

An overview of 6PPD-quinone: where we started, where we are now, and where we are headed

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Coho salmon (*Oncorhynchus kisutch*)



Paul Kaiser/USFWS



Image from nativefishsociety.org

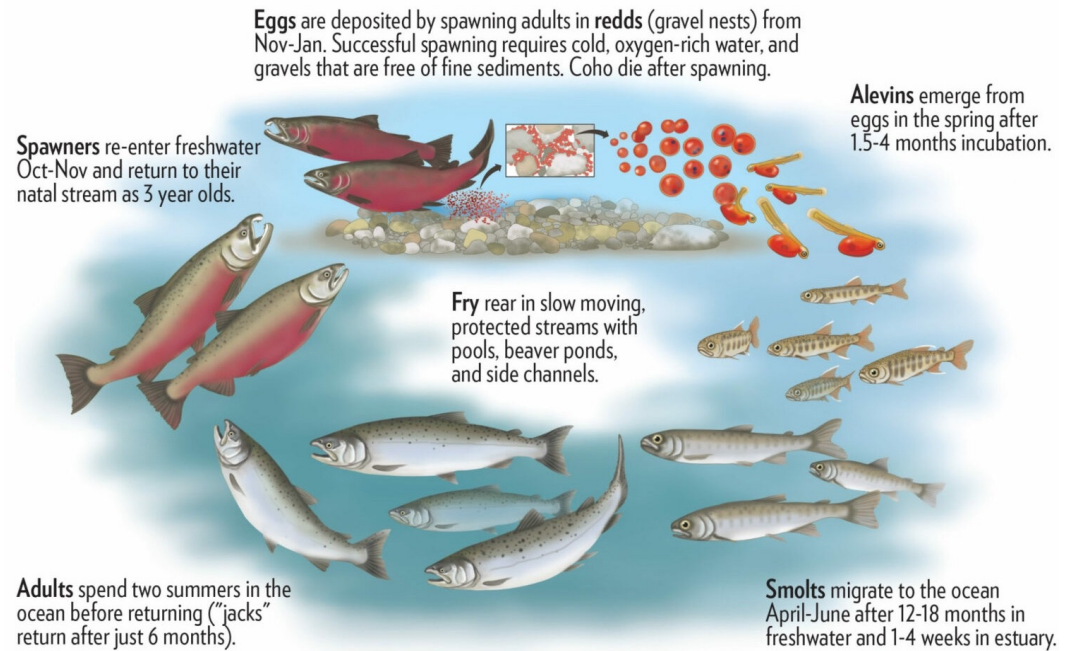


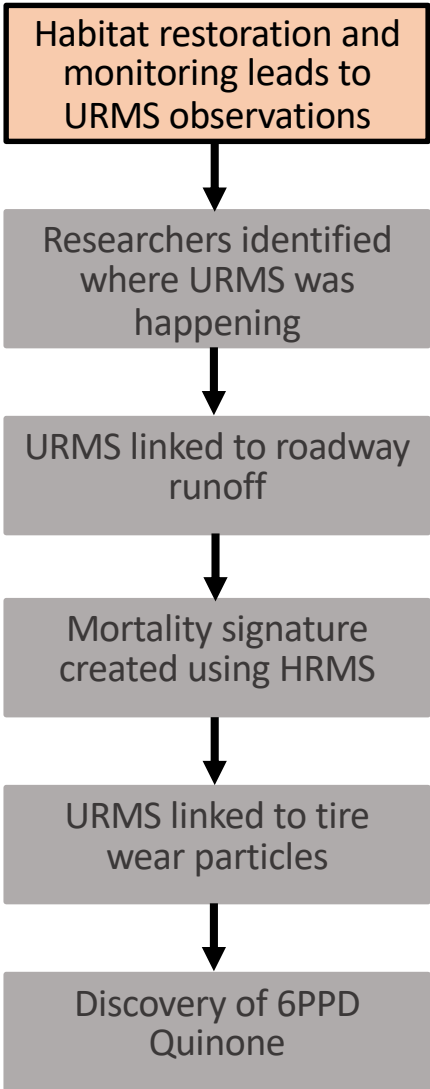
Image from wildsalmoncenter.org

Urban Runoff Mortality Syndrome (URMS)

- Also known as pre-spawn mortality (PSM)
- First documented in the late 1980s
- Restoration and monitoring efforts in the early 2000s led to more widespread observation of URMS



Longfellow Creek, November 16th, 2022

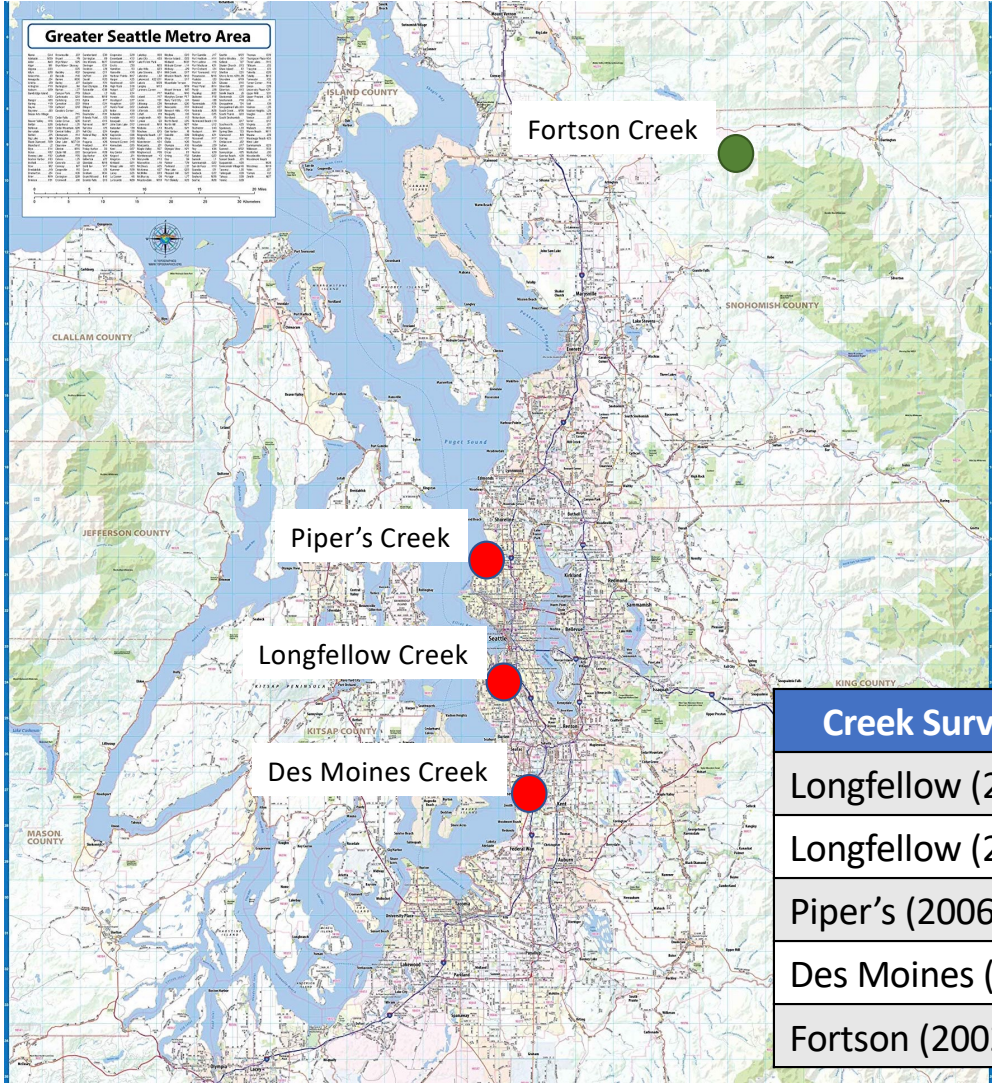
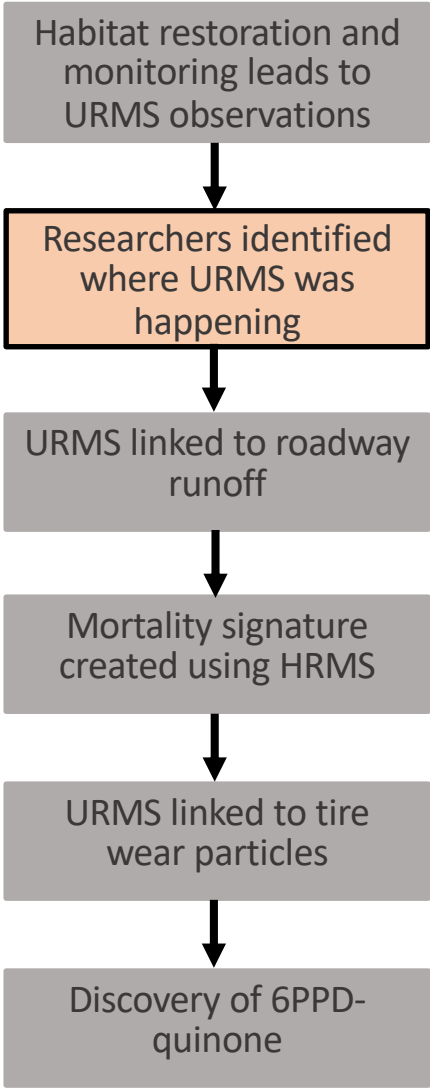


Extensive physical and biological restoration in 1990s

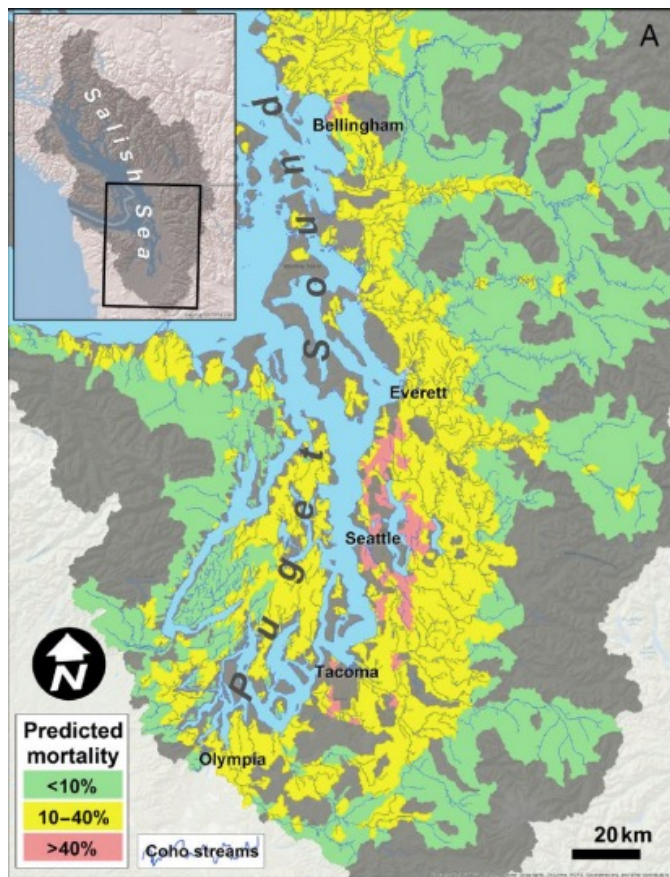
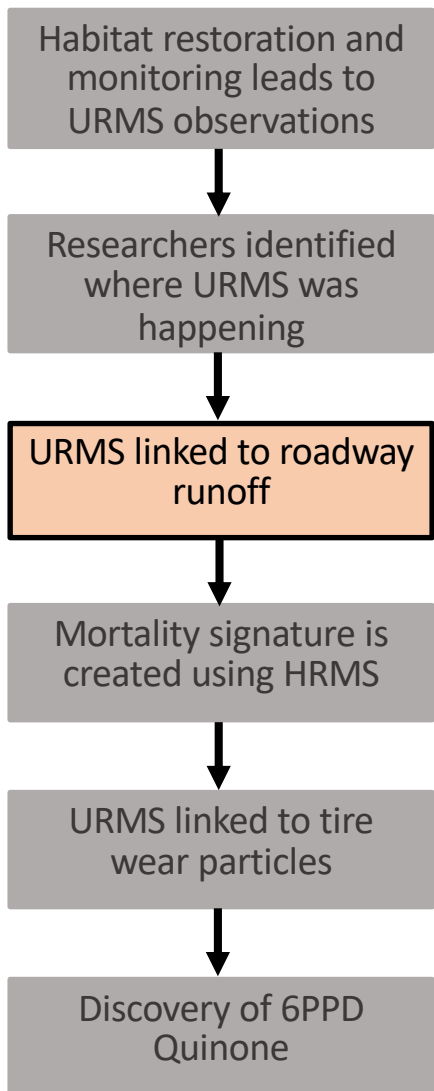
- Removal of culverts
- Placement of large woody debris and gravel substrate
- Removal of noxious weeds
- Planting of native vegetation

Early monitoring efforts (1999-2001) identified unusual pre-spawn mortality in adult coho





Creek Surveyed	Urban Stream?	% PSM
Longfellow (2002)	Yes	86
Longfellow (2009)	Yes	79
Piper's (2006)	Yes	100
Des Moines (2004)	Yes	63
Fortson (2002)	No	0.9



Feist et al. 2017. Ecol. Appl.

Exposure to artificial stormwater containing PAHs and metals

Exposure (h)	Mortality	
	Unexposed	PAHs/Metals mixture
24	25% (1/4)	0% (0/4)
24	33% (1/3)	0% (0/3)
24	0% (0/4)	50% (2/4)
24	0% (0/4)	0% (0/4)

Exposure to highway run-off stormwater before and after biofiltration

Exposure (h)	Mortality		
	Unexposed	Unfiltered	Filtered
4	0% (0/4)	100% (4/4)	0% (0/4)
24	0% (0/4)	100% (4/4)	0% (0/4)
24	0% (0/4)	100% (4/4)	0% (0/4)
24	0% (0/4)	100% (4/4)	0% (0/4)
24	0% (0/4)	100% (4/4)	0% (0/4)

Spromberg et al. 2016. J Appl Ecol

Habitat restoration and monitoring leads to URMS observations



Researchers identified where URMS was happening



URMS linked to roadway runoff



Mortality signature is created using HRMS



URMS linked to tire wear particles



Discovery of 6PPD Quinone



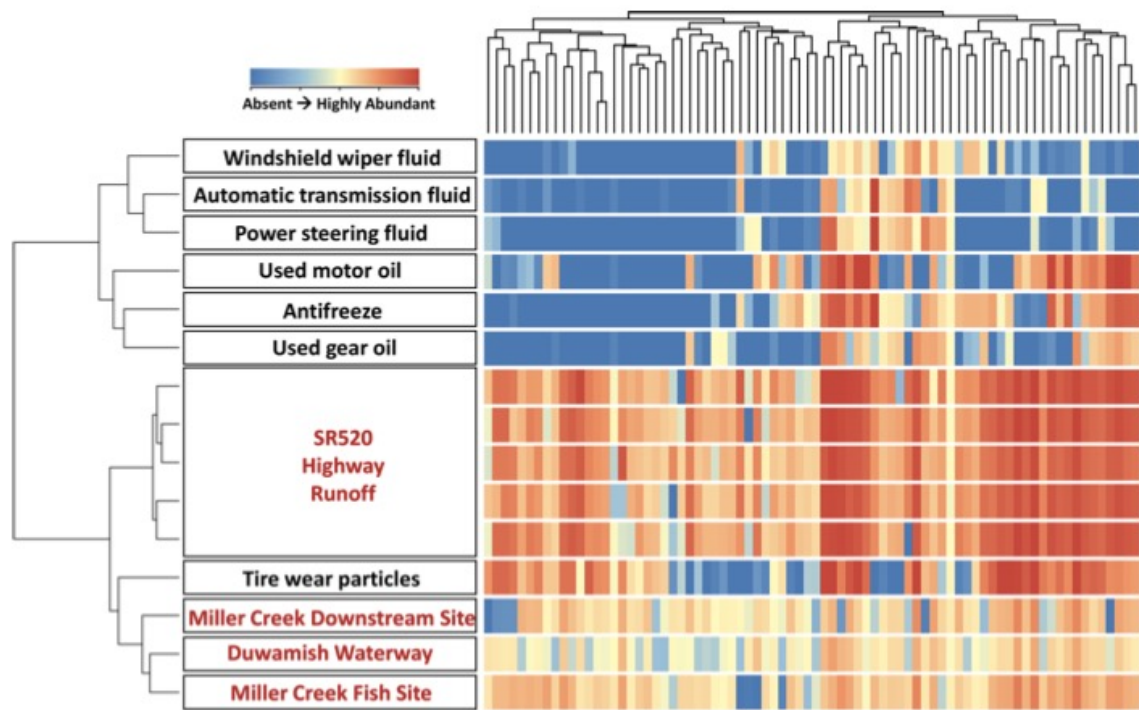
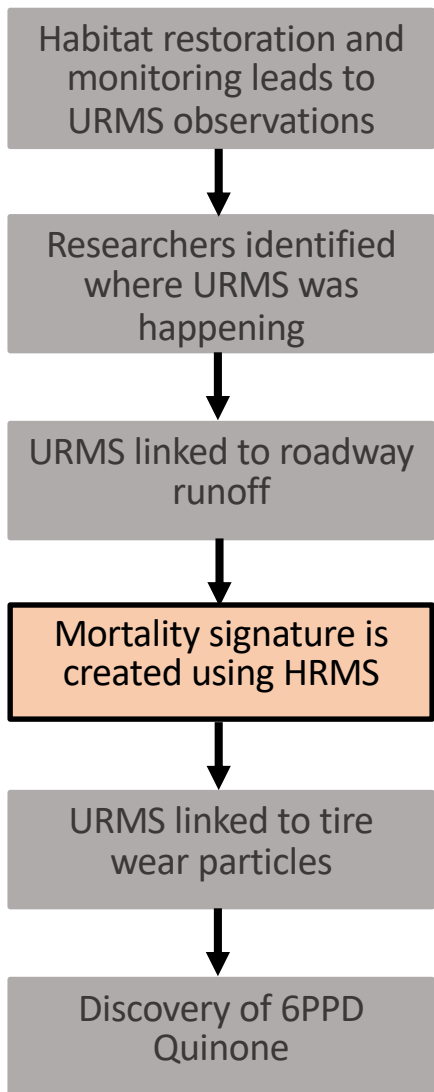
State Route 520



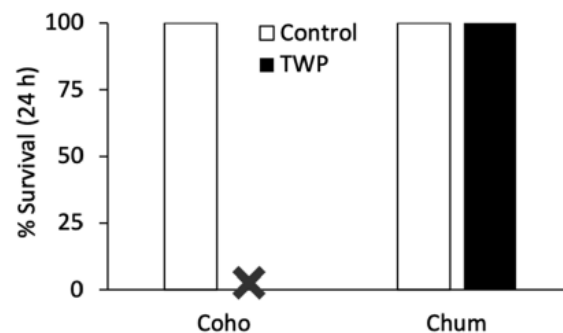
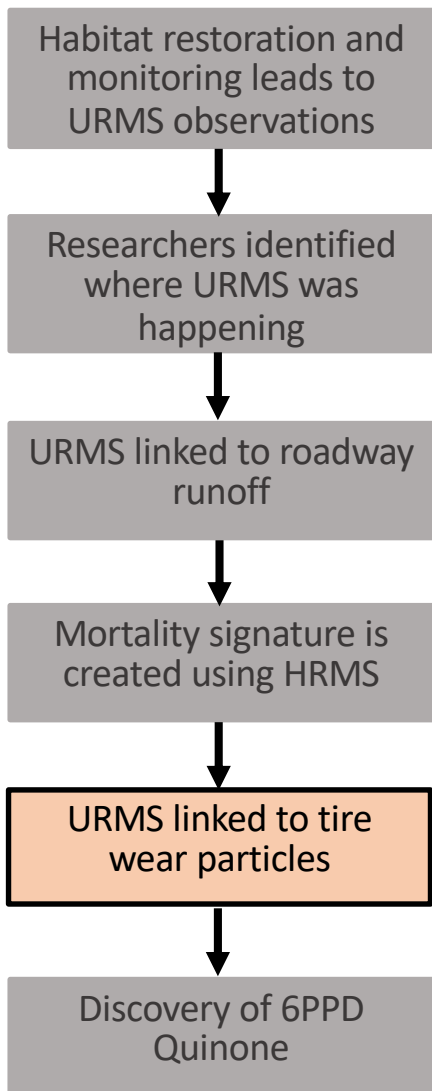
Miller Creek



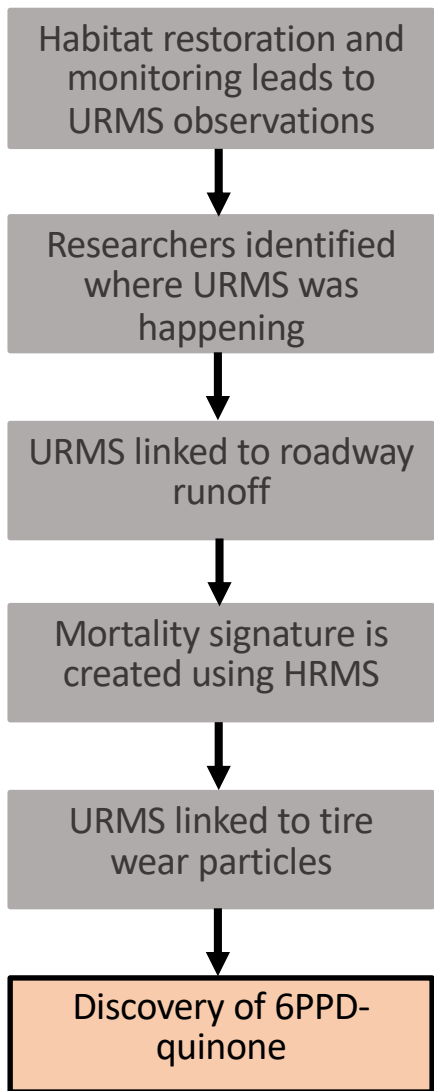
Lower Duwamish Waterway



Peter et al. 2018. Environ. Sci. Technol.



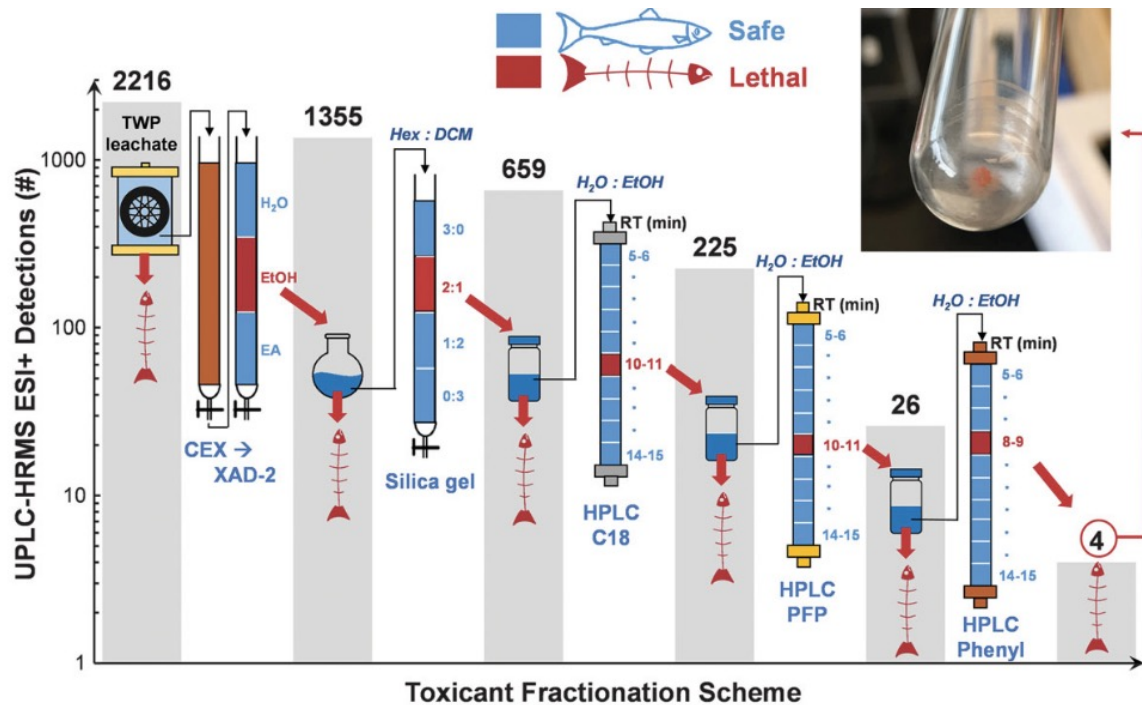
- Exposed coho and chum to tire wear particle (TWP) leachate
- TWP leachate was acutely lethal to coho at concentrations similar to roadway runoff with similar symptoms
- As seen in the wild, chum salmon were not sensitive to TWP leachate at concentrations lethal to coho
- Confirms that TWP exposure causes coho mortality



ECOTOXICOLOGY

A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon

Zhenyu Tian^{1,2}, Haoqi Zhao³, Katherine T. Peter^{1,2}, Melissa Gonzalez^{1,2}, Jill Wetzel⁴, Christopher Wu^{1,2}, Ximin Hu³, Jasmine Prat⁴, Emma Mudrock⁴, Rachel Hettinger^{1,2}, Allan E. Cortina^{1,2}, Rajshree Ghosh Biswas⁵, Flávio Vinicius Crizóstomo Kock⁵, Ronald Soong⁵, Amy Jenne⁵, Bowen Du⁶, Fan Hou³, Huan He³, Rachel Lundeen^{1,2}, Alicia Gilbreath⁷, Rebecca Sutton⁷, Nathaniel L. Scholz⁸, Jay W. Davis⁹, Michael C. Dodd³, Andre Simpson⁵, Jenifer K. McIntyre⁴, Edward P. Kolodziej^{1,2,3*}

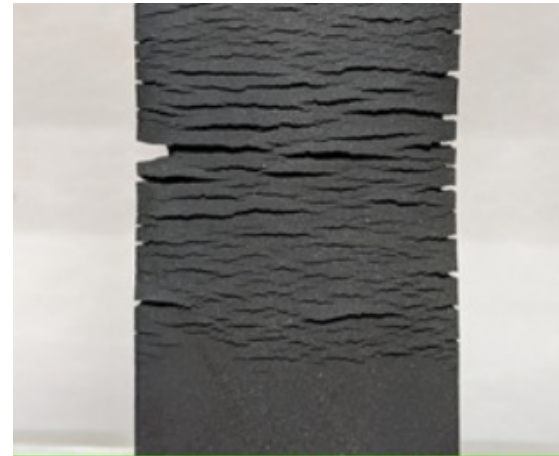


Tian et al. 2020. Science.

Why are antiozonants important?



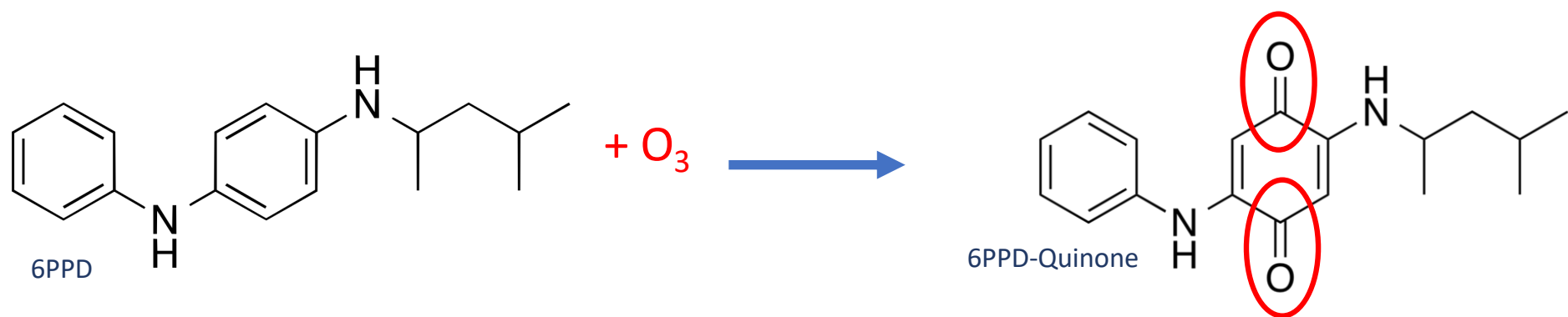
Rubber with 6PPD



Rubber without 6PPD

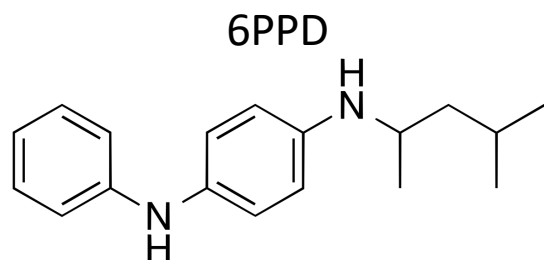
USTMA

6PPD vs 6PPD-Quinone



Toxic Transformation Product

Physicochemical Properties

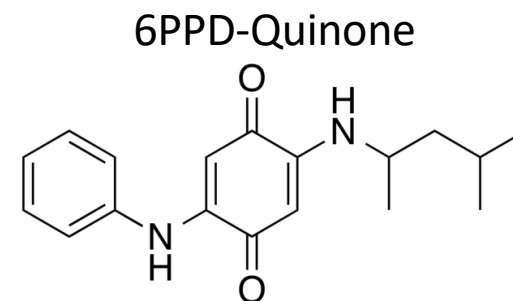


Molar mass: 268.402 g/mol

Water solubility: 1000 µg/L (50° C) (ECHA 2021)
563 ± 204 µg/L (23° C) (Hiki *et al.*)

Log K_{ow}: 4.68 *estimated* (OSPAR, 2006)

Aqueous half life: 6.8hr in sterile DI water
3.9hr in sterile river water with traces of
heavy metals (OSPAR, 2006)



Molar mass: 298.38 g/mol

Water solubility: 38 ± 10 µg/L (Hu *et al.*, 2023) (20° C)
67 ± 5 µg/L (Hiki *et al.*) (23° C)

Log K_{ow}: 4.30 ± 0.02 (Hu *et al.* 2023)

Aqueous half life: 33hr in dechlorinated tap water (Hiki *et al.*)
13-16 days in river water (Di *et al.*, 2022)

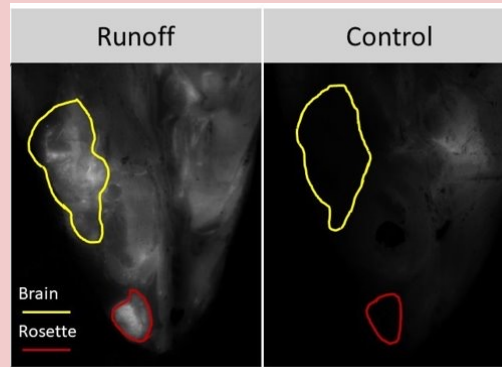
6PPD and 6PPDQ have a strong tendency to adsorb to organic matter. It has been suggested that until further evidence is obtained, these chemicals be considered persistent in soils and sediments and future monitoring should take this into account.

Research at WSU

Stormwater Treatment



Mechanism of Action



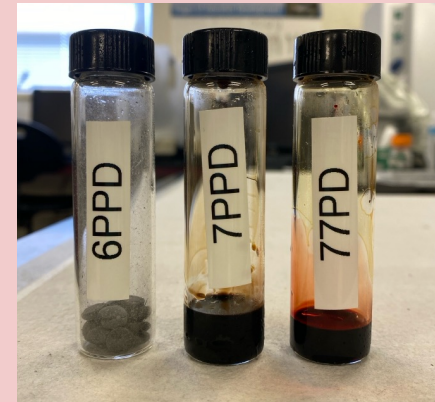
Life Stage Toxicity



Toxicity in the Environment



Alternatives Assessment

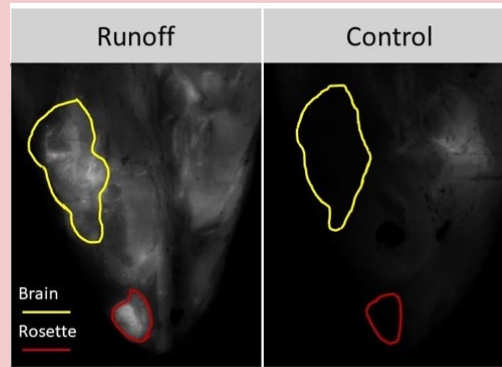


Research at WSU

Stormwater Treatment



Mechanism of Action



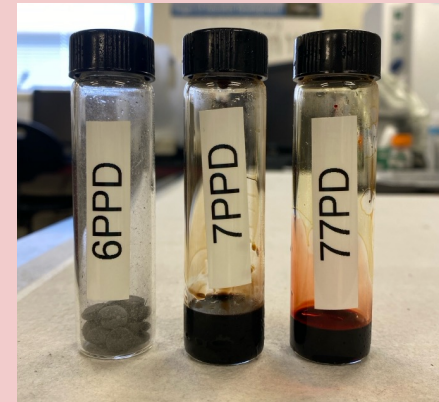
Life Stage Toxicity



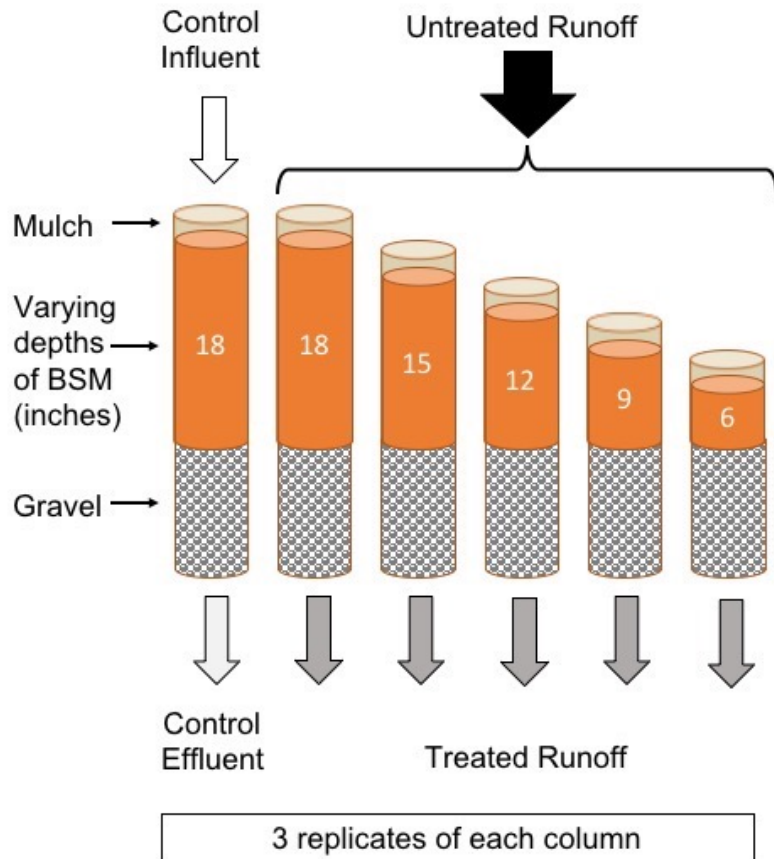
Toxicity in the Environment



Alternatives Assessment



Longevity of Bioretention for Treating Stormwater



Research questions:

- What depths of bioretention are necessary to treat runoff?
- For how long are they effective?

Accelerated Aging:

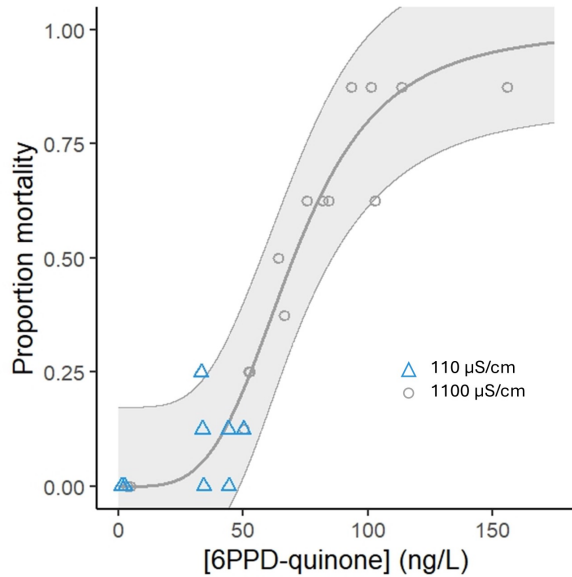
- Dosing with collected runoff
- 10 water years across 2-yr study
- Assess chemical and biological performance at end of every water year



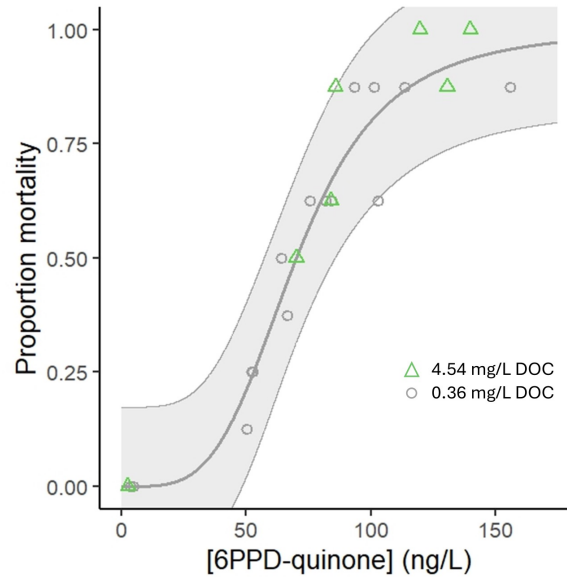
Lane Maguire



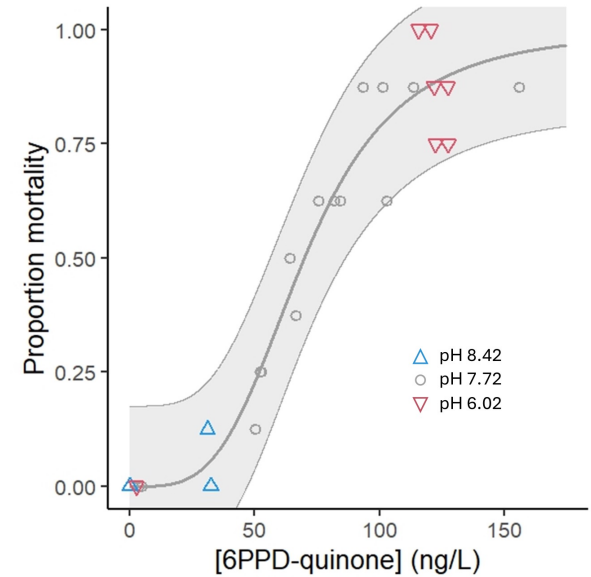
6PPD-Quinone Toxicity and Habitat Factors



Salinity



Organic matter



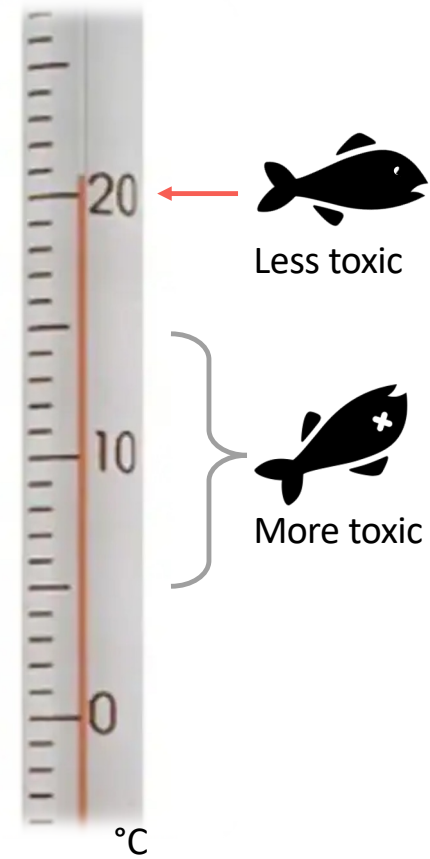
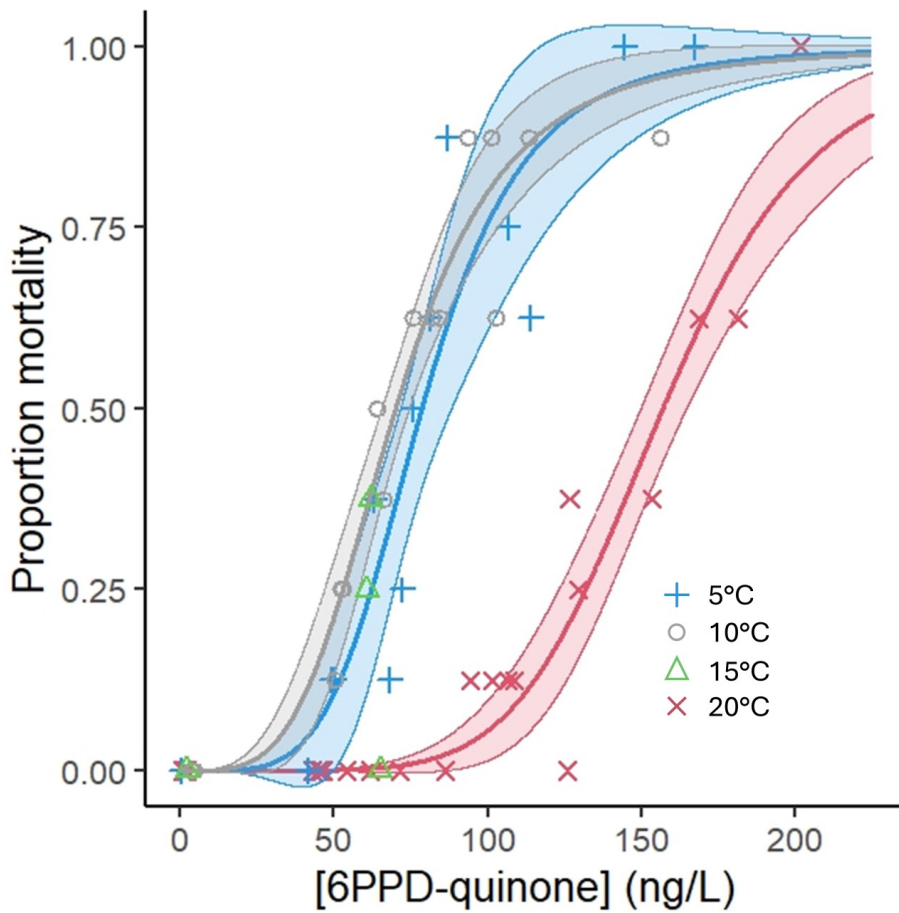
& pH

...do **not** affect toxicity

Garrett Foster



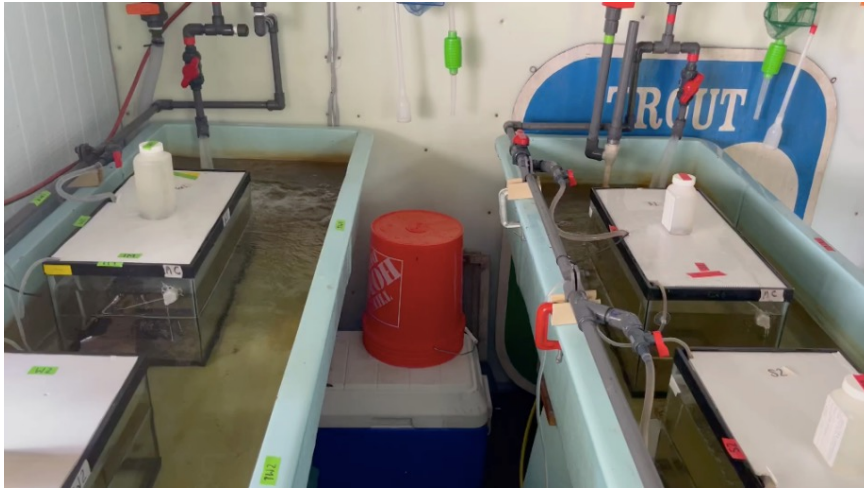
6PPD-Quinone Toxicity and Habitat Factors



Garrett Foster



Miller Creek Project



- Documenting the effect of spring storms on health of juvenile coho in an urbanized watershed
- Storm 1: April 25-30, 2024 caused 80% mortality of juveniles
- Confirms that juveniles are in fact vulnerable to real stream waters and that fall storms are not the only risk



Funded by: Puget
Sound Partnership



Nathan Ivy

Investigating Safer Alternatives to 6PPD

Goals:

1. Determine and compare toxicity of antiozonants to coho salmon.
2. Determine and compare the toxicity of antiozonant transformation products to coho salmon
3. Identify the transformation products formed during ozonation of the alternatives



Caitlin Lawrence

Toxicity of PPD Family of Antiozonants

Chemical	Known LC50?
6PPD	0.51mg/L, 24hr <i>Oncorhynchus kisutch</i>
7PPD	0.028 mg/L, 96hr <i>Oryzias latipes</i>
IPPD	1.2 mg/L, 96hr <i>Danio rerio</i>
44PD	No data available
77PD	0.06 mg/L, 96hr <i>Pimephales promelas</i>

Chemical	Known LC50?
CPPD	No data available
CCPD	No data available
DPPD	No data available
DTPD	No data available
DOPD	No data available



PPD anti-ozonants in tires:
6PPD > DTPD > DPPD > 7PPD (IPPD <LOQ)

Quinone-derivative:
6PPD-Q > DPPD-Q > DTPD-Q > 7PPD-Q (IPPD-Q <LOQ)



Zhao et al. 2023

Washington State Regulatory Actions

6PPD Action Plan

- **Actionable recommendations**, including regulatory, policy, or legislative
- 52-member advisory committee
 - 12 Tribal representatives
- Developed 37 recommendations
 - 20 supported by 2025-27 budget package
- Progress report to the Legislature in **December 2024**



Slide adapted from Tanya Williams, WA DOE

6PPDQ and WA Aquatic Life Toxics Criteria

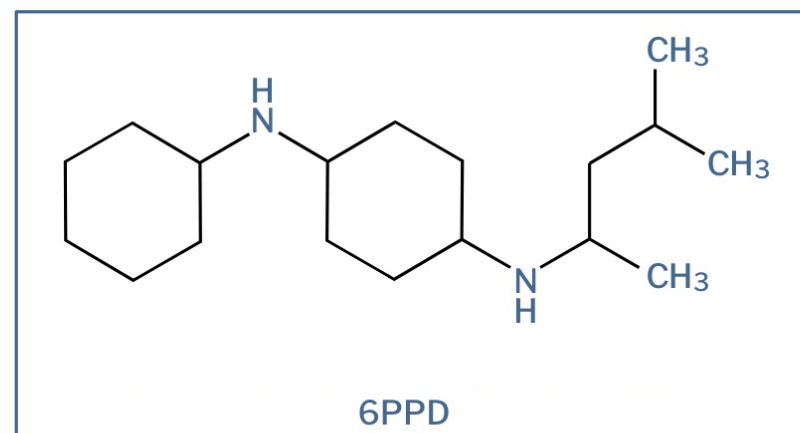
The screenshot shows the Washington Department of Ecology website. At the top left is the logo for the Department of Ecology, State of Washington. To the right are navigation links for 'Regulations & Permits', 'Research & Data', 'Blog', and 'Contact Us', along with a search bar. Below this is a horizontal menu with 'Home', 'Air & Climate', 'Water & Shorelines', 'Waste & Toxics', and 'Spills & Cleanup'. The main content area features a breadcrumb trail: 'About us > Who we are > News > 2024 news stories > Aug 14 - Aquatic Life Toxics Criteria'. The news release is dated 'August 14, 2024' and has the title 'State sets new limits for toxic chemicals in water'. The sub-headline is 'PFAS, 6PPD-quinone among chemicals listed'. The text states that Washington's waters have new protections due to a major update to state water quality rules, which protect aquatic life from toxic chemicals. It mentions that the Washington Department of Ecology developed these changes based on updated science and research, and recommendations from the U.S. Environmental Protection Agency (EPA) and Tribal governments. An image of Commencement Bay is shown, with a caption stating: 'Ecology's latest rule protects both fresh and marine waters, including Commencement Bay, pictured here.'

Freshwater Acute:
0.012µg/L

Finding safer alternatives to 6PPD

Published **hazard criteria** for alternatives in 2023

- Chemicals assessed must have:
 - Data on acute aquatic toxicity to:
 - Coho
 - Rainbow trout
 - Two other trophic levels
 - Data on transformation toxicity after exposure to ozone
- Placed a limit on acute toxicity of alternatives (LC_{50} 0.1mg/L)



Safer Products for WA

- 6PPD added as a priority chemical
- Tires added as a priority consumer product
- Tires are not subject to the statutory exemption for motor vehicles



Developing and evaluating measurement methods

- Laboratory standard operating procedures (SOPs)
- Field Sampling SOPs
- Product testing SOPs (crumb rubber study)



Photos: Ecology field sampling.

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

US Federal Regulations

Citizen Petition under TSCA

Earthjustice submitted a petition on behalf of three Pacific Northwest Tribes to the US EPA to establish regulations prohibiting manufacturing, processing, use and distribution of 6PPD.



EPA Granted Petition

Identified first actions:
1. Published advance notice of proposed rulemaking
2. Require manufacturers to submit unpublished health and safety studies



Affiliated Tribes of Northwest Indians passed resolution supporting the TSCA petition

“...the high toxicity and ubiquity of 6PPD-q presents an unreasonable risk to treaty rights and to tribal communities that rely on salmon and steelhead for cultural, subsistence and ceremonial purposes.”



EPA Announces Screening Values

Screening values for 6PPD (8,900ng/L) and 6PPD-q (11ng/L) were announced. States and Tribes may consider these values in their water quality protection programs.

Is 6PPD-Quinone Impacting BC?

Tire Wear Toxins

Daily Occurrence

Point Source

Data Interrogation

Tire Wear Toxins Website



BRITISH COLUMBIA CONSERVATION FOUNDATION

Tire Wear Toxins

1698 Samples Analyzed

Select a Watercourse
No data

6-PPDQ Concentration Per Day

2024/05/21	6-PPDQ: not detected
2024/05/29	Daily Mean 6-PPDQ: 215 ng/L
	6-PPDQ: 6 ng/L
2023/09/22	6-PPDQ: not detected

Tire Toxicant 6-PPDQ Concentration (ng/L)

Total Samples For This Site
1,631

Map displays maximum 6-PPDQ concentrations

1 of 10

Northfield Creek Beach-Estates-Park
Lower LCS50 (coho); Upper LCS50 (coho)

Graph How to Interpret Graph

1 of 251

Beck Creek_DS-Cedar-Road -

Thank You!



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