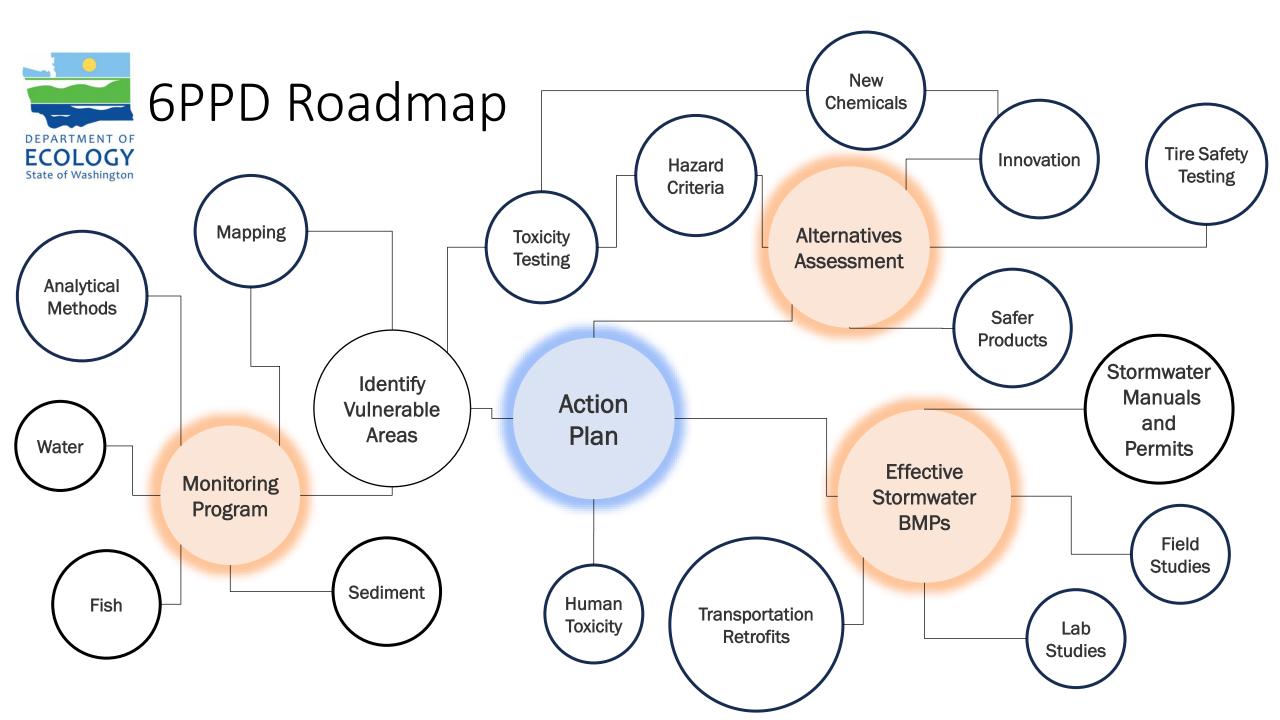


1,4-Benzenediamine, N(1,3-dimethylbutyl)-N'-phenyl CH3 CH3 CASRN 793-24-8

2-anilino-5-[(4-methylpentan-2-yl)amino] cyclohexa-2,5-diene-1,4-dione CH3 CH3 CCH3 CCH3 CCH3

Figure 1. Chemical structures for 6PPD and 6PPD-quinone.

Graphic Courtesy of ITRC: "What We Know: 6PPD and 6PPD-quinone"



Early-to-Mid 2000s Longfellow Creek, Seattle











Mid 2010's Grover's Creek Hatchery Suquamish Tribal Land











2019-2020
University of Washington
Center for Urban Waters









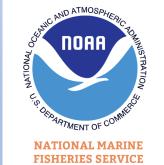


https://youtu.be/vxmojuC dJE

2019 University of Washington Center for Urban Waters

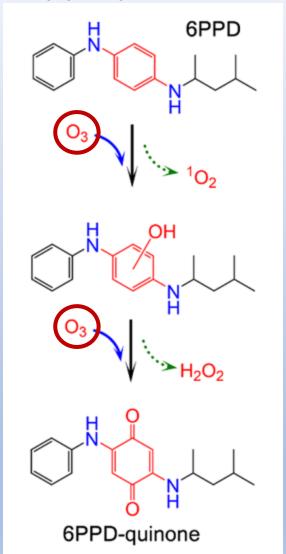


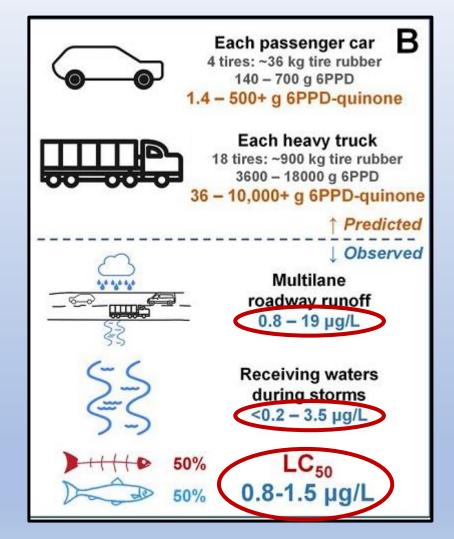






6-p-phenylenediamine





Previously unknown to chemistry

2020 – Washington State Legislature, Universities, and Agencies

6PPD "lines of inquiry" and active groups*

Product Replacement

Ecology HWTR
Interstate (CA, others)
USEPA
USTMA
Salmon Safe

Analytical Methods

UW Tacoma Ecology MEL USEPA Private labs

Biological Effects

WSU Puyallup NOAA USFWS WDFW Toxics Workgroup

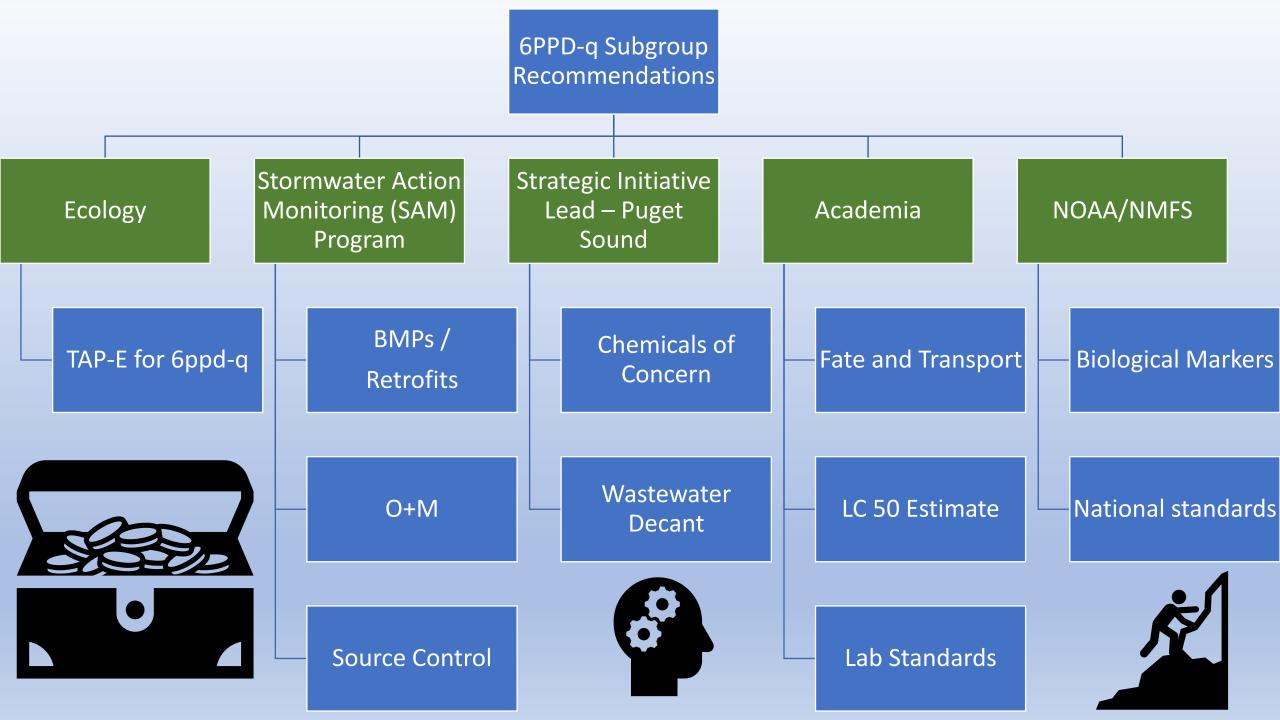
Stormwater Management

Ecology WQP
SAM
WSDOT
WA Stormwater Center
PS Recovery SIL
SWG 6PPD Subgroup

Geography/ Priorities

NOAA/USFWS WDFW/WDNR UW Tacoma Ecology EAP Tribes <u>SWG 6PPD Subgroup</u>







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



Washington State Department of Ecology

STORMWATER TREATMENT OF TIRE CONTAMINANTS BEST MANAGEMENT PRACTICES EFFECTIVENESS

Final Report | June 2022























6PPD: Stormwater Research and Action around Toxic Tire Chemicals

Stormwater Work Group 6PPDQ Subgroup Meeting October 4, 2024



Introductions



Madison Rose Bristol
6PPD Stormwater Planner



Shelby Giltner
6PPD Environmental Engineer



Tanya Williams6PPD Agency Lead



Agenda

- Updates on stormwater best management practices (BMP) effectiveness research
- Policy Updates
- Action Plan Update



Our Research Projects

- Over 20 contracted research projects using 6PPD Funding
 - Stormwater characterization for different land uses
 - Testing BMP Effectiveness: Street sweeping, grassy swales, road embankments, sorbent media, bioretention soil mixes, media filters, proprietary treatment (TAPE) devices
 - Testing runoff from crumb rubber mulch or turf
 - Developing sampling and analytic methods

6PPD Stormwater Best Management Practices Research Website is Live!!

Use the following link for the site:

6PPD Stormwater Best
Management Practices Research

Most research results will be published by Summer 2025





6PPD Stormwater Best Management Practices Research

This page is run by the Washington State Department of Ecology and is a space for sharing publications from 6PPD stormwater research.

Ecology is supporting several research projects and identifying best management practices (BMPs) that are effective at managing 6PPD and 6PPD-quinone (6PPDQ) in stormwater. These studies will help inform appropriate policy, regulatory, and rulemaking processes around 6PPD and 6PPDQ to protect aquatic life, ecosystems, and human communities.

Summary Publications

The following publications provide a big picture overview of our 6PPD BMP effectiveness research:

- Focus On: Best Management Practices for 6PPDQ (2023)
- Saving Washington's salmon from toxic tire dust (2023)
- . 6PPD in Road Runoff: Assessment and Mitigation Strategies (2022)

Overview of Research Projects

We describe each of our research projects below, including:

- The partner organization that Ecology contracted to conduct research
- Study title
- Study description
- . Contract status, including if the study is completed or ongoing
- . Who the study is funded by, including:
 - · Ecology's 6PPD Funding
 - o Stormwater Action Monitoring Program (SAM)
 - Puget Sound National Estuary Program Stormwater Strategic Initiative Lead (Stormwater SIL)
 - Water Quality Combined Funding Program (WQ CFP)
- Contact information of the project manager
- · Links to publications and the year it was published

List of Research Projects

To learn about research projects, click on the project below or scroll down this page.

- . City of Redmond Redmond Paired Watershed Study
- . City of Spokane Bioretention Soil Media Study: Development of Non-Vegetated BMPs
- . City of Tacoma Monitoring for Stormwater Contaminants of Emerging Concern in Western Washington

New Project - EA Engineering Unamended Soils

- Test unamended soils for potential to reduce 6PPDQ in stormwater
 - Unamended soils will meet SMMWW Site Suitability Criteria which includes parameters for infiltration rates, percent organic, and cation exchange capacity. Ecology's default bioretention soil mix (BSM 60:40) will be used as a control to compare removal rates.
- Test the reduction of 6PPDQ in soil-vegetation systems and evaluating potential uptake in vegetation
 - Vegetation blends include SWMMWW recommended blends for wet biofiltration swales.

New Project - NV5 6PPD Study

- Verification of BMP effectiveness Phase I
 - Literature Review to identify BMPs to be sampled and monitored
 - QAPP Development
- Crumb Rubber Investigation
 - Leachate test on crumb rubber samples of various ages
 - Stormwater sample collected from turf field drainage systems
- Street Sweeping and Traffic Density Characterization
 - Collecting street sweeping solids and stormwater samples from areas with different traffic densities, street sweeping frequencies, and land uses

New Project - Tacoma Sediment Method

- The City of Tacoma's Environmental Services Laboratory is developing a standard operating procedure (SOP) to evaluate 6PPDQ in sediment.
 - The draft SOP has been submitted to Ecology for comment and review.
 - The method will be used by the City of Tacoma in two contaminant of emerging concern (CEC) monitoring projects that will begin sampling this fall.

Completed Project: King County HPBSM

- Columns of Bioretention Soil Media
 (BSM) and High
 Performance Bioretention Soil Mixes
 (HPBSM) were dosed with stormwater
 collected from the I-5 WSDOT Ship Canal
 runoff test site.
- Juvenile Coho were exposed to untreated stormwater and treated effluent to determine % survivability.



Photo: Shelby Giltner

Completed Project: <u>King County HPBSM</u> (cont.)

Study Results:

- All mixes showed high 6PPDQ removal rates with >96% reduction in all samples
- 0-5% of juvenile coho exposed to untreated stormwater survived
- 100% of coho exposed to treated effluent survived, regardless of mix
- HPBSMs provided small but significant 6PPDQ treatment improvements over BSM
- HPBSM effluent concentrations were always below 8 nanograms/L
 - below proposed Aquatic Life Toxics Criteria of 12 nanograms/L

Completed Project: <u>Herrera 6PPDQ in Highway</u> Runoff, BMP Effectiveness, and Field Protocol

- Collected storm event samples to characterize 6PPDQ from highway runoff
- Evaluated the ability of selected propriety treatment devices to reduce 6PPDQ. Devices included:
 - High flow rate biofilters
 - Membrane filter
 - Horizontal bed media filter
- Collected data to develop field sampling protocol for collecting stormwater composite samples for 6PPDQ analysis

Completed Project: <u>Herrera</u> (cont.)

Results:

- Median concentrations of 6PPDQ for untreated highway runoff ranged from 600-700ng/L. During storm events, 6PPDQ concentrations typically exceed the LC50 for juvenile coho salmon of 95 ng/L, often by an order of magnitude.
- Proprietary BMPs tested in were able to consistently remove 6PPDQ but at varying degrees of effectiveness.

Table: Herrera Environmental Consultants. Percent reduction of 6PPDQ from five treatment technologies.

Table 6. Stormwater BMP Performance.										
	Type of Treatment		6PPD-q Percent Reduction			Median 6PPD-q Concentration ^b				
Location	Technology	na	Min	Median	Max	Influent	Effluent			
SCTF-TB1	High flow rate biofilter	10	59.4%	87.3%	97.9%	760	110			
SCTF-TB2	Membrane filter	8	-2.9%	38.3%	59.4%	652	527			
SCTF-TB2.5	Horizontal bed media filter	10	7.2%	17.9%	64.7%	580	385			
SCTF-TB4	Cartridge-based media filter	6	19.7%	54.1%	68.5%	570	275			
STTC-TB1	High flow rate biofilter	6	55.0%	81.2%	85.4%	713	154			

Completed Project: <u>UW-Tacoma Evaluation of</u> 6PPD-Quinone Sorption to Treatment Media and Engineered Soil Mixtures

- Compared the contaminant capture of engineered medias, commercial sorbent components, and simplified soils
 - Examples of media studied included but were not limited to compost, mulch, sands, perlites, and zeolites

 Purchased and installed an accelerated solvent extraction (ASE) system to develop an ASE analytical methods to extract 6PPDQ from soil and treatment media

Completed Project: <u>UW-Tacoma</u> Evaluation of 6PPD-Quinone Sorption to Treatment Media and Engineered Soil Mixtures (cont.)

• Results:

- The research generate previously unknown partitioning coefficients for soil and media components
- Sorbent treatment media including the HPBSM, BSM, stormwater compost, granular activated carbon, and biochar can reduce 6PPD-q
- Paper Authors and Contributors: Alana Hildebrandt, Ximin Hu, Hailey Germeau, Melissa Gonzalez, Frances Yih, Craig Rideout, Edward P. Kolodziej

Water Quality Policy Actions



- Reissued <u>Municipal Stormwater Permits and Manuals</u> in July 2024
 - Reduced project thresholds, retrofits, street sweeping
- Published <u>draft Industrial Stormwater General Permit</u> (ISGP) in Summer 2024
 - Monitoring and reporting 6PPDQ; no standards or limits
 - Currently responding to comments. Response to comments and the final ISGP will be reissued in late 2024.
- 6PPDQ <u>Aquatic Life Toxics Criteria</u> for freshwater and acute mortality of <u>12 ng/L</u> has been adopted by WA State.
 - Criteria must be reviewed approved by the EPA, including ESA consultations, before there are any regulatory impacts

Questions?





ADA Accessibility

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For more information:

Shelby Giltner
6PPD Environmental Engineer
Shelby.Giltner@ecy.wa.gov





6PPD Action Plan

Science, Policy, and Action



6PPD and 6PPD-quinone

- 6PPD is a chemical in tires that prevents the rubber from cracking
- 6PPD transforms into 6PPD-quinone (6PPDQ) when exposed to ozone
- Both are emitted in tire wear particles and are found everywhere
- 6PPDQ is acutely toxic to coho salmon

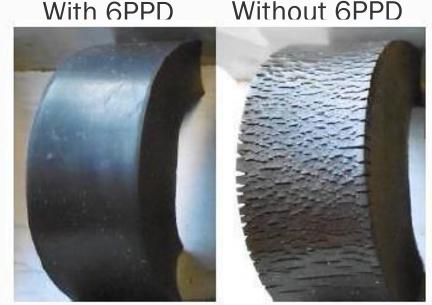


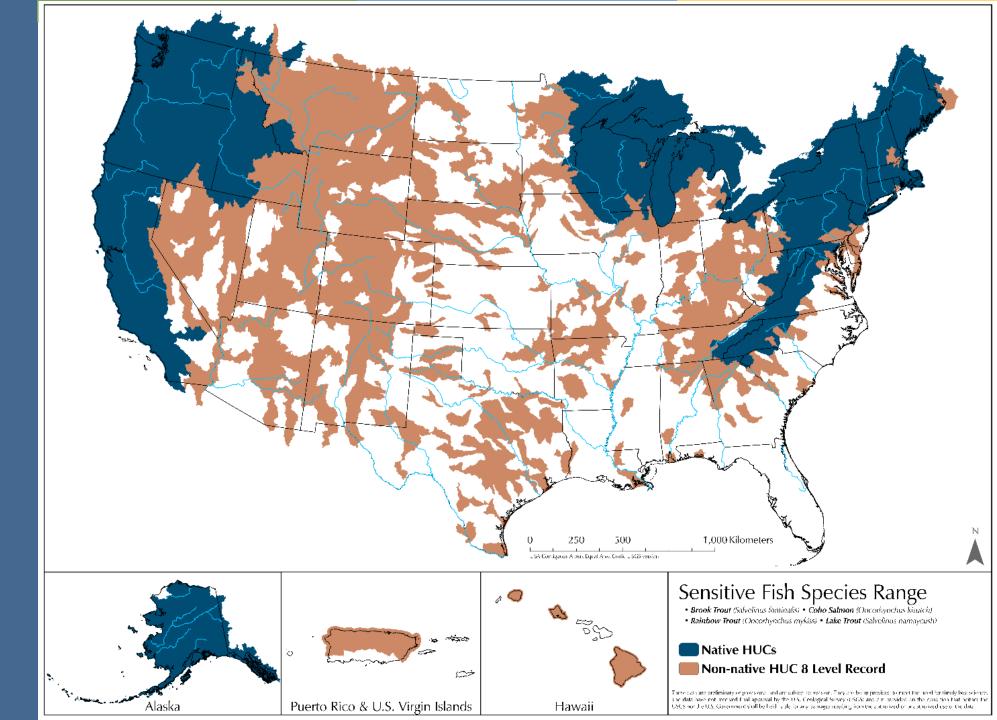
Photo: U.S. Tires Manufacturer's Association



Photo: Clear Creek coho (courtesy of Wild Fish Conservancy, 2021)

6PPDQ is toxic to:

Coho salmon
Brook trout
Lake trout
Rainbow trout
Steelhead
Coastal
cutthroat trout

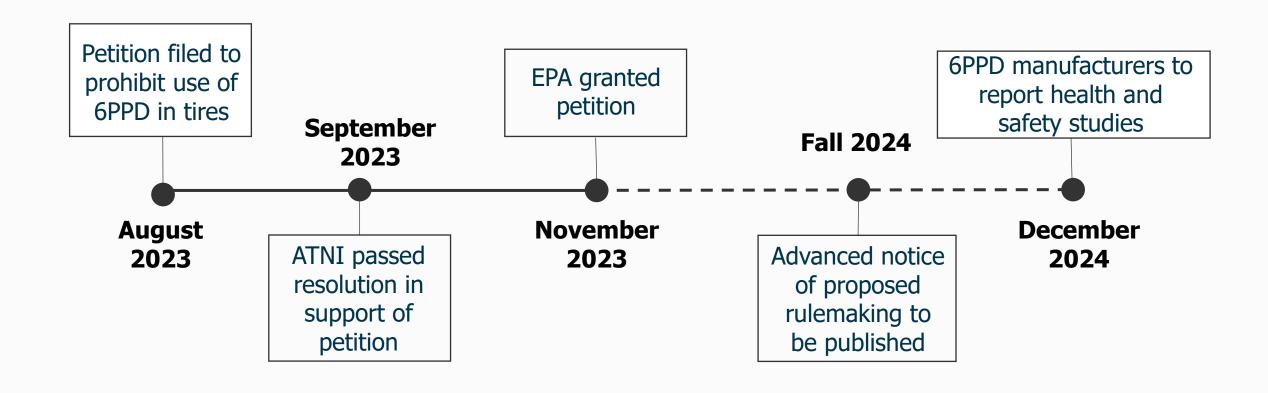




Policy Update



Federal Action





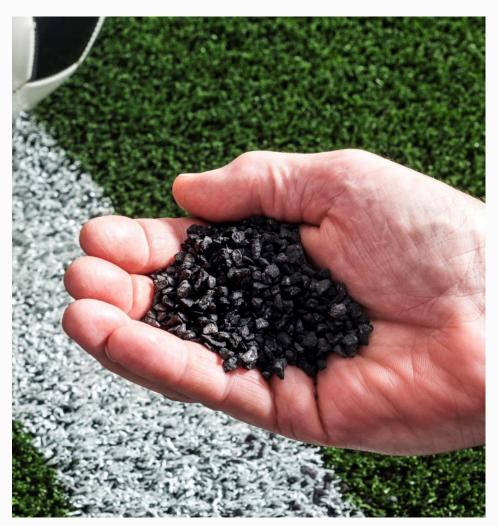
Safer Products for WA

- 6PPD added as a priority chemical
- Tires added as a priority consumer product
- Other recycled tire products being considered as a priority products
- Next steps: Public comment period, then issuance of report in June 2025



Photo credit: <u>Rubberecycle Mulch</u> Changes made: cropped to square

Artificial Turf Runoff Study



- Are toxic chemicals from artificial turf entering the environment through stormwater runoff?
- Data will inform the product replacement program
- Measure 6PPDQ and PFAS
- Various field ages and with different infill types, including crumb rubber
- Actively looking for participants in Central and Eastern Washington

Photo: recycled tires used for artificial turf fields.

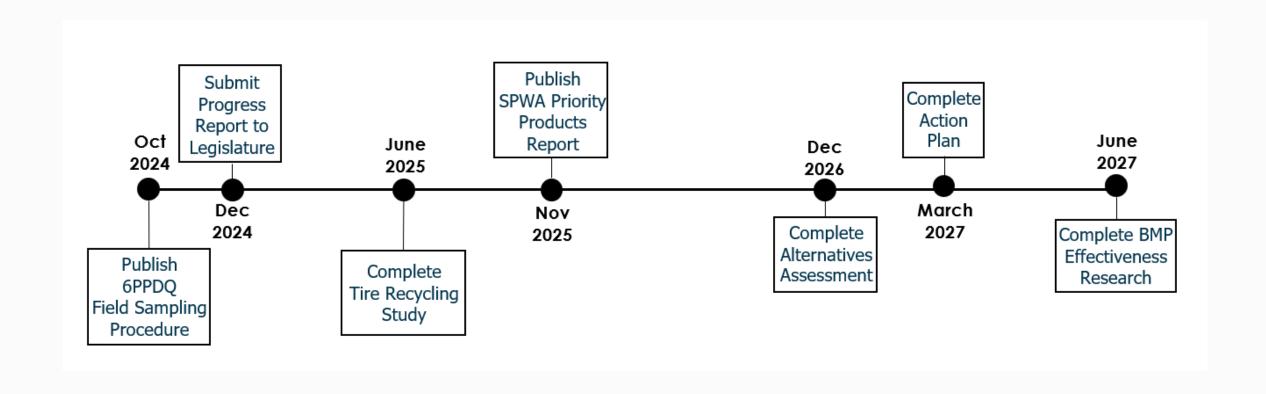
Aquatic Life Toxics Criteria: 6PPD-quinone

- August 2024: Ecology adopted rule and submitted to the EPA for review and approval.
- Next step: Endangered Species Act consultation (NOAA)

	FW Acute (μg/L)	FW Chronic (μg/L)	SW Acute (μg/L)	SW Chronic (μg/L)
Washington	-	-	-	-
EPA	0.011	-	-	-
Final Rule	0.012	-	_	-
	(1-hour)			



Ecology's 6PPD Project Timeline

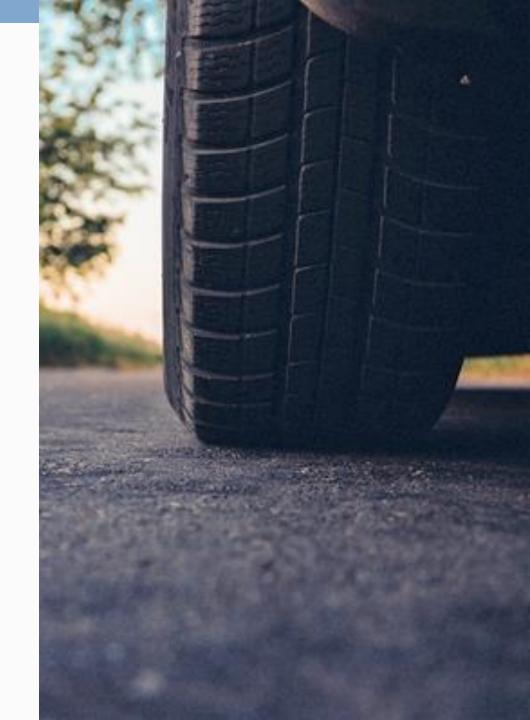


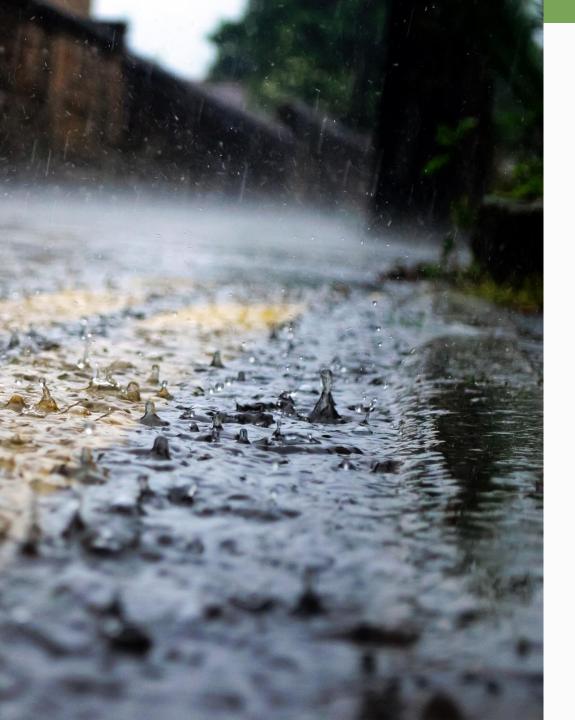


Action Plan: Phase 1

Plan Development Process

- 52-member advisory committee
 - 12 Tribal representatives
 - Federal, state, municipalities, industry, NGOs
- Developed 37 recommendations
- 6PPD Decision Package
 - \$8.9 million requested for 25-27
- Progress report to the Legislature in December 2024







Research

- Alternatives testing
- Field sampling and lab methods
- Field monitoring
- Collaboration and technical assistance
- Stormwater BMP effectiveness in lab & field

Policy

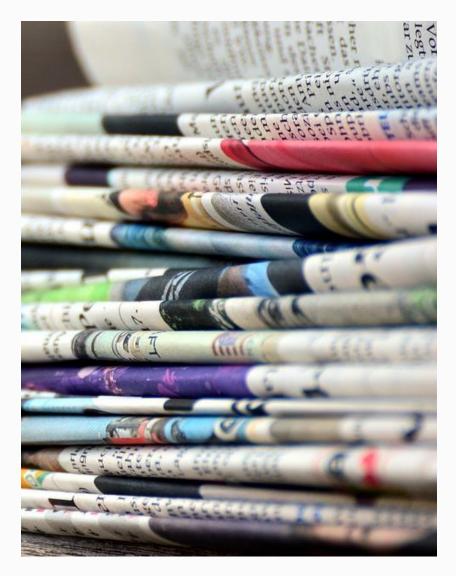
- Assess hazards of other PPD chemicals
- Rubber-based recreational surfaces
- Fish toxicity studies
- Prioritize waste tire cleanups
- Stormwater permit management
 - Toolbox for 6PPDQ





Management

- Maintain lab capacity
- Continued collaboration with partners
- Technical assistance
- Communications collaborative



Other agencies

- Monitoring of high priority tire-related compounds (DFW)
- Human exposure health hazards, drinking water, consumption of aquatic species, holistic effects on people's health (DOH)
- Tire Pile Removal Program (DNR)
- State programs that are intended to reduce vehicle miles traveled (DOT)
- Implement the low-risk, high-reward stormwater treatment demonstration projects (DOT)



Photo credit: WSDOT, 2024.



Identifying impacted communities



Photo: Affiliated Tribes of Northwest Indians Winter Convention 2024; Credit: ATNI

- Tribes, indigenous people, and populations
- Subsistence fishers
- Workers who are disproportionately exposed to 6PPD compounds
- Communities and groups that live, work, or play near areas potentially contaminated with 6PPD compounds



6PPD Action Plan

Scan QR code for a direct PDF download of the Data Gaps, Research Needs, and Recommendations to Inform Future 6PPD Action Plan Work





Funding Opportunities & Staying Informed



PS Stormwater Strategic Initiative Lead Request for Proposals

- Climate Resiliency in Stormwater Management
 - \$2.5 million
- Developing Stormwater Parks and Regional Facilities
 - \$1.6 million
- Chemical Action Plan Implementation
 - \$1 million
- Contaminants of Emerging Concern Research
 - \$1 million
- Addressing Toxic Hotspots on Juvenile Chinook Salmon
 - \$2.5 million



Interested? Fill out this form for proposal assistance.



ATNI – 6PPD Workshop

- ATNI Natural Resources Summit
- November 18-20, Tulalip Tribe Resort & Casino

Stormwater Projects

Human Health and Exposure Potential

Ecotoxicology

Fish Tissue Sampling

Safer Alternatives Salmon Recovery Planning Sampling and Monitoring Training



Stay Informed

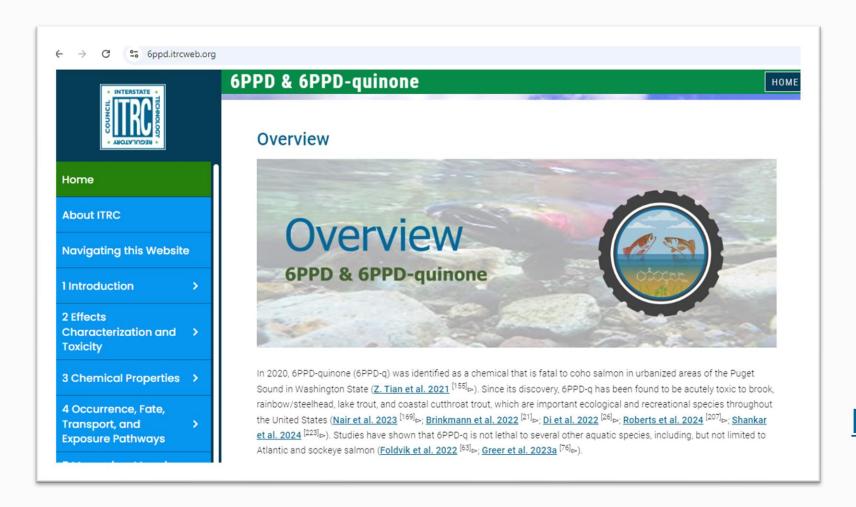
- Monthly 6PPD newsletter
 - Research updates
 - Upcoming meetings
- 6PPD Science Network
- 6PPD State of the Science meeting (Fall 2025): Seattle, WA

6PPD and 6PPD-quinone email list





ITRC 6PPD Guidance Document





https://6ppd.itrcweb.org

Questions?





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For more information:

Tanya Williams

6PPD Agency Lead

tanya.williams@ecy.wa.gov



BREAK TIME!!



Table 1. Reported 6PPD-quinone LC₅₀ concentrations (50% observed mortality) of salmonids.

Species	LC ₅₀ (μg/L)	Test duration (h)	Toxicity Key
Coho salmon (Oncorhynchus kisutch)	0.04, ²⁴ 0.08, ²⁵ 0.095 ²	24	Higher
White-spotted char (Salvelinus leucomaenis pluvius)	0.51 26	24	
Brook trout (Salvelinus fontinalis)	0.59 ³	24	
Rainbow trout/steelhead (Oncorhynchus mykiss)	0.64, ²⁹ 1.0, ³ 2.26 ⁵	96	
Chinook salmon (Oncorhynchus tshawytscha)	67.3 ²⁴ , 82.1 ²⁵	24	
Sockeye salmon (Oncorhynchus nerka)	Not acutely toxic at 50 ²⁵	24	Lower
Atlantic salmon (Salmo salar)	Not acutely toxic at 12.2 ²⁸	48	
Brown trout (Salmo trutta)	Not acutely toxic at 12.2 ²⁸	48	
Arctic char (Salvelinus alpinus)	Not acutely toxic at 12.7 ³	24	
Southern Dolly Varden (Salvelinus curilus)	Not acutely toxic at 3.8 ²⁶	48	
Cherry salmon (Oncorhynchus masou masou)	Not acutely toxic at 3.5 ²⁶	48	

Graphic Courtesy of ITRC: "What We Know: 6PPD and 6PPD-quinone"









Scientific Technical Services is a department within Western Washington University.

- Service the entire university
- Not within any specific college
- House, manage and have expertise on a suite of instrumentation
- Prioritize student hands-on experience











Capabilities

SEM EDS: Scanning Electron Microscopy with Energy Dispersive Spectroscopy

HPLC: High Performance Liquid Chromatography

Micro-CT: X-Ray Microtomography

MALDI: Matrix-Assisted Laser Desorption Ionization Mass Spectrometry

LC-MS QTOF: Liquid Chromatography Mass Spectrometry

GC-MS: Gas Chromatography Mass Spectrometry

Raman Spectroscopy

Fluorescent Confocal Microscopy

Find more detailed information on our website **SciTech.wwu.edu**







EPA Draft Method 1634







Solid Phase Extraction - SPE













Solid Phase Extraction



- Preparatory cleaning of sample
- Wash cartridges with acetonitrile then water
- Pull samples through with vacuum
- Rinse with water and methanol
- Extract 6PPD-Q with acetonitrile









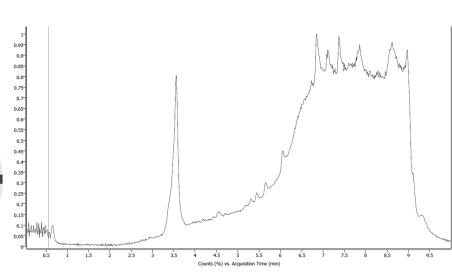
High Performance Liquid Chromatography, HPLC



- Pressurize liquid up to thousands of bar
- Flow through reverse phase column
- Run a 10 min gradient between water and acetonitrile
- Within column separate complex mixture into parts
- Flow separated mixture into mass spectrometer











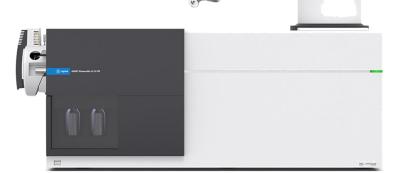


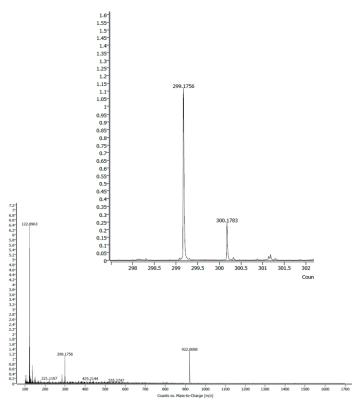
Mass Spectrometry



- Charge analyte within source
- Accelerate sample into first mass analyzer, quadrupole
- Flow through collision cell
- Accelerate into second mass analyzer, time-of-flight tube
- Acquire spectra that clearly resolve isotopic distributions











Partnerships

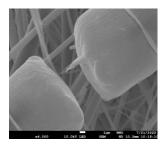
Dr. Karin Lemkau

Assistant Professor, Chemistry and Marine and Coastal Science Program

Current/Past Projects

- Oil weathering
- Polyunsaturated aldehydes
- Polycyclic aromatic hydrocarbons
- Wastewater epidemiology







Very interested in partnering on 6PPD-Q work and has established lab setup for sample processing.

Dr. Ian Moran

Visiting Assistant Professor, Environmental Sciences

Current/Past Projects

- Collaboration with NOAA Fisheries on sublethal toxicity of 6PPD-Q on juvenile salmonids
- · Contaminated sites/Superfund
- Aquatic toxicology





Already immersed in 6PPD-Q work and has samples that could be processed.





Afternoon Tour Logistics

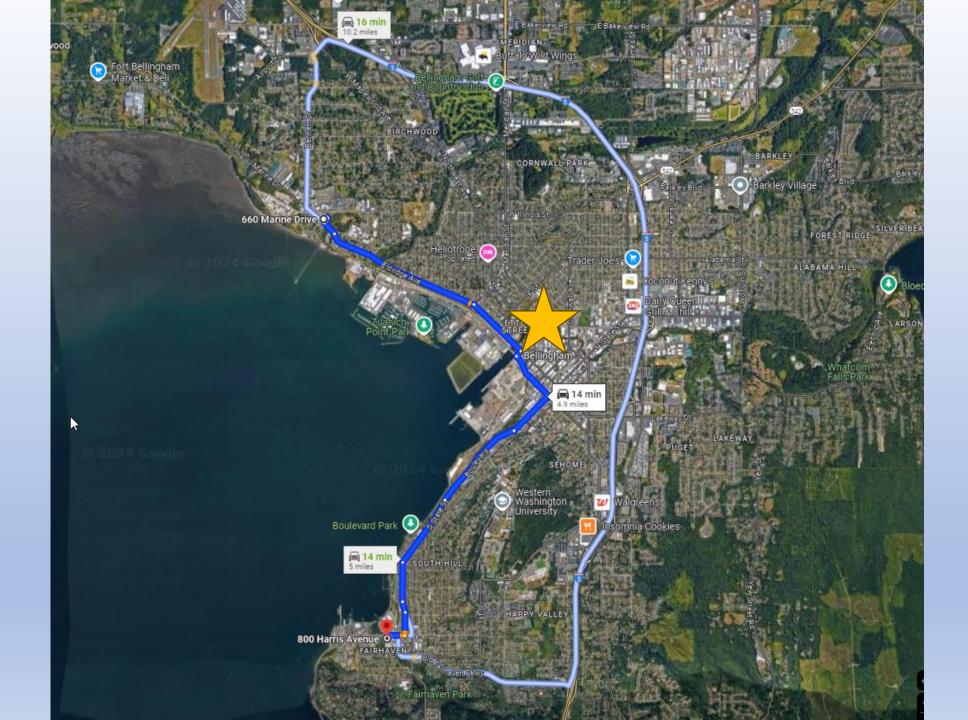
Site "A" Little Squalicum Estuary



Site "B" Harris Street Water Quality BMP



Two Tours at Each Site, First leaves at 1pm, Second at ~2:15pm, with 30 minutes between for driving/parking





THANK YOU!!

6PPD-q Subgroup Meeting October 4, 2024



1,4-Benzenediamine, N(1,3-dimethylbutyl)-N'-phenyl CH3 CH3 CH3 CH3 CH3

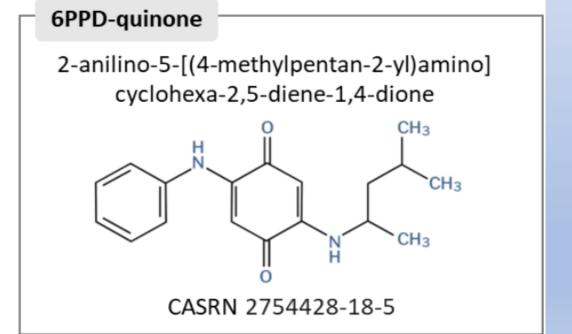


Figure 1. Chemical structures for 6PPD and 6PPD-quinone.

Graphic Courtesy of ITRC: "What We Know: 6PPD and 6PPD-quinone"