

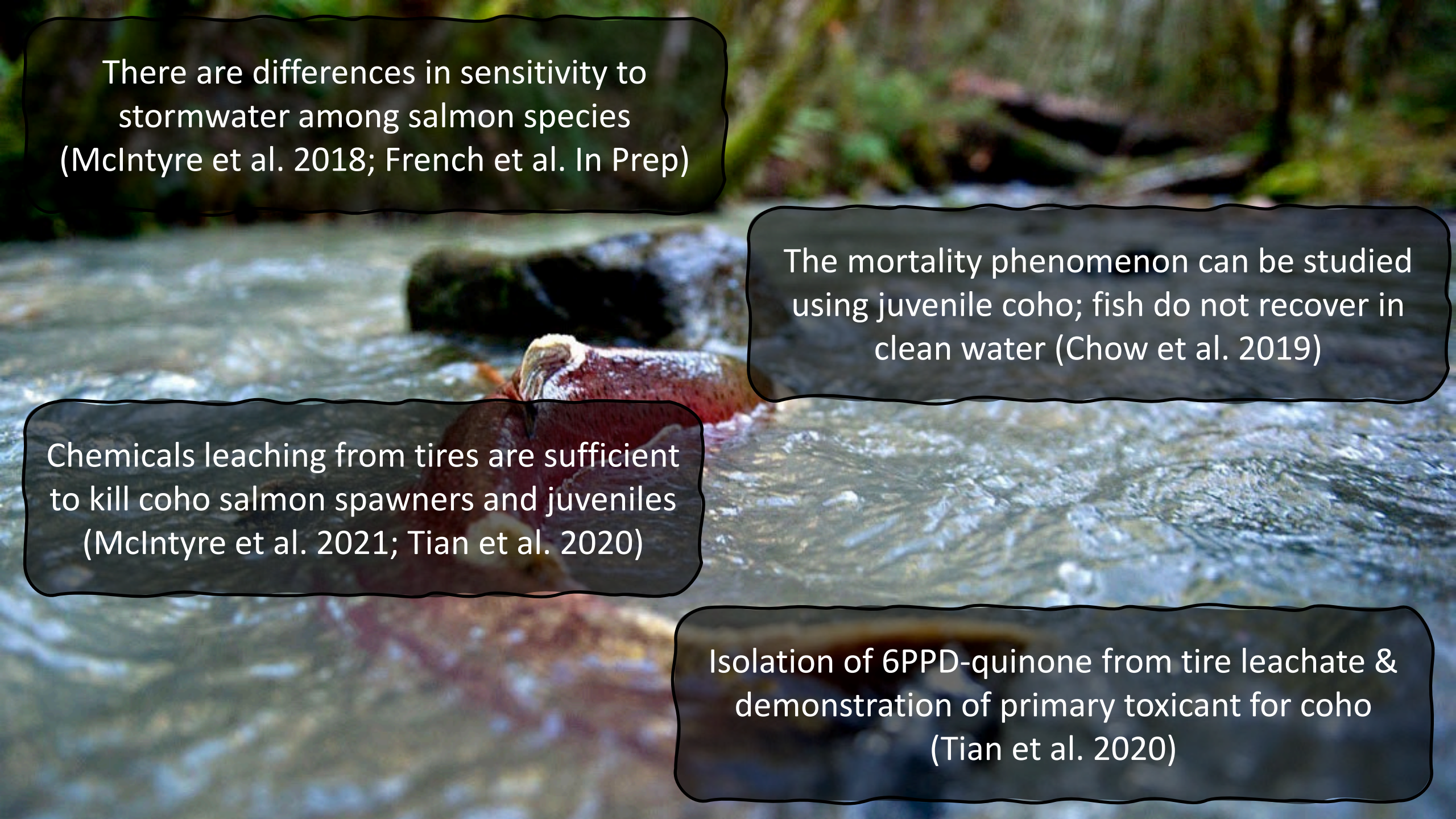
State of the Science: 6PPD-Q Toxicology



Dr. Jenifer McIntyre

WA State University | School of the Environment
Puyallup Research & Extension Center | WA Stormwater Center






There are differences in sensitivity to stormwater among salmon species (McIntyre et al. 2018; French et al. In Prep)

The mortality phenomenon can be studied using juvenile coho; fish do not recover in clean water (Chow et al. 2019)

Chemicals leaching from tires are sufficient to kill coho salmon spawners and juveniles (McIntyre et al. 2021; Tian et al. 2020)

Isolation of 6PPD-quinone from tire leachate & demonstration of primary toxicant for coho (Tian et al. 2020)

The background image shows a shallow stream with clear, rippling water. A large, weathered log with a reddish-brown hue is partially submerged, extending from the foreground towards the center. The surrounding environment is lush with green moss and ferns on the banks. A dark circular overlay with a white border is positioned on the right side of the image, containing the text.

Toxicology of
6PPD-quinone
2021-2022

6PPD-Q Revised Toxicity to Coho Salmon

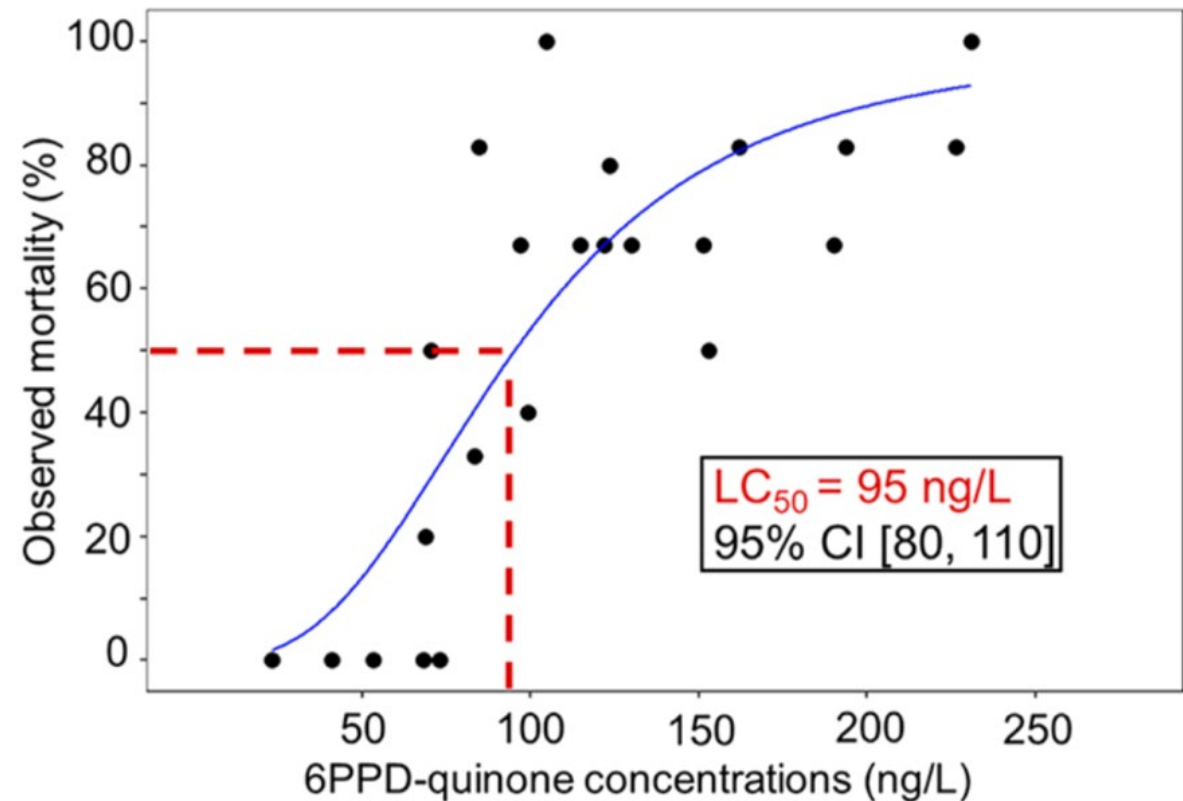
Commercial standard for 6PPD-Q
(HPC Standards)

- Higher purity
- Correction for recovery

Result:

Revised environmental concentrations & effects concentrations ~8X lower than reported in Tian et al. 2020.

(Tian et al. 2022 ES&T Letters)



Coho LC50 revised from 790 ng/L to 95 ng/L

6PPD-quinone toxicity for other species

Common Name	Species	Time (h)	Non-lethal µg/L	LC50 (95% CL) µg/L	Reference
Coho	<i>O. kisutch</i>	24		0.10 (0.08-0.11)	Tian et al. 2022
Brook trout	<i>S. fontinalis</i>	24		0.59 (0.49-0.63)	Brinkmann et al. 2022
Rainbow trout	<i>O. mykiss</i>	24		1.00 (0.95-1.05)	Brinkmann et al. 2022
Zebrafish	<i>D. rerio</i>	24		308.7 (258.3-368.9)	Varshney et al. 2021
White sturgeon	<i>A. transmontanus</i>	96	>12.7		Brinkmann et al. 2022
Arctic char	<i>S. alpinus</i>	96	>12.7		Brinkmann et al. 2022
Medaka	<i>O. latipes</i>	96	>34		Hiki et al. 2021
Daphnia	<i>D. magna</i>	48	>46		Hiki et al. 2021
Amphipod	<i>H. azteca</i>	96	>43		Hiki et al. 2021
Zebrafish	<i>D. rerio</i>	96	>54		Hiki et al. 2021

Toxicity of 6PPD-quinone vs other chemicals

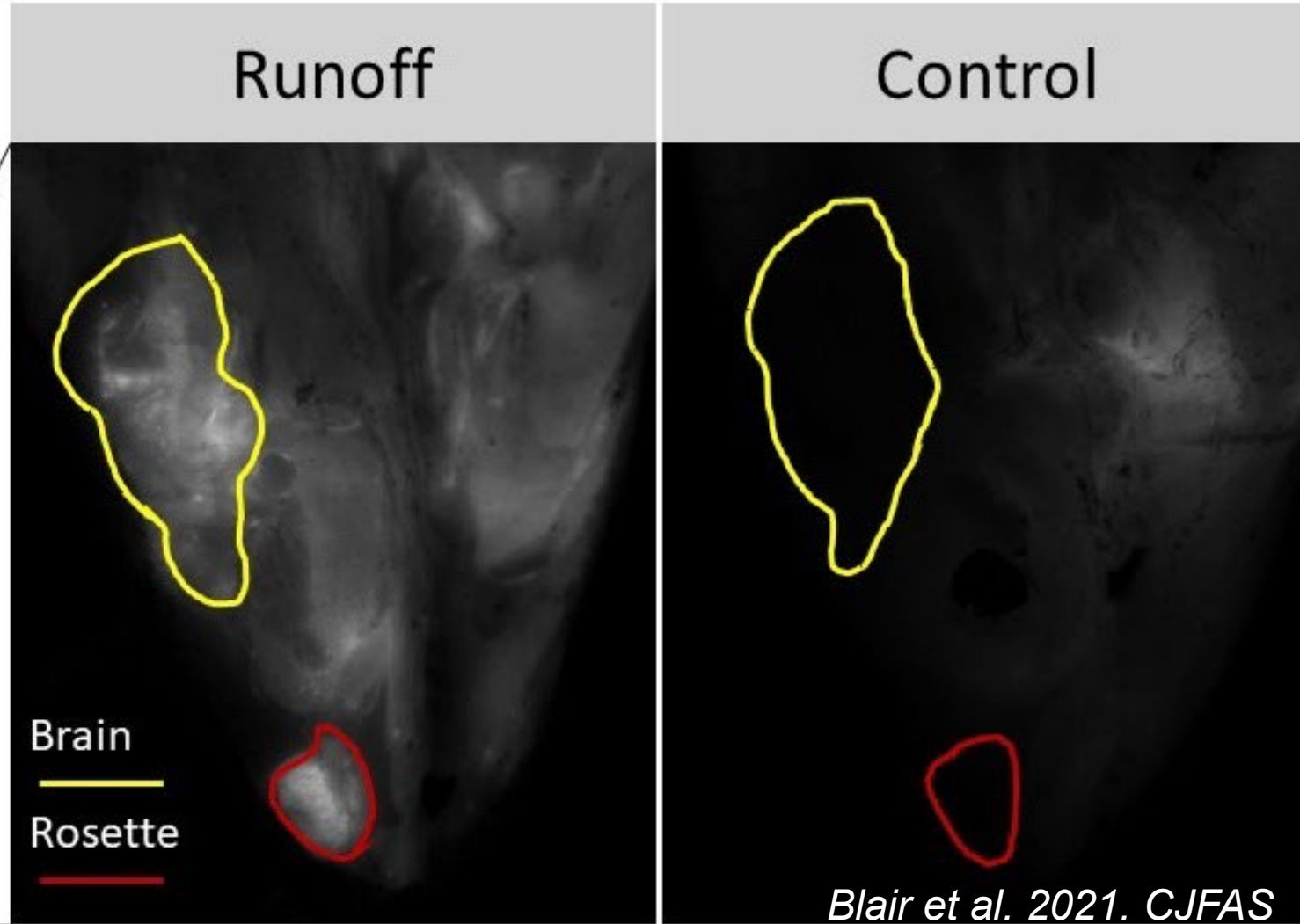
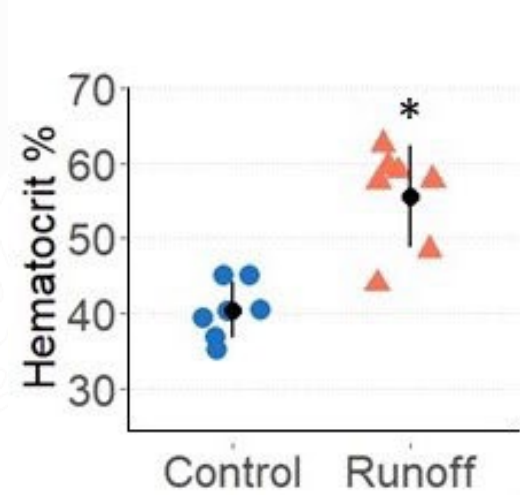
(Tian et al. 2022 ES&T Letters)

chemical class	name	most sensitive species	LC ₅₀ (ppb)	95% CI
OP	parathion	<i>Orconectes nais</i>	0.04	0.01–0.2
quinone	6PPD-Q	<i>O. kisutch</i>	0.10	0.08–0.11
OC	mirex	<i>Procambaris blandingi</i>	0.10	not reported
OP	guthion	<i>Gammarus fasciatus</i>	0.10	0.073–0.014
OP	chlorpyrifos	<i>Gammarus lacustris</i>	0.11	not reported
OC	endrin	<i>Perca flavescens</i>	0.15	0.12–0.18
OC	4,4'-DDT	<i>O. nais</i>	0.18	0.12–0.30
OP	diazinon	<i>Ceriodaphia dubia</i>	0.25	not reported
metal	cadmium	<i>Oncorhynchus mykiss</i>	0.35	not reported
OC	methoxychlor	<i>O. nais</i>	0.50	0.25–1.8
OC	dieldrin	<i>Pteronarcella badia</i>	0.50	0.37–0.67
OP	malathion	<i>G. fasciatus</i>	0.76	0.63–0.92
OC	toxaphene	<i>Ictalurus punctatus</i>	0.8	0.5–1.2

6PPD-quinone is among the most toxic chemicals know for aquatic life



Blood brain barrier of coho becomes leaky

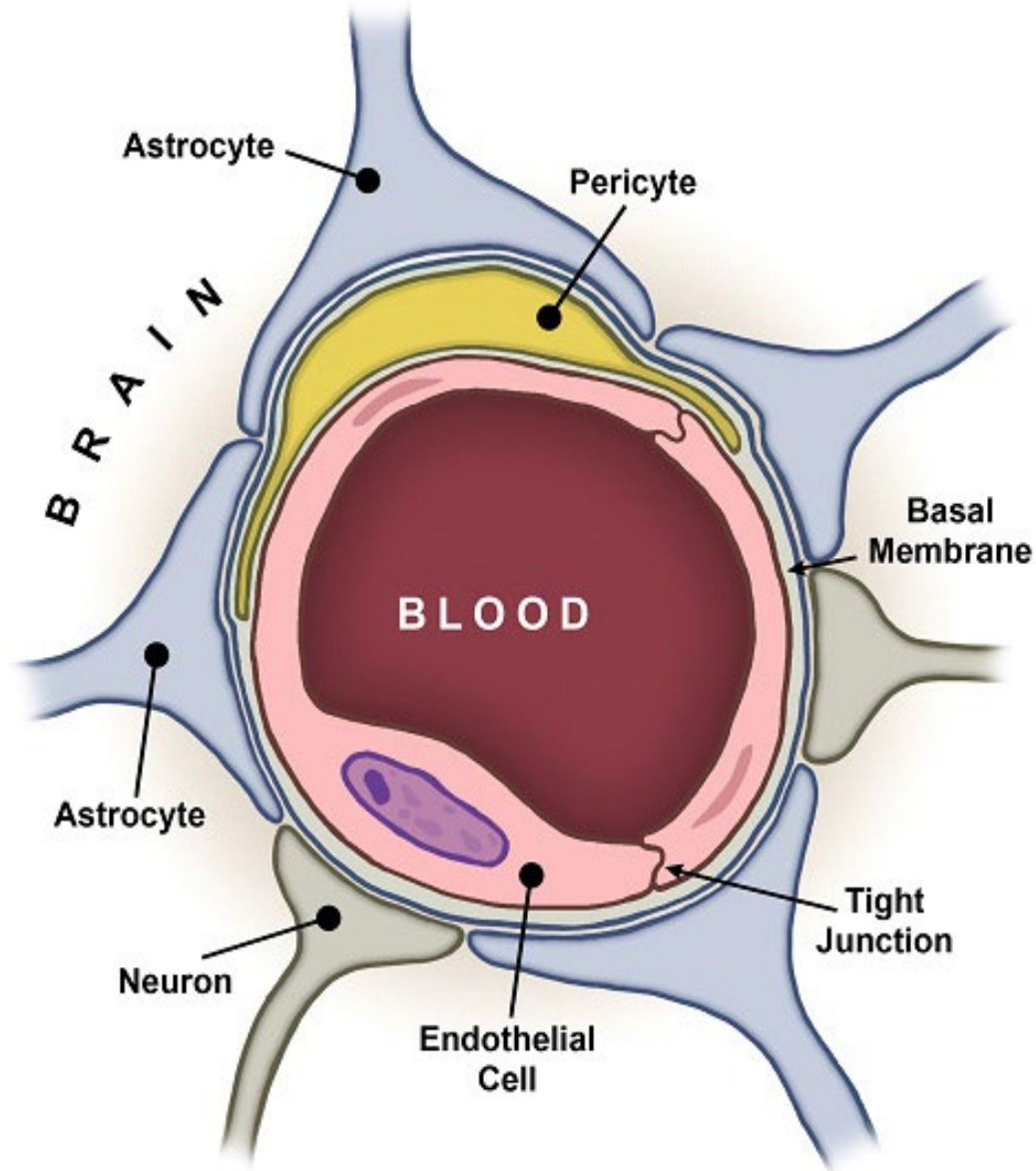


Stephanie Blair
Ph.D. candidate
WSU SOE

Hemoconcentration linked to plasma leaking from vascular system



Timing and Severity of Plasma Leaking



Timing: Track BBB permeability at time/end points during exposure to runoff:

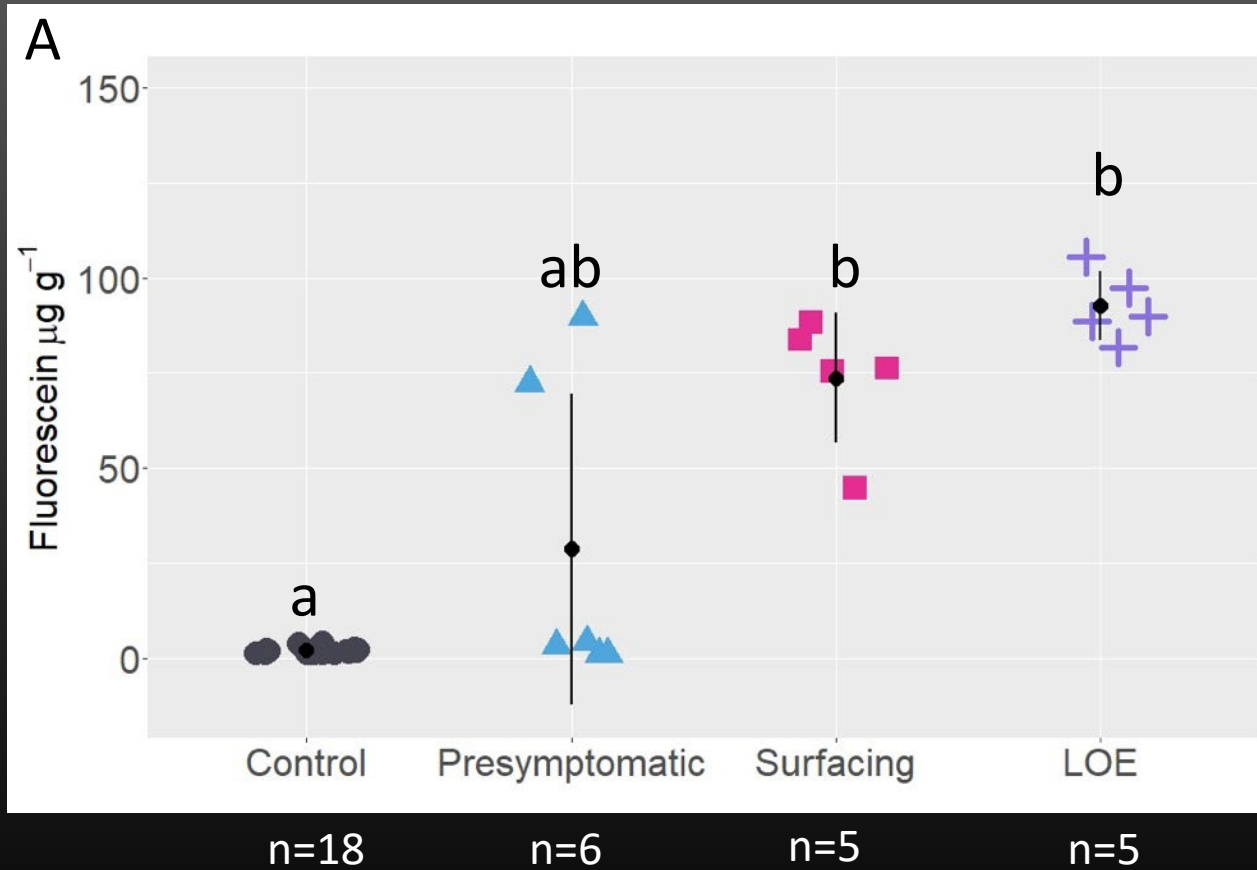
- pre-symptomatic
- surfacing
- loss of equilibrium

Severity: Use high- and low-molecular weight tracers

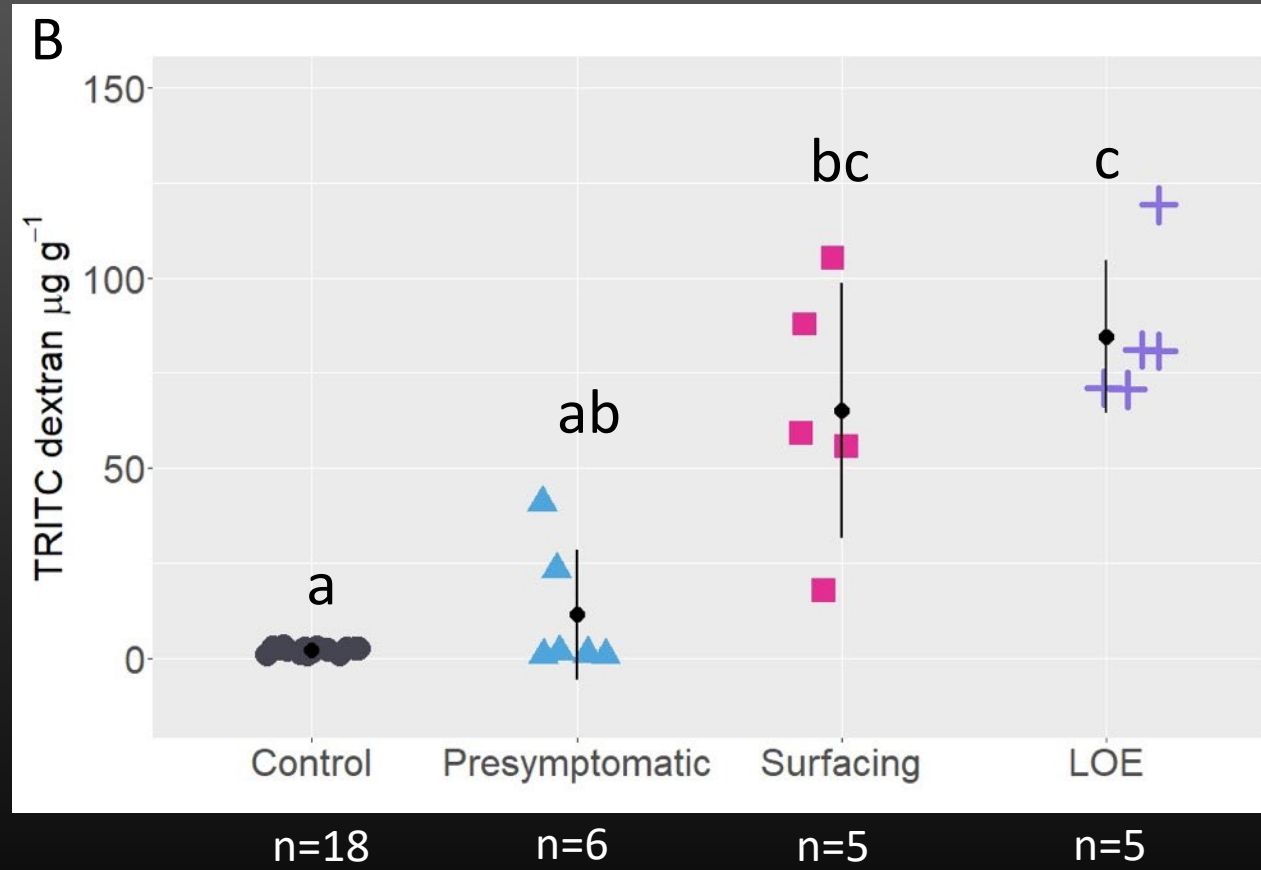
- Low = mild opening of BBB
- High = severe opening of BBB

Goals: Molecular initiating events & sublethal impacts

Brain content of low mw tracer



Brain content of high mw tracer



Exposure Time \longrightarrow

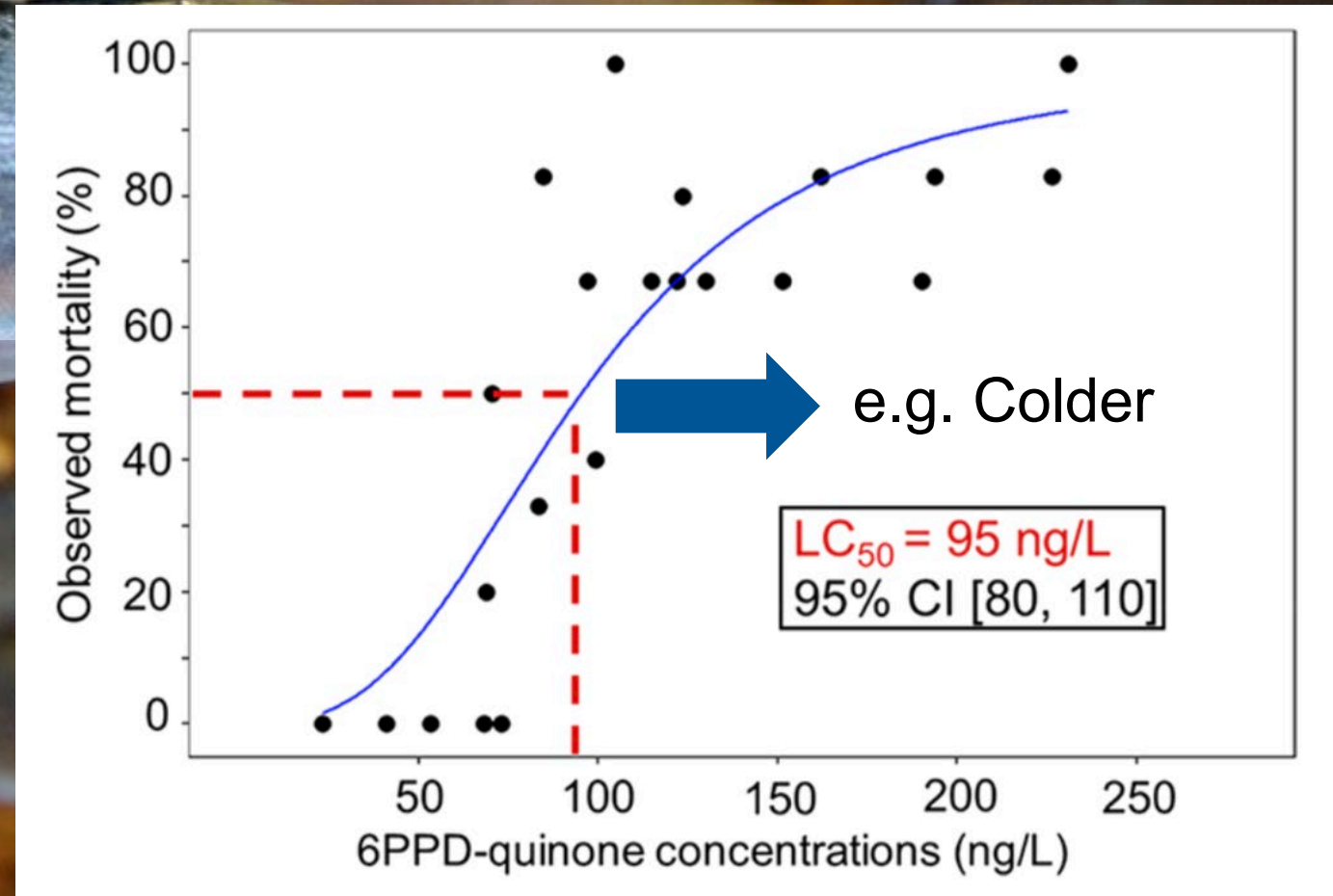
6PPD-quinone concentrations
50% Runoff: 211 ng/L
Control tanks: Non-detect

6PPD-quinone toxicity: Environmental variables



Garrett Foster
M.S. student
WSU SOE

- Temperature
- pH
- Ionic strength
- Dissolved organic matter
- Life phase
- Physical activity



Treatment: Green Stormwater Infrastructure



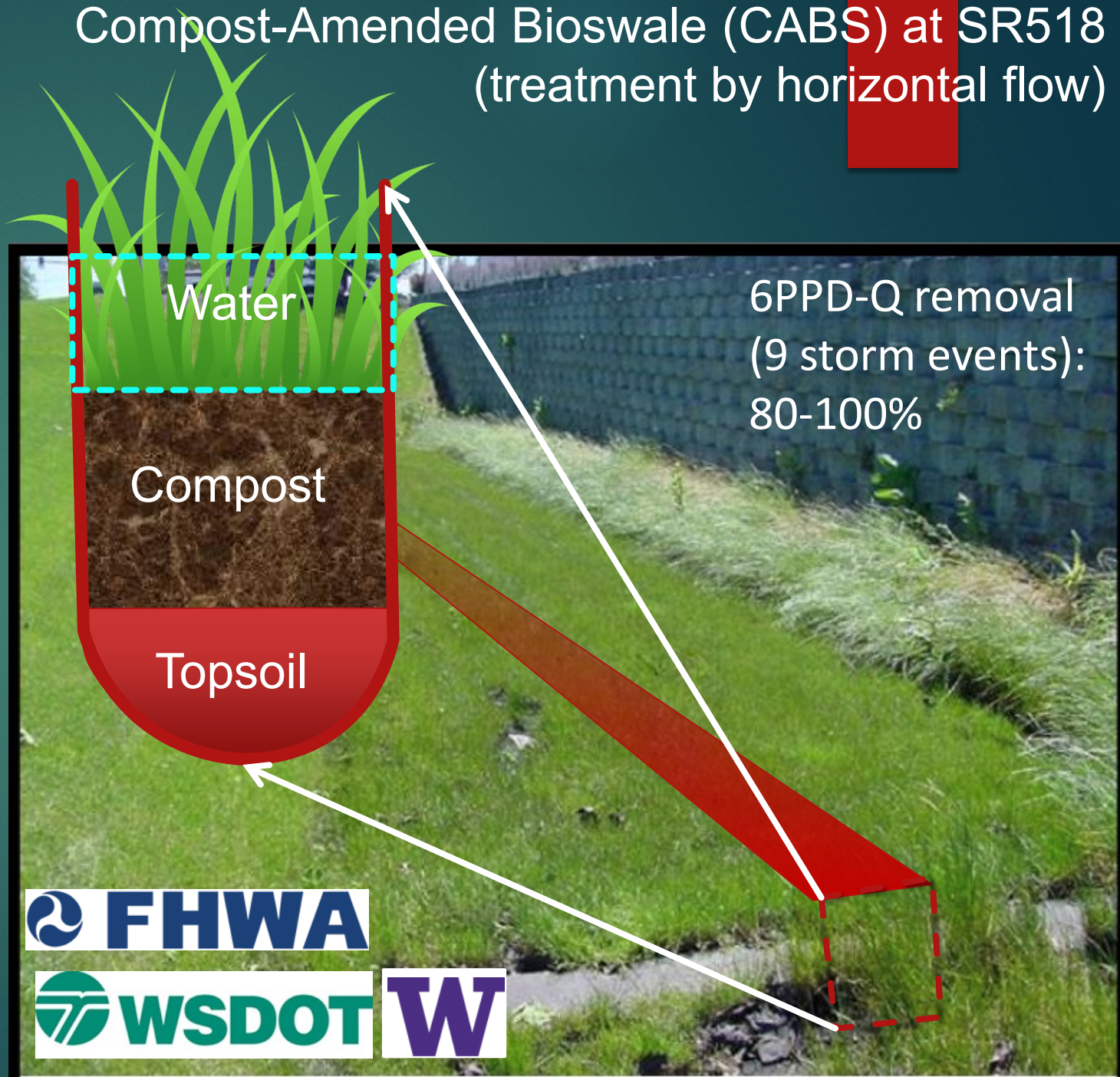
Bioretention at Ship Canal (I-5) (treatment by vertical infiltration)

6PPD-Q removal
(8 storm events):
~100%

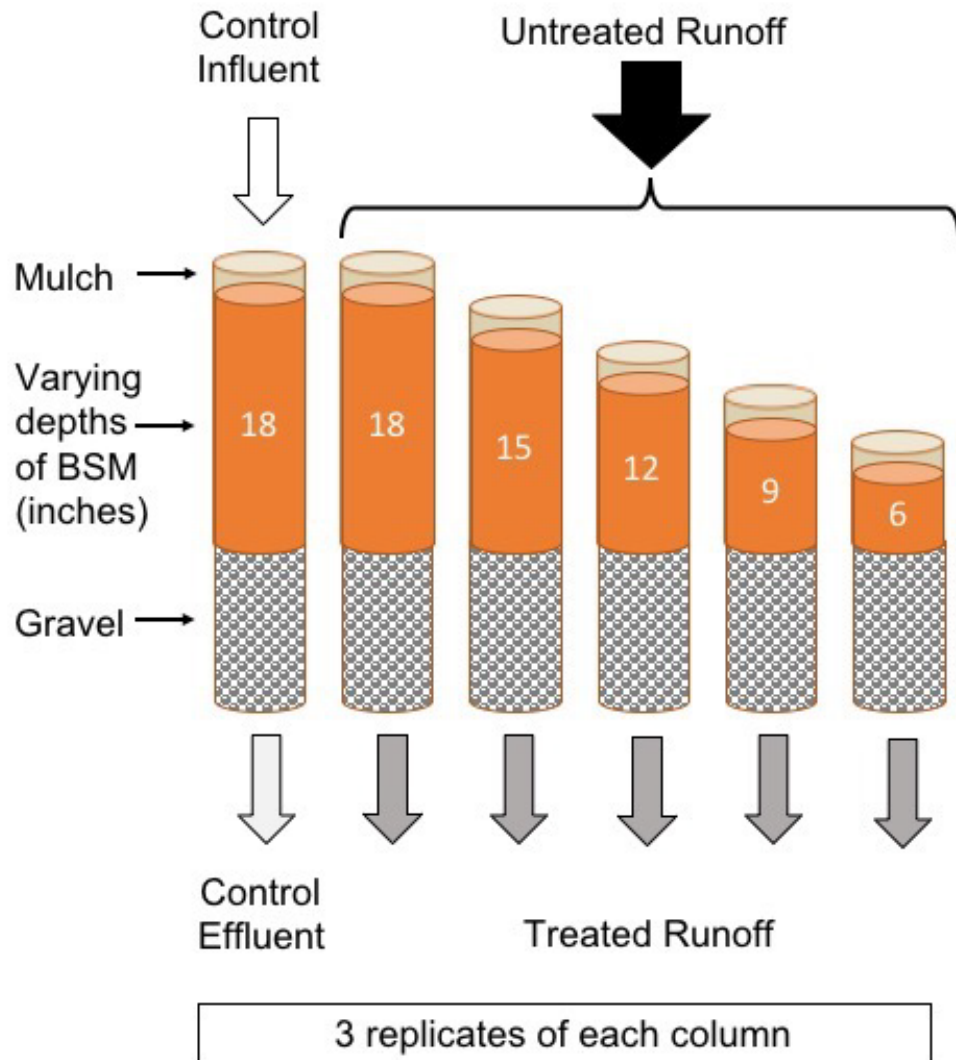


Compost-Amended Bioswale (CABS) at SR518 (treatment by horizontal flow)

6PPD-Q removal
(9 storm events):
80-100%



6PPD-Q treatment with bioretention depth?



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

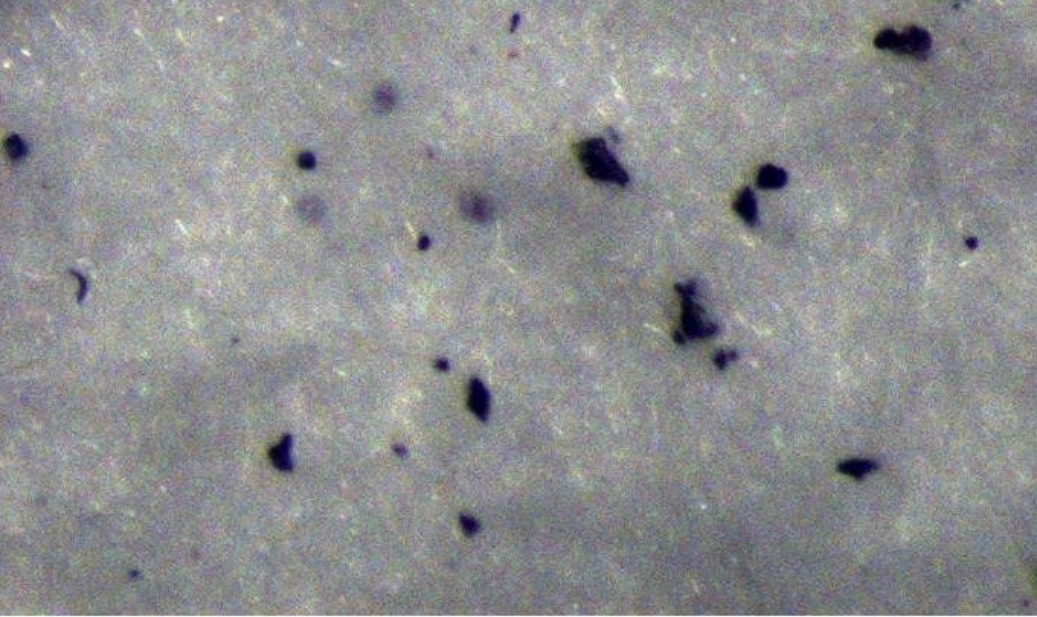


Lane Maguire
M.S. 2021

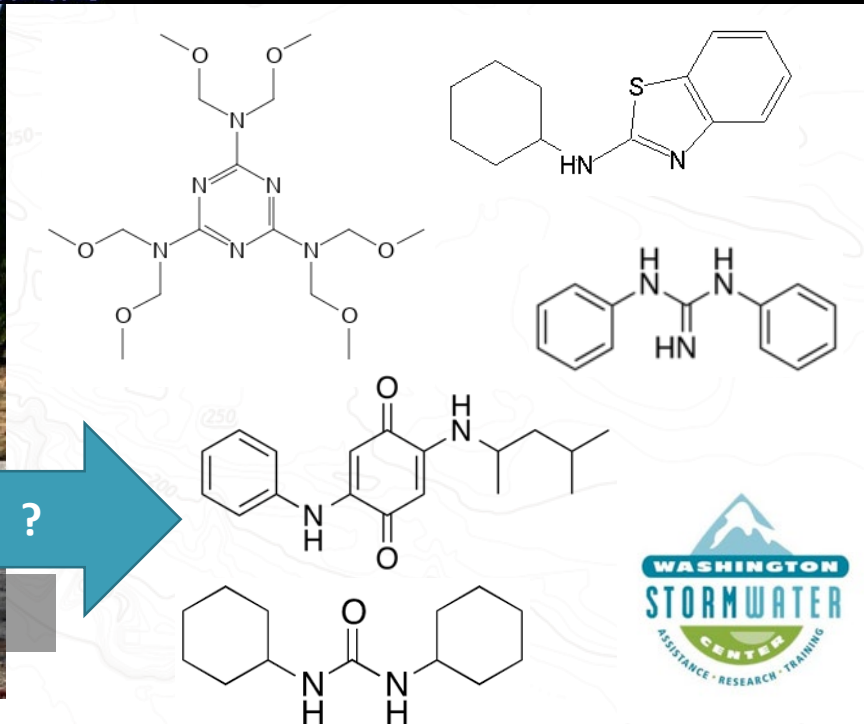
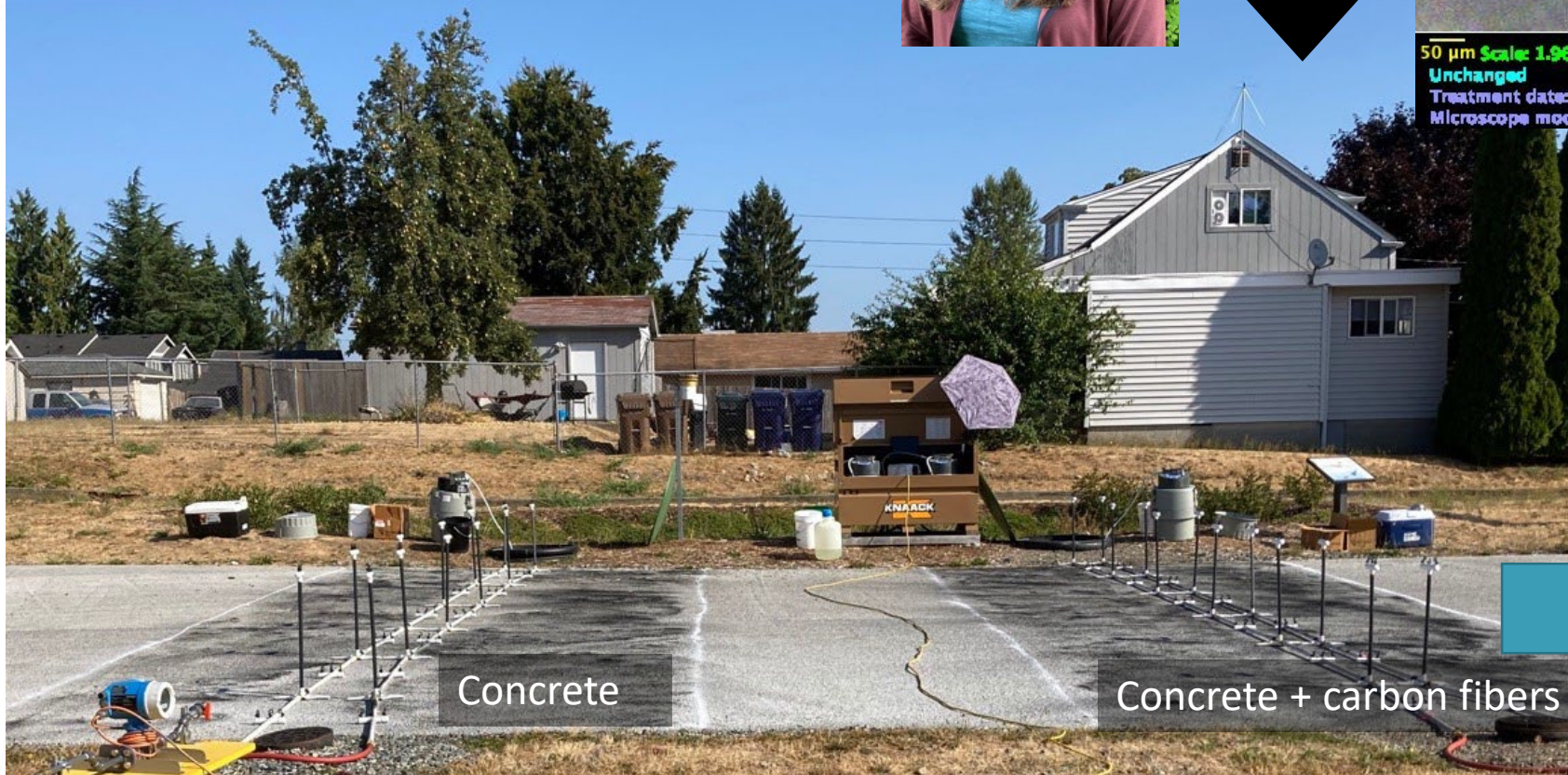


Can permeable pavements mitigate chemical and microplastics emissions from tire wear?

Chelsea Mitchell (WSU PhD candidate)
Anand Jayakaran



50 μm Scale: 1.960 μm / pixel
Unchanged
Treatment date: Mon 14-Mar-2022 Time: 18:59:22
Microscope model: zoom3



Mitigation: Source Control



Ongoing conversation about
safer alternatives to 6PPD

LisaRozmyn@wsu.edu

jen.mcintyre@wsu.edu

Send
Help!

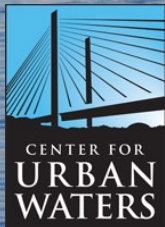
*Questions Shall Be Entertained,
Unless We've Gone Over-Time*



6PPD-Quninone: Background and Observations



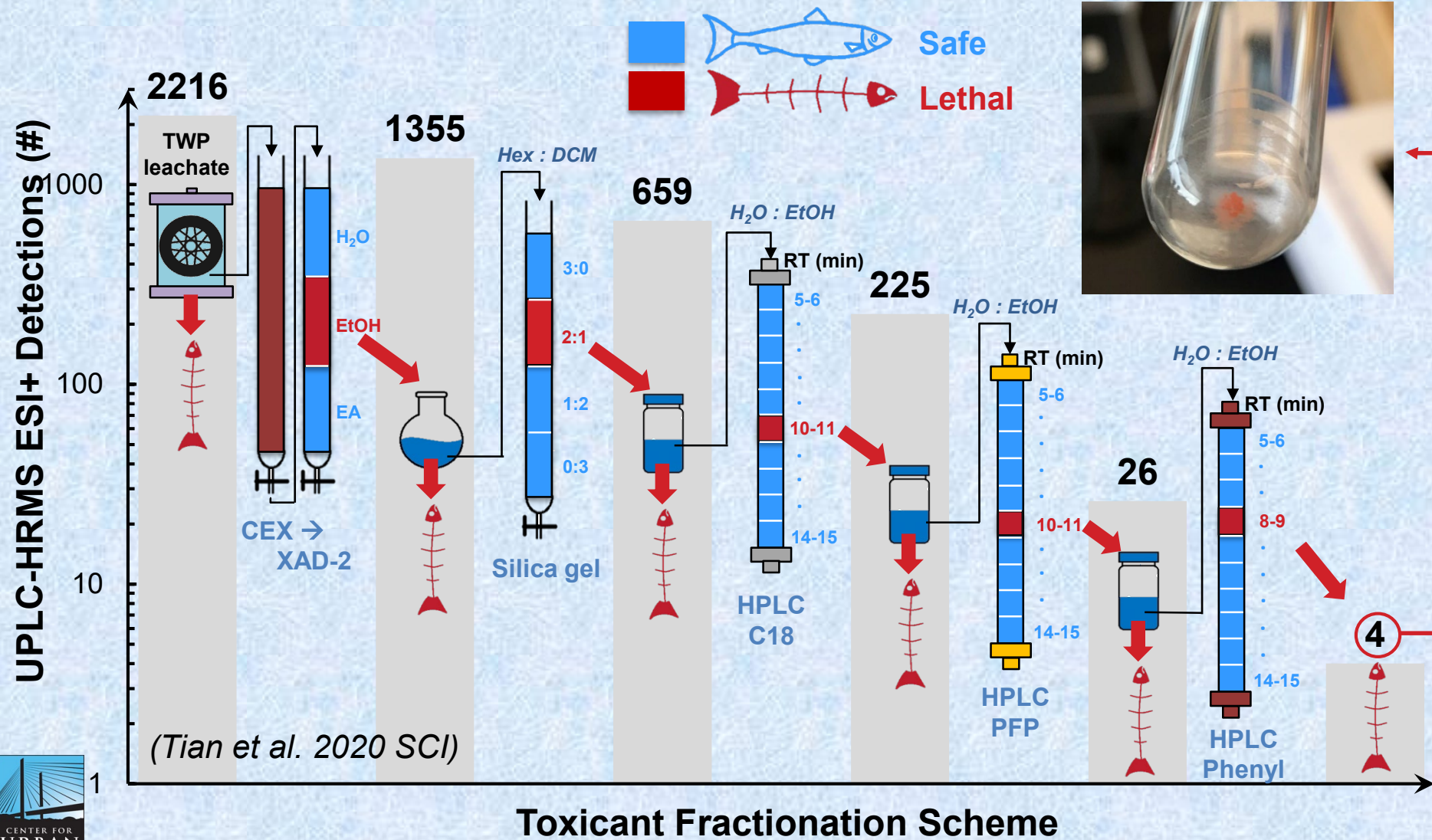
Edward P. Kolodziej,
Center for Urban Waters Research Group,
and various awesome collaborators



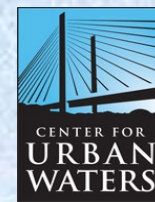
Finding a Toxic Chemical.

+Control: TWP leachate, 27 exposures, 135 coho, 98.5% mortality

-Control: Solvent and Exposure water blanks, 125 coho, 0% mortality



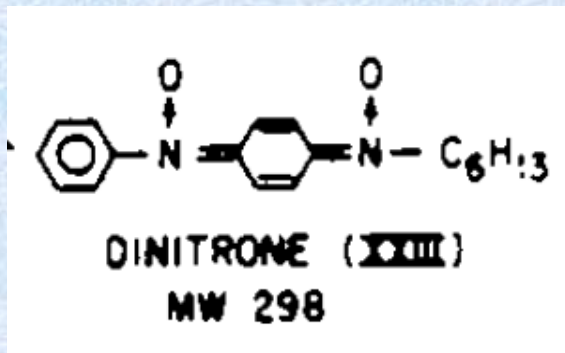
Final Toxic Fraction: What Was $C_{18}H_{22}N_2O_2$??



- $C_{18}H_{22}N_2O_2$ NOT found in literature/databases for environment or tire rubber chemicals “True Unknown”
- Assumed transformation product, held C and N constant.. Looked for matches → $C_{18}H_{24}N_2$ (“6PPD”) in EPA Crumb Rubber report

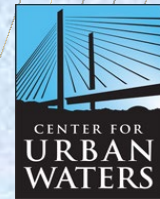
Lattimer et al., 1983
Rubber. Chem. Technol.

$C_{18}H_{22}N_2O_2$
 “dinitrone”

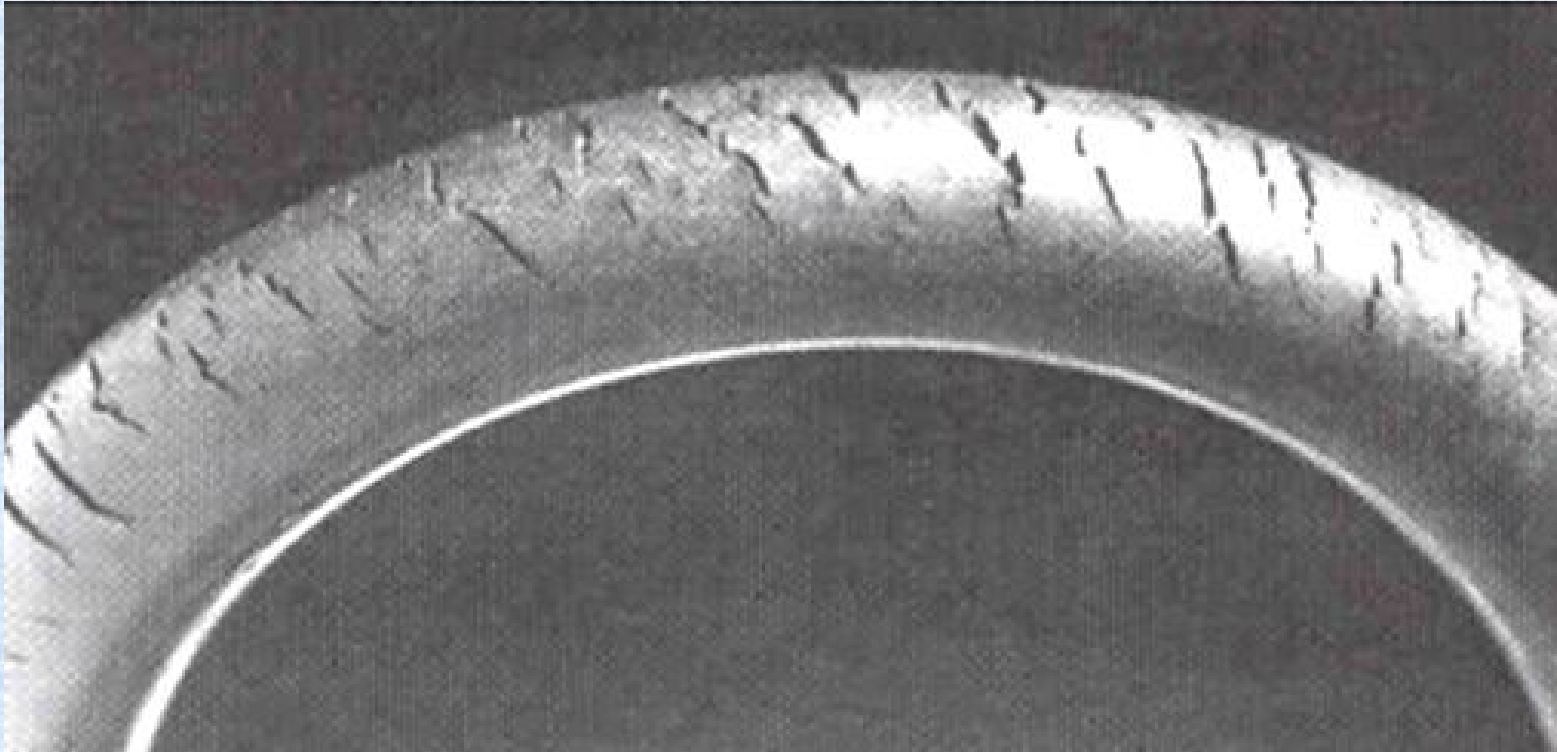


Measured mass ^a	Atomic composition	Calculated mass ^b
184.0997 ^c	$C_{12}H_{12}N_2$	184.1000
198.0793 ^c	$C_{12}H_{10}N_2O$	198.0793
214.0742 ^c	$C_{12}H_{10}N_2O_2$	214.0742
268.1579 ^c	$C_{17}H_{20}N_2O$	268.1576
268.1944 ^c	$C_{18}H_{24}N_2$	268.1939
211.1235	$C_{14}H_{15}N_2$	211.1235
282.1734 ^c	$C_{18}H_{22}N_2O$	282.1732
225.1023	$C_{14}H_{13}N_2O$	225.1028
296.1889 ^c	$C_{19}H_{24}N_2O$	296.1888
298.1688 ^c	$C_{18}H_{22}N_2O_2$	298.1681
534.3716 ^c	$C_{36}H_{46}N_4$	534.3722
477.3011	$C_{32}H_{37}N_4$	477.3018
546.3356 ^c	$C_{36}H_{42}N_4O$	546.3358
503.2819	$C_{33}H_{35}N_4O$	503.2811
489.2654	$C_{32}H_{33}N_4O$	489.2654

What Does 6PPD Do??



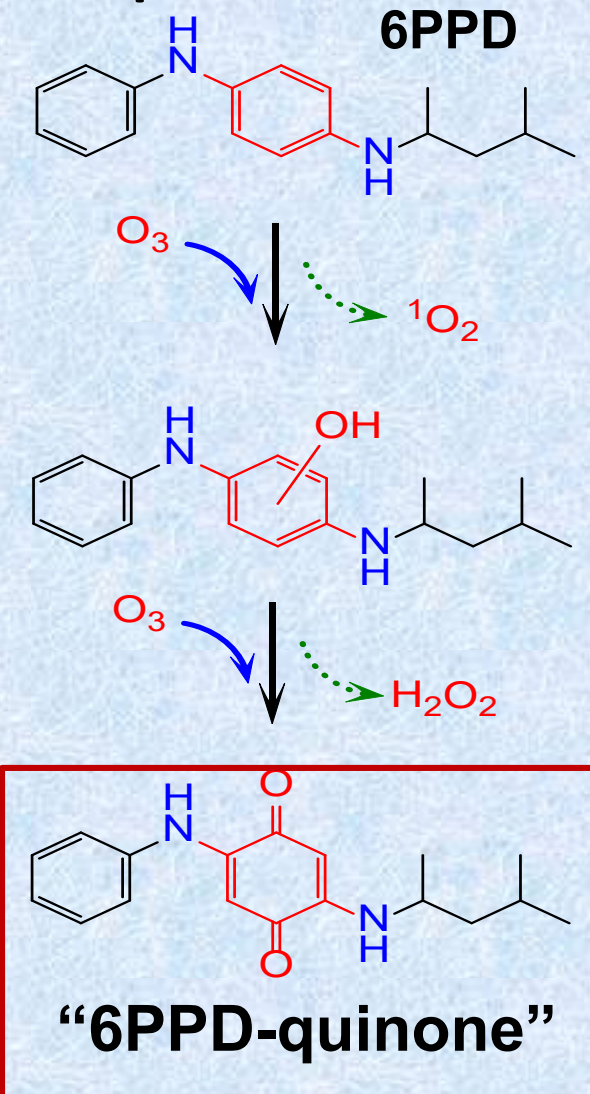
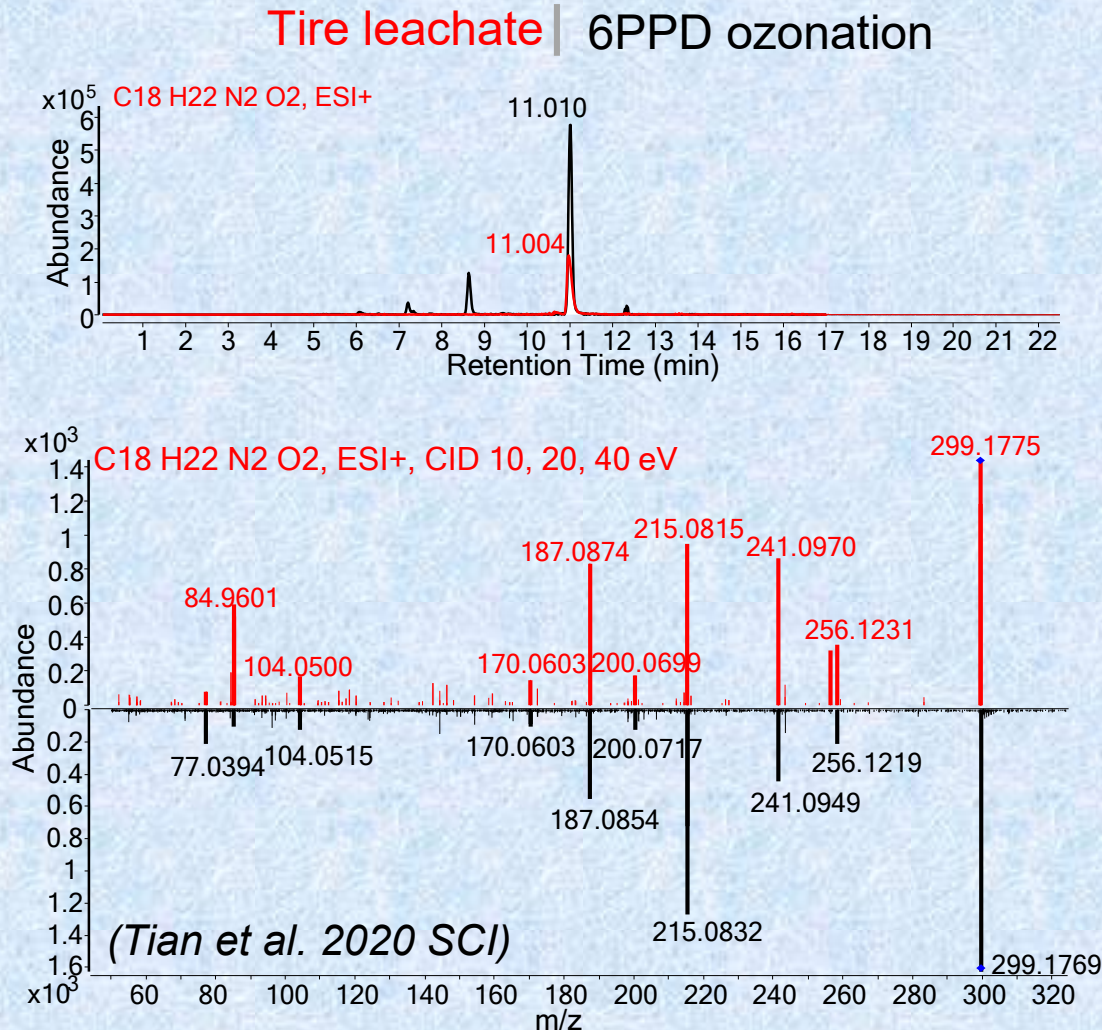
“Anti-Ozonant”: Prevents tires from cracking
This provides strength, long life, good gas mileage, safety



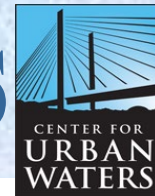
**We all own/purchase 6PPD:
Each car, ~100 lbs rubber, ~1 lb 6PPD
Heavy trucks: >2000 lbs rubber, maybe 2% 6PPD?**

Purified $C_{18}H_{22}N_2O_2$ from Tire Leachate and Ozonation

-Andre Simpson, U. Toronto NMR Analysis:
Identical structures, O_3 synthesized ~98% pure



Past References and Technical Details



EMBARGOED UNTIL 2:00PM US ET, THURSDAY 3 DECEMBER 2020

Science

REPORTS

Cite as: Z. Tian *et al.*, *Science*
10.1126/science.abd6951 (2020).

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*}

ENVIRONMENTAL
Science & Technology

Cite This: *Environ. Sci. Technol.* 2018, 52, 10317–10327

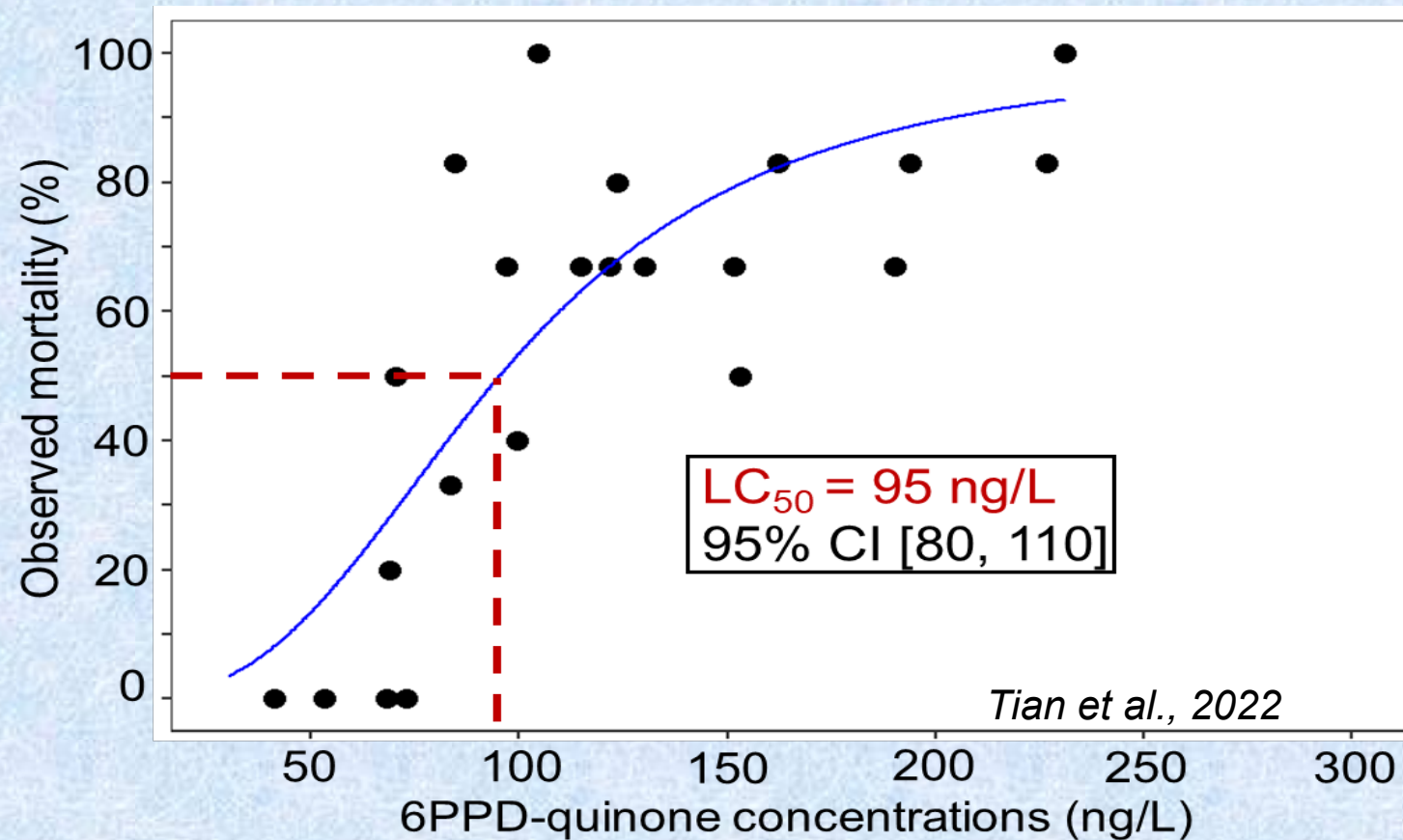
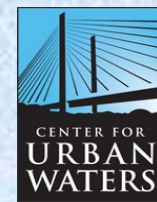
Article

pubs.acs.org/est

Using High-Resolution Mass Spectrometry to Identify Organic Contaminants Linked to Urban Stormwater Mortality Syndrome in Coho Salmon

Katherine T. Peter,^{*,†,‡,§} Zhenyu Tian,^{†,‡,§} Christopher Wu,[‡] Peter Lin,[‡] Sarah White,[‡] Bowen Du,^{||} Jenifer K. McIntyre,[⊥] Nathaniel L. Scholz,[#] and Edward P. Kolodziej^{†,‡,§}

6PPD-Quinone Revised LC₅₀ Value

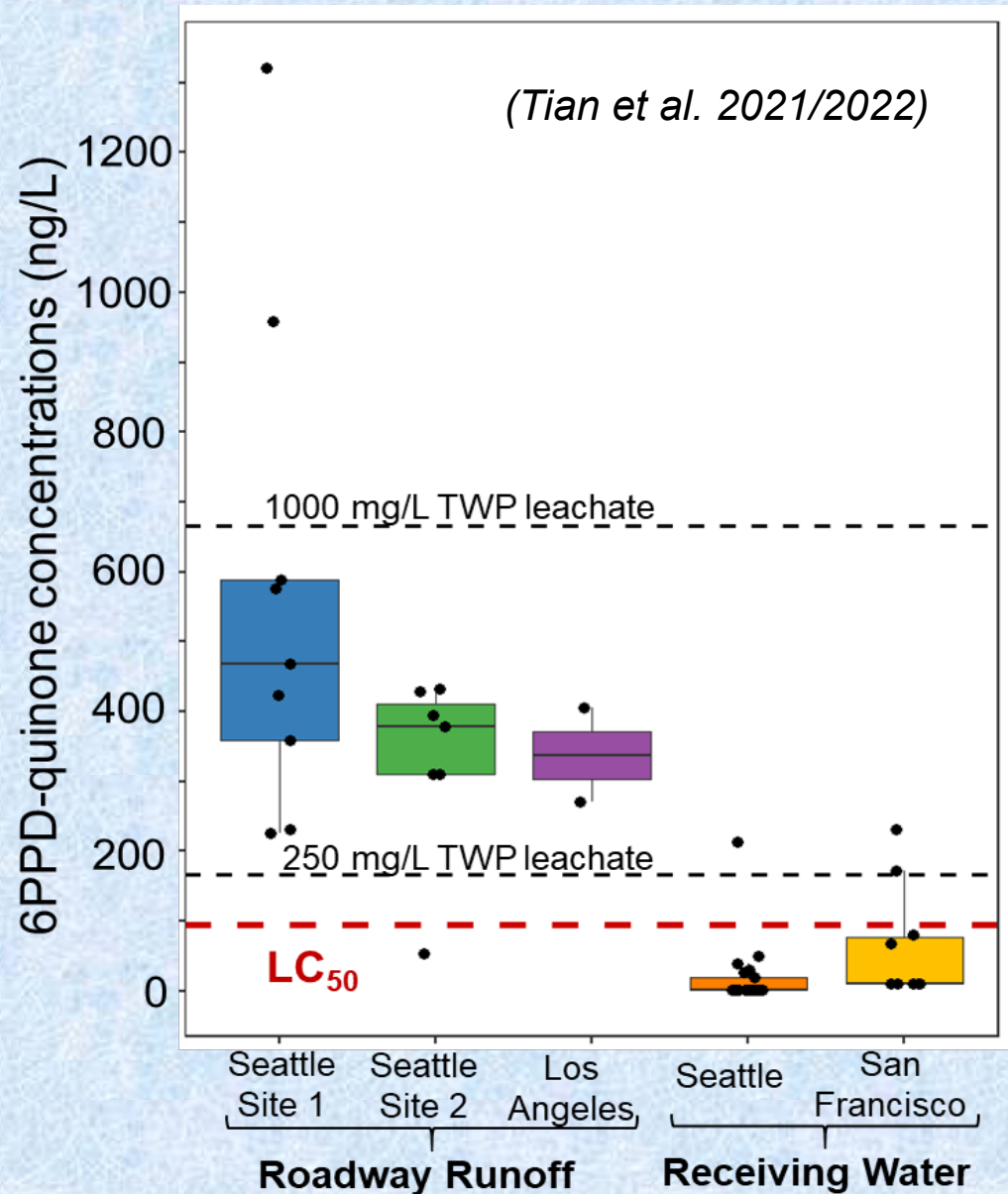


-Juvenile coho salmon, triplicate exposure, N=129

-Lower LC₅₀ with HPC standard: **95 ng/L** VS **790 ng/L**

6PPDQ is one of the 5-6 most toxic chemicals ever identified

Environmental Relevance-Revised LC50



- **Detected in 18/18 road runoff, nearly all above LC₅₀ value**
- **Detected in 6/7 creeks sampled during URMS events, concentrations near and above LC₅₀**
- **Detected in Seattle, Los Angeles, San Francisco samples**

Recent References for Technical Details



Quantitative LC/MS/MS method, current 6PPDQ toxicity value



Tian et al. *ES&T Letters* 2022, 9 (2) 140-146.

pubs.acs.org/journal/estlcu

Letter

6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard

Zhenyu Tian,* Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C. Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej*

6PPD mass balance, 6PPDQ yield, other 6PPD-ozone products



Hu et al. *ES&T Letters* 2022, *Research ASAP*

pubs.acs.org/journal/estlcu

Letter

Transformation Product Formation upon Heterogeneous Ozonation of the Tire Rubber Antioxidant 6PPD (*N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine)

Ximin Hu, Haoqi Nina Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd,* and Edward P. Kolodziej*

Key Global Studies



Challis et al. 2021:

- Cold climate runoff and snowmelt (high conc. in snowmelt)
- 6PPDQ concentrations: 80-1400 ng/L in roadway runoff
- 6PPDQ mass loadings: 2-380 g/storm event
- High concentrations of other TWP chemicals (DPG at >200 ug/L)



Challis et al. ES&T Letters 2021, 8, 961-967.



pubs.acs.org/journal/estlcu

Letter

Occurrences of Tire Rubber-Derived Contaminants in Cold-Climatic Urban Runoff

J. K. Challis, H. Popick, S. Prajapati, P. Harder, J. P. Giesy, K. McPhedran, and M. Brinkmann*



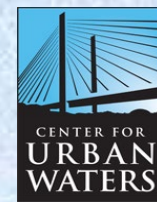
Cite This: *Environ. Sci. Technol. Lett.* 2021, 8, 961–967



Read Online

Other similar studies from Australia, Canada, China.

Key Global Studies



Brinkmann et al. 2022:

6PPDQ toxic to other salmonids:

-Brook trout LC50 (24 hr): 590 ng/L

**-Rainbow trout LC50 (72 hr): 1000 ng/L
(versus 95 ng/L for coho salmon)**



Brinkmann et al. ES&T Letters 2022, 9, 333-338.

pubs.acs.org/journal/estlcu

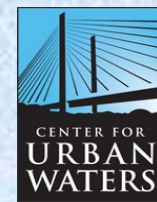
Letter

Acute Toxicity of the Tire Rubber-Derived Chemical 6PPD-quinone to Four Fishes of Commercial, Cultural, and Ecological Importance

Markus Brinkmann, David Montgomery, Summer Selinger, Justin G. P. Miller, Eric Stock, Alper James Alcaraz, Jonathan K. Challis, Lynn Weber, David Janz, Markus Hecker,* and Steve Wiseman

No toxicity to some aquatic species: expect species specific effects

Key Global Studies



Zhang et al. 2021:

- 6 different PPD antioxidants in urban air**
- 6PPD and 6PPDQ both present at pg/m³ concentrations**
- 81% of urban PM_{2.5} contained detectable 6PPDQ**



Zhang et al. ES&T 2021.

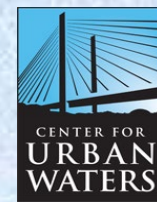
pubs.acs.org/est

Article

***p*-Phenylenediamine Antioxidants in PM_{2.5}: The Underestimated Urban Air Pollutants**

Yanhao Zhang, Caihong Xu, Wenfen Zhang, Zenghua Qi, Yuanyuan Song, Lin Zhu, Chuan Dong, Jianmin Chen, and Zongwei Cai*

Key Global Studies



Cao et al. 2022:

- 5 PPD antioxidants in urban water, air, soil**
- corresponding PPD-quinones detected for all**
- PPD quinones were at higher concentrations**

ENVIRONMENTAL
Science & Technology

Cao et al. ES&T 2022 56(7) 4142-4150.



pubs.acs.org/est

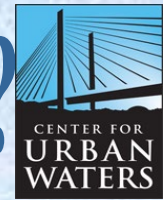
Article

New Evidence of Rubber-Derived Quinones in Water, Air, and Soil

Guodong Cao,[†] Wei Wang,[†] Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu,
and Zongwei Cai*

Broader environmental issues around PPD antioxidants exist

Source Control: Make “Salmon Safe” Tires??



??



Tire companies need to take out (all) the toxic chemicals...



Evaluating 6PPD Alternatives

Craig Manahan, Safer Ingredients Chemist

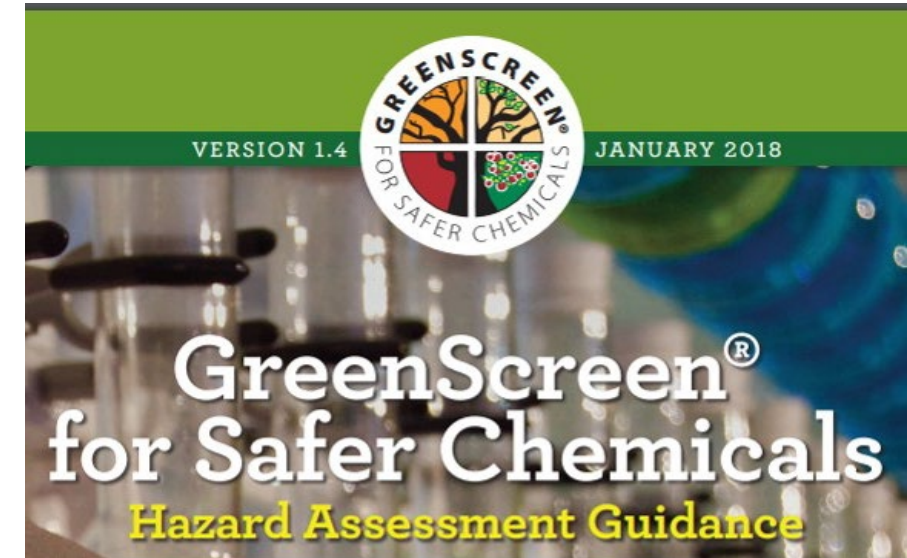
Department of Ecology, Hazardous Waste and Toxics Reduction Program

2021 Budget Proviso – HWTR Program

- Operating Budget, Section 302 (22)
 - \$195,000 MTCA appropriation
 - Assess “potential hazards of 6PPD and other chemicals or chemical classes and breakdown products used as antioxidants and/or antiozonants in tires”
 - Submit technical memo by December 1, 2021
- Perform Greenscreen[®] assessments of 6PPD and nine potential alternatives
- Final technical memo submitted November 29, 2021
- Ecology EAP and Water Quality programs are also using proviso money to work on a report due in Nov. 2022.

Greenscreen[®] for Safer Chemicals

- Free tool to assess and compare hazards of different substances
- 18 hazard endpoints, including:
 - Persistence
 - Bioaccumulation
 - Carcinogenicity
 - Reproductive and developmental toxicity
 - Endocrine disruption
 - Aquatic toxicity
- Rates chemicals Benchmark 4 (preferred chemicals) through Benchmark 1 (hazardous chemicals)



Benchmark 4
Prefer-Safer Chemical

Benchmark 3
Use but Still Opportunity for Improvement

Benchmark 2
Use but Search for Safer Substitutes

Benchmark 1
Avoid-Chemical of High Concern

GreenScreen[®] Results

Chemical and Chemical Abstract Service (CAS) Number	GreenScreen [®] Benchmark Score
6PPD (#793-24-8)	BM-1 – Avoid: Chemical of High Concern
77PD (#3081-14-9)	BM-2 – Use but Search for Safer Substitutes
CCPD (#4175-38-6)	BM-1 – Avoid: Chemical of High Concern
IPPD (#101-72-4)	BM-1 – Avoid: Chemical of High Concern
7PPD (#3081-01-4)	BM-1 – Avoid: Chemical of High Concern
TMQ (#26780-96-1)	BM-2 – Use but Search for Safer Substitutes
6QDI (#52870-46-9)	BM-1 – Avoid: Chemical of High Concern
NBC [Nickel dibutyldithiocarbamate] (#13927-77-0)	BM-1 – Avoid: Chemical of High Concern
Ethoxyquin (#91-53-2)	BM-2 – Use but Search for Safer Substitutes
Dilauryl thiodipropionate (#123-28-4)	BM-3 _{DG} -- Use but Still Opportunity for Improvement

Industry concerns about alternatives

Alternative	Benchmark	Industry Comments
77PD	BM-2	<p>“...provides a shorter period of protection than 6PPD.... It is unclear how long the protection would last in a modern tire.”</p> <p>“Equally important is the fact that as a member of the PPD family, it would be expected to form a quinone like 6PPD.”</p>
TMQ	BM-2	<p>“By itself, it has been shown to have only 52% of the activity of 6PPD. By itself, it does not provide sufficient antiozonant protection to the rubber.”</p>
Ethoxyquin	BM-2	<p>“In early studies, it was shown to be 87% as effective as 6PPD in the initial reaction with ozone...it is unclear how long protection would last. It is classified as mildly to moderately toxic.”</p>
Dilauryl thiodipropionate	BM-3 _{DG}	<p>“It is expected to have little, if any antiozonant activity.”</p>

Current Hurdles to Overcome

- Still developing toxicity data – we don't know whether alternatives are also toxic to salmon or other species
- Lack of information, especially about feasibility and performance needs – we aren't materials or manufacturing experts
- Don't want to duplicate other efforts, but currently there's no official coordination between researchers (*e.g.*, an MOA or clearinghouse)
- Still developing mitigation techniques – we know 6PPD-quinone is harder to treat and doesn't behave like other contaminants
- Solution will need to be multi-faceted – tires with 6PPD will be on the road for 10 or more years after manufacturers stop using it

Future Actions

- Funding further research to address data gaps
- 2022 Budget Proviso:
 - \$1,322,000 MTCA appropriation
 - “complete a full safer alternatives assessment of the 6PPD compounds used in tires. The assessment shall incorporate and evaluate toxicity data of alternatives on Coho and other species.”
 - “if the department finds safer alternatives exist, include recommended regulatory, policy, or legislative actions to advance safer alternatives.”
 - No date specified for completion.





Questions?

Roads to Sea

Rhea Smith

Toxics Studies Unit

Environmental Assessment Program

April 27, 2022



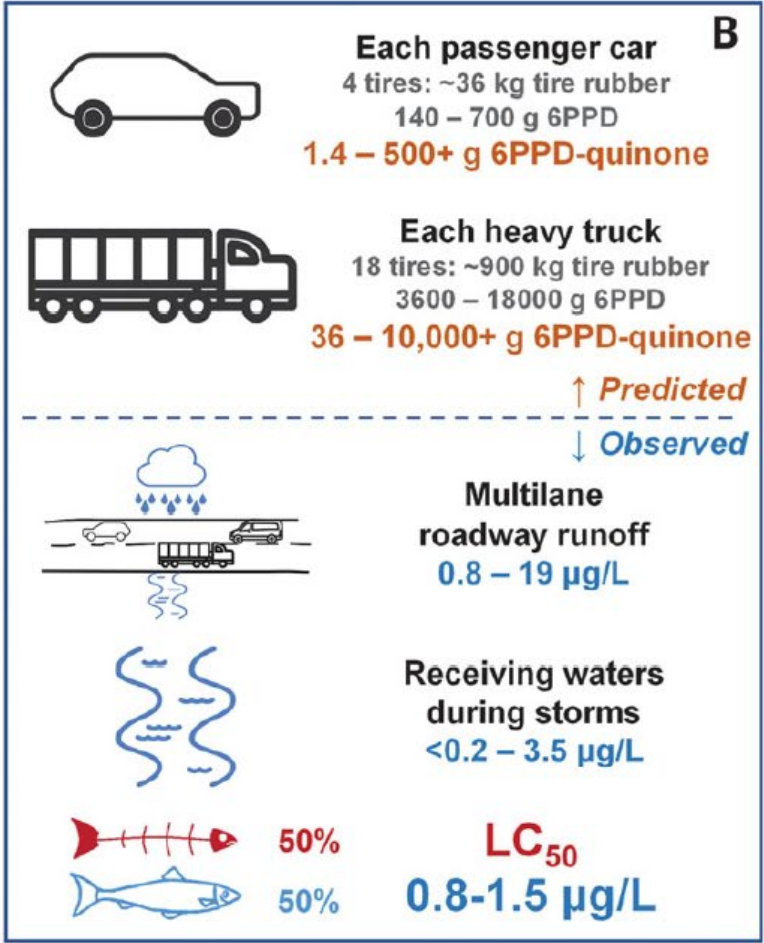
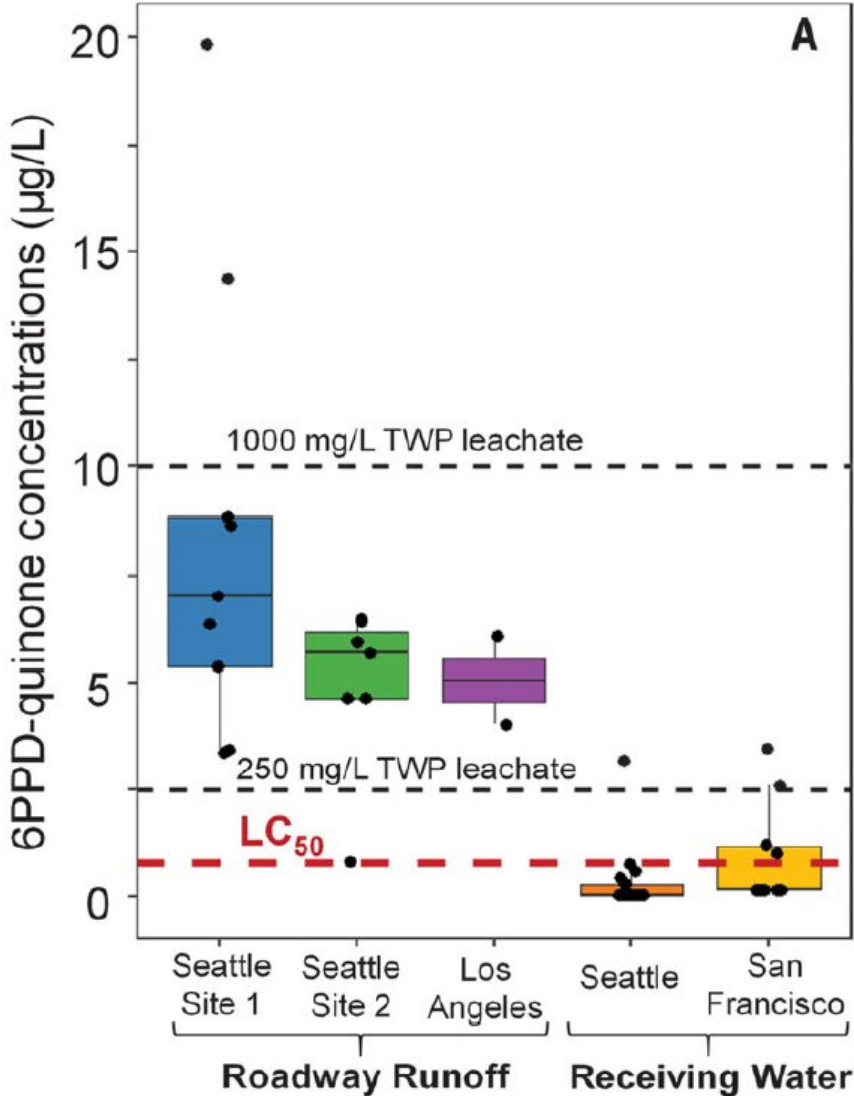
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State of Washington



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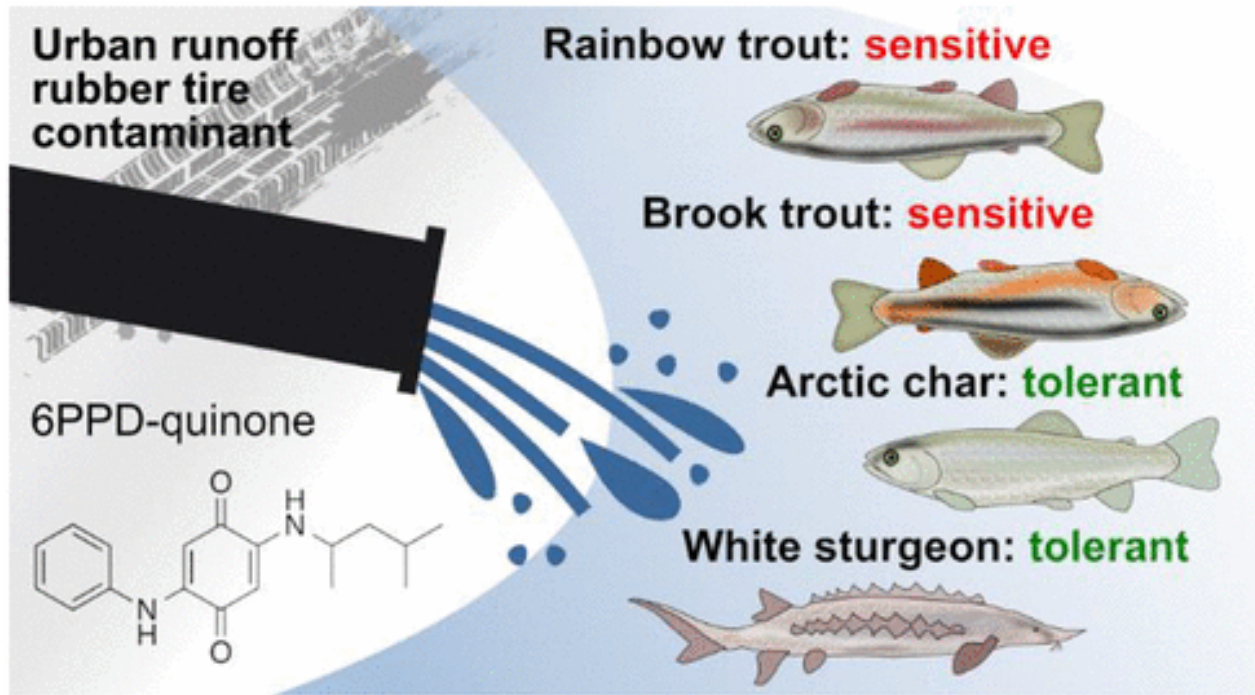
- 1 Problem: Toxic Tire Chemicals
- 2 Process: Research to Action
- 3 Report: Model Toxics Control Act Proviso
- 4 Research: 6PPD Data Visualization
- 5 Research: Monitoring Strategies
- 6 Response: Ecology Wide

The Problem: Toxic Tire Chemicals

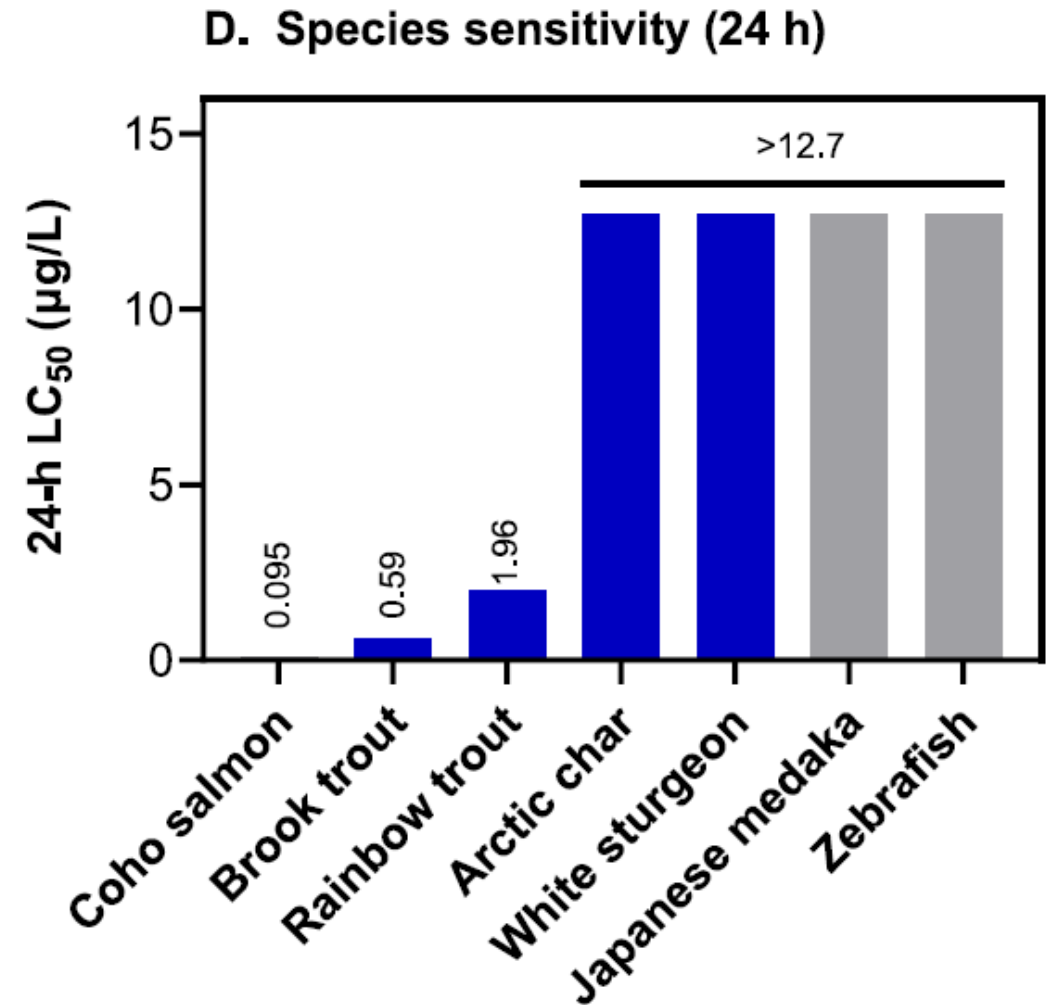


Tian et al. 2020, 2022

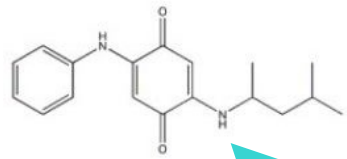
Variable Sensitivities to 6PPD-Quinone



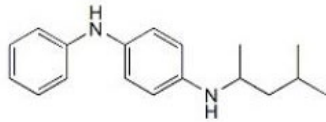
Brinkmann et al. 2022



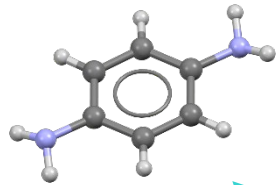
The Problem: “We live in a chemical world”



6PPD - Quinone – $C_{18}H_{22}N_2O_2$



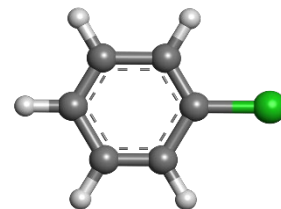
6PPD – (N^1 -(4-Methylpentan-2-yl)- N^4 -phenylbenzene-1,4-diamine) - $C_{18}H_{24}N_2$



PPD - p-Phenylenediamine – $C_6H_4(NH_2)_2$



PNCBO - 4-Nitrochlorobenzene – $ClC_6H_4NO_2$

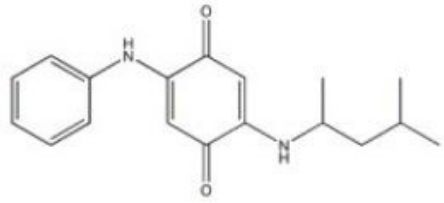


Chlorobenzene – C_6H_5Cl

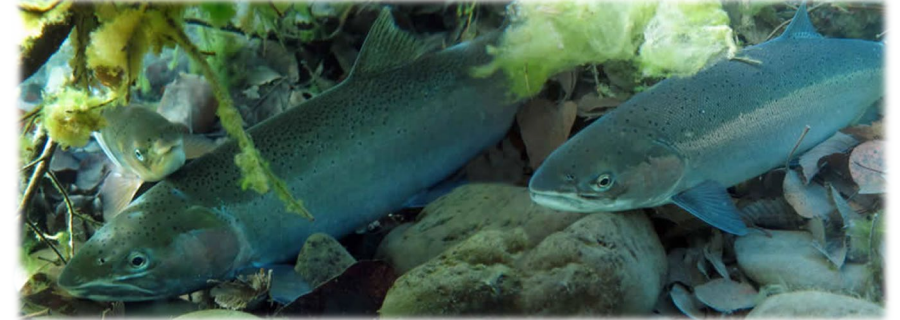


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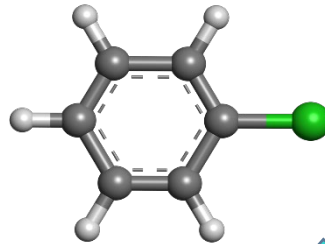
The Problem: Collateral damage



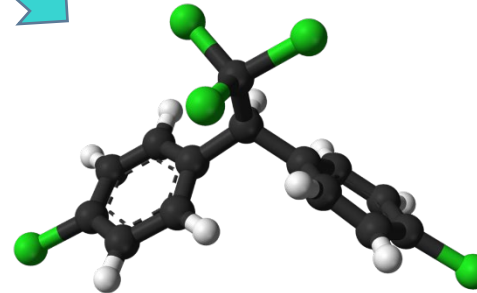
6PPD -
Quinone -
 $C_{18}H_{22}N_2O_2$



Toxic Cousins



Chlorobenzene - C_6H_5Cl



DDT - C_6H_5Cl



Ecology 6PPD **Science** Review

ACTIONS

Reviewing alternative preservative chemicals for tires

Working with our partner agencies and organizations to coordinate action plans

Sharing new and developing information with partners

Interstate and international coordination on method development and environmental research

Spatial data compilation of toxics and vulnerable aquatic habitats for the State of Washington

Non-point source “hot spot” spatial mapping and modeling framework to support toxic reduction planning

Stormwater engineers are assessing best management practices on short-term and long-term time scales

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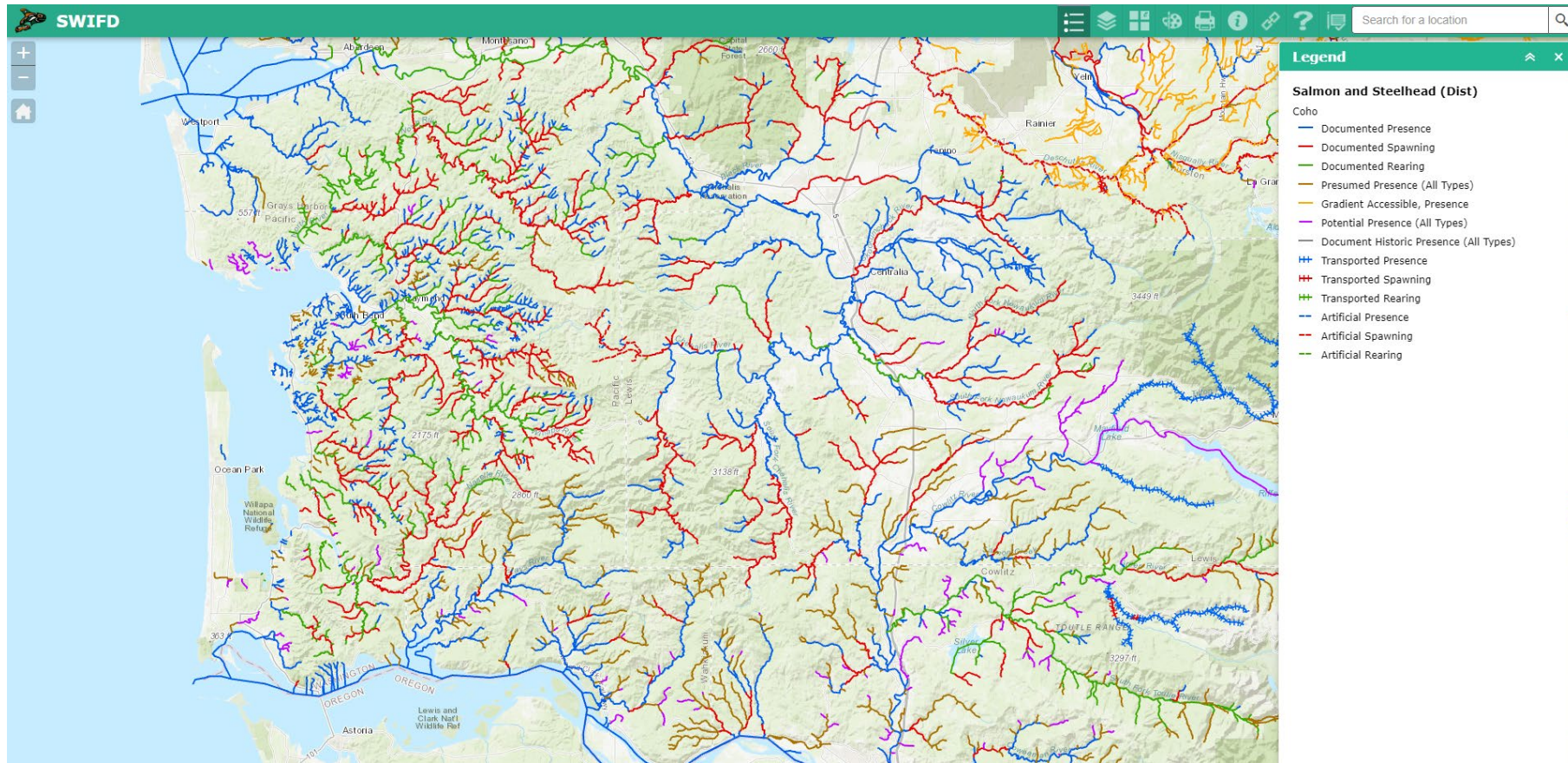
Non-point source “hot spot” spatial mapping and modeling framework to support toxic reduction planning

Stormwater engineers are assessing best management practices on short-term and long-term time scales

Wild Salmon habitat is co-managed with WA Tribes

- Ecology works with Tribes in a government-to-government relationship to protect and manage shared natural resources and to cooperate across jurisdictions. The unique legal status of Tribes and the presence of treaty-reserved rights and cultural interests throughout the state create a special relationship between Tribes and agencies responsible for managing and protecting the state's natural resources.
- Tribes retained about 6 million acres of reservation land and specifically retained the right to take fish in their “usual and accustomed” areas along with the privilege of hunting on “open and unclaimed lands,” among other things.
- Tribes possess property and self-government rights that are guaranteed under treaties and federal laws and each tribal reservation in the state constitutes a bordering jurisdiction subject to federal and tribal environmental laws.

Where are the fish? SWIFD (nwifc.org)



Statewide Salmonid Habitat Mapping Portal - NWIFC* and WDFW co-managed

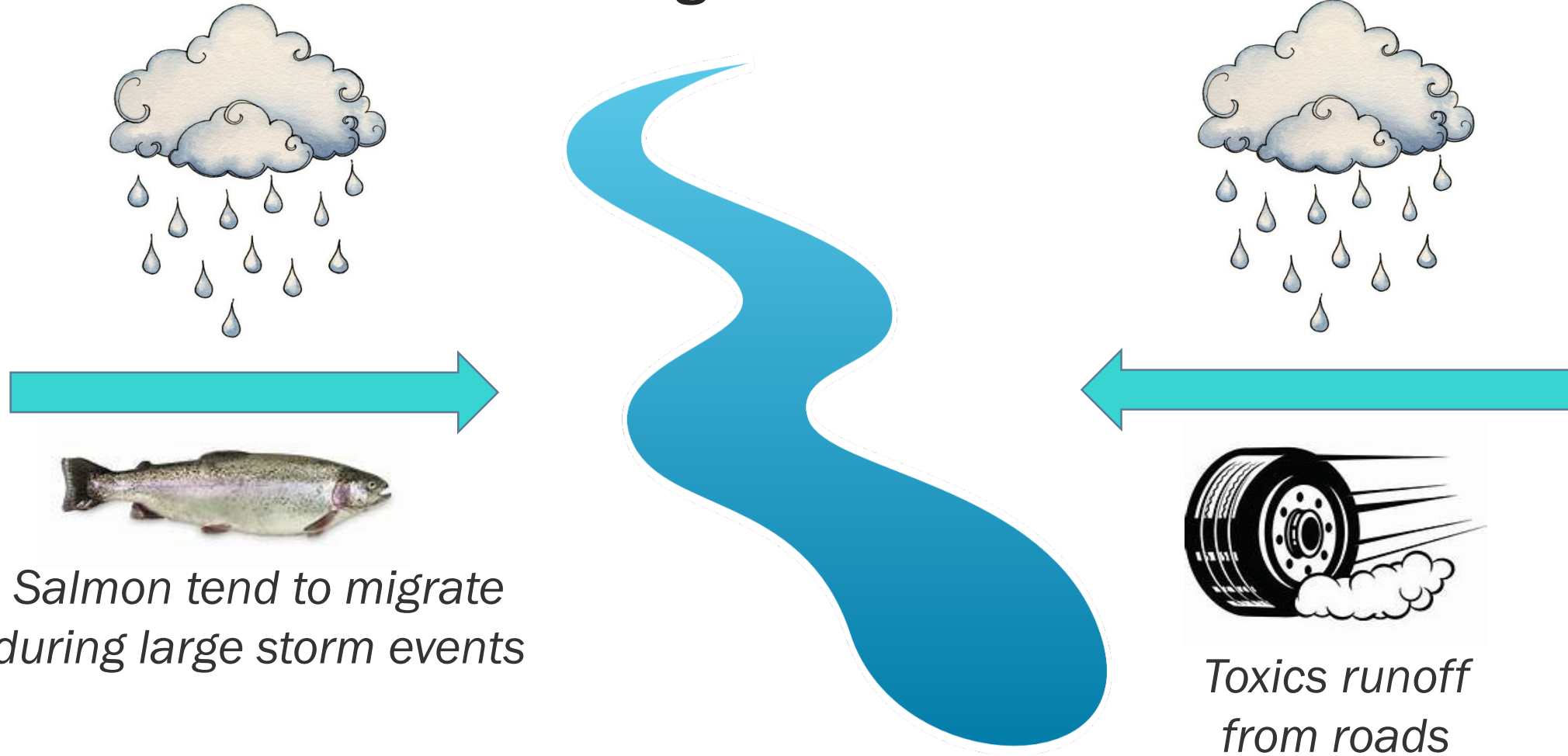
* NWIFC is a natural resources management support service governed by the Western WA Treaty Tribes

Visualization Tools for the Puget Sound

Conservation mapping & modeling efforts

Tool	POC Organizations
Stormwater Heatmap	TNC & Geosyntec
Roads to Ruin Vulnerability Mapping	NOAA, USFW, CUW, WSC
Prioritizing conservation actions in urbanizing landscapes	TNC & NOAA
Watershed Characterization Project	SEA Program, Ecology
High Resolution Change Detection	WDFW
Puget Sound Mapping Project	Department of Commerce
StreamCAT	EPA
Freshwater Explorer	EPA
VELMA	EPA
SWIFD aka Salmonscape	NWIFC, WA Tribes & WDFW

Modeling and monitoring Strategies: Salmon and car habitat convergence



Salmon and Storm Phenology

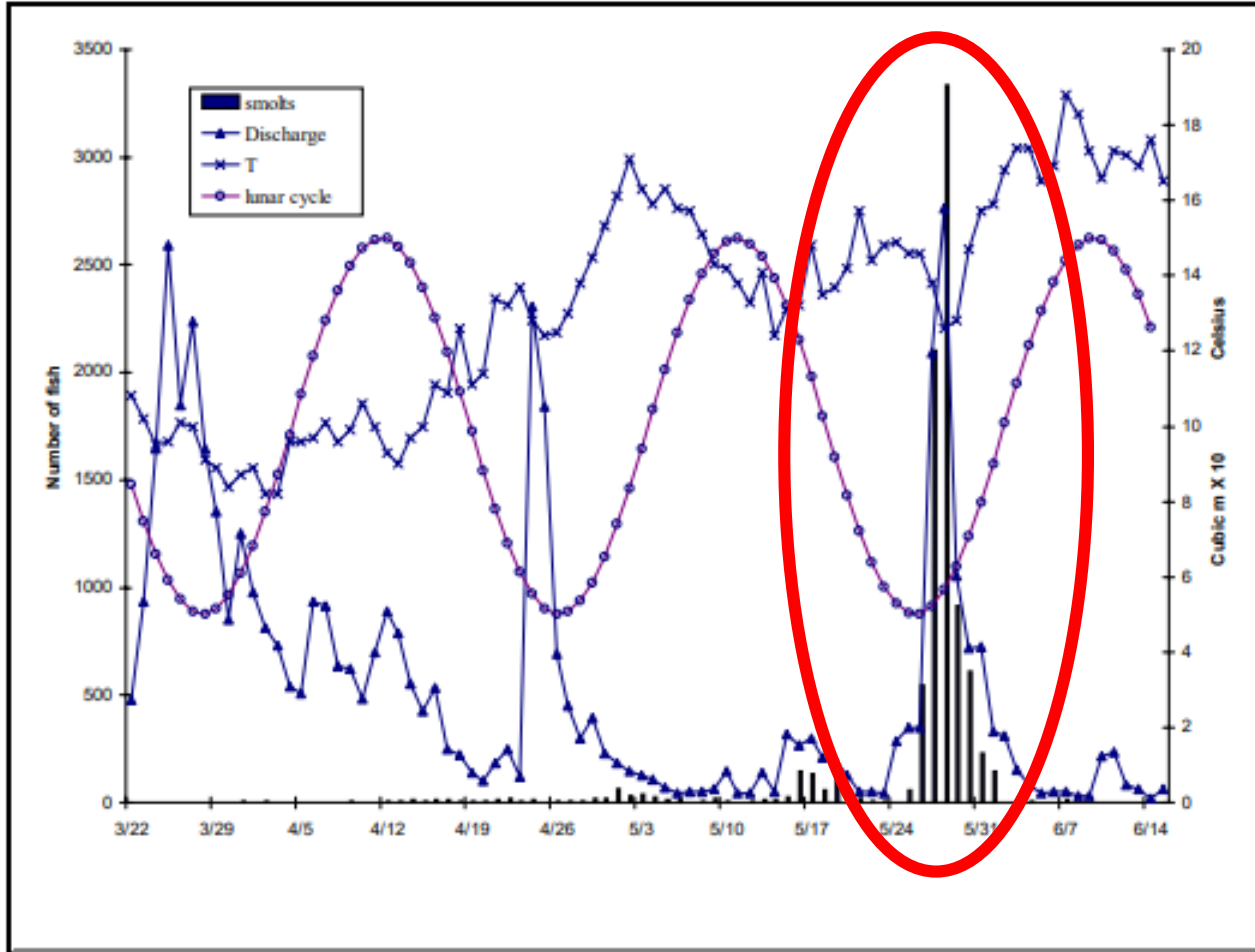


Figure 1. Temporal distribution of coho, cutthroat and steelhead smolt outmigration with respect to temperature, discharge, and lunar cycle from Squalicum Creek between 22 March and 15 June 1998. Maxima of lunar cycle series correspond to full moons and minima correspond to new moons.

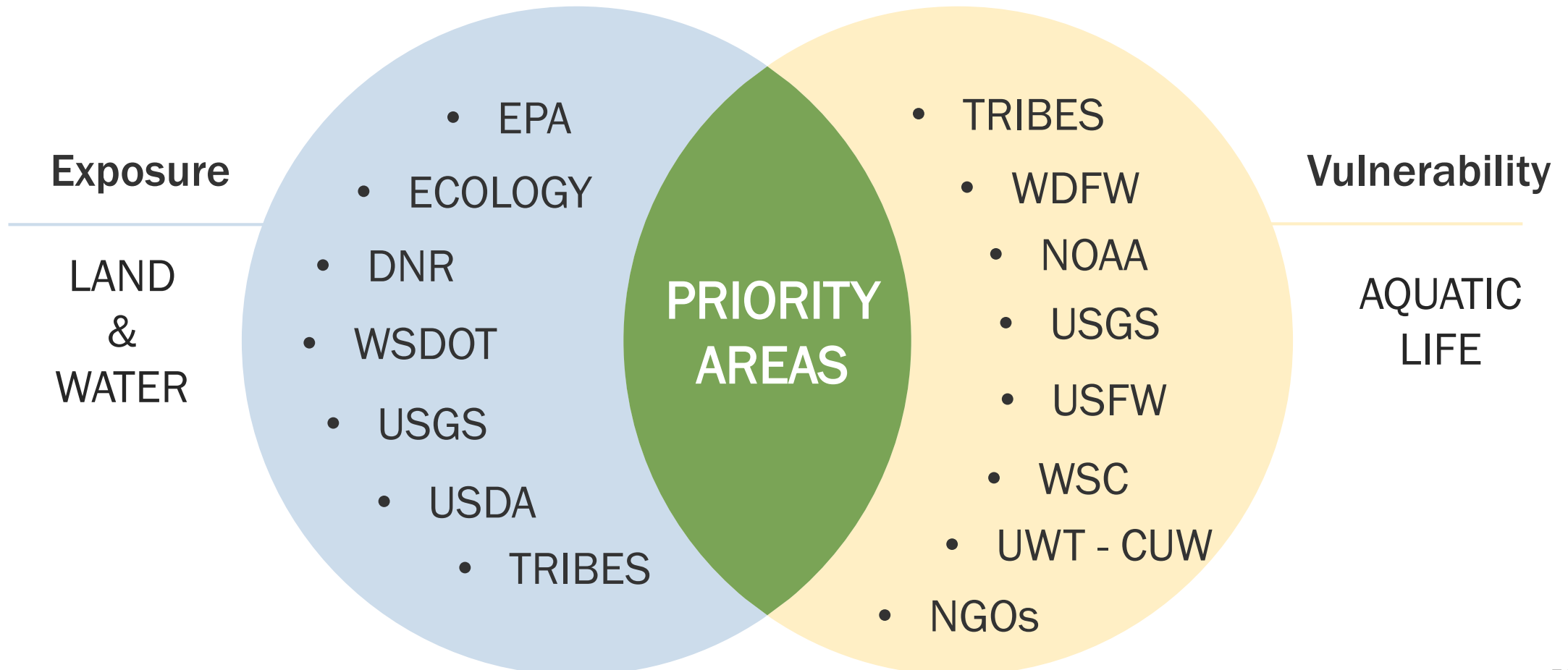
Smolt outmigration timing

1. Large rain event
2. Stream discharge high peak
3. New moon
4. Rapid temperature change

Downen & Mueller 1999

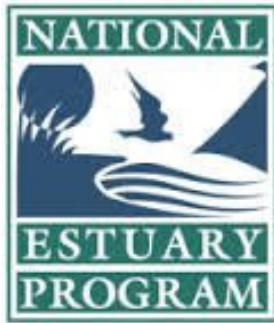
Exposure & Vulnerability Action Planning

Need both to effectively accomplish environmental goals





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Thank you

Rhea Smith

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*There will be a 6PPD Panel discussion
at Salish Sea Conference, hope to see
you there!*



Ecology's strategic priorities



Support and engage our communities, customers, and employees



Reduce and prepare for climate impacts



Prevent and reduce toxic threats and pollution



Protect and manage our state's waters



Protect and restore Puget Sound



Stormwater solutions to reduce tire wear, 6PPD & 6PPD-quinone

Brandi Lubliner, PE (she/her)

Stormwater Monitoring and Engineering

Washington Department of Ecology – Water Quality Program

Salish Sea Environmental Conference April 27, 2022

Stormwater toxicity activities - since Dec 2020

- Assigned staff to cover 6PPD projects in several Ecology programs
- Coordinate with all these groups mentioned by panelists
- Launch and staff a new 6PPD subgroup of the PSEMP Stormwater Work Group
- Updates to stormwater guidance
- Working on 2 legislative assignments



- 2021: Identify best management practices (BMPs) for reducing the toxicity to Coho and other aquatic life (Report due November 2022)
- 2022: Study and develop BMPs to treat stormwater containing tire wear

Legislative Proviso Assignments to Ecology's WQ Program

Road water



Coho water



Why is the focus on Best Management Practices (BMPs) for stormwater?

- Stormwater permits use Ecology's **Stormwater Management Manuals (SWMMs)** to achieve the permit's requirements:
 - flow control
 - Stormwater source control
 - runoff treatment
- These SWMMs (Eastern and Western WA) describe BMPs in detail. When to use BMPs, how to size them, how to choose which to use for site conditions, etc.

What are BMPs and who does this work?

Each BMP describes the kind of work needed:

- Prevention
- Education/Outreach
- Maintenance
- Structural facility



Selection and implementation of BMPs depend on the site/basin needs.

Example: trash

- Placement of garbage cans
- Litter education
- Street sweeping, litter crews
- Trash screens on catch basins



2021 Assignment – BMPs to reduce toxicity

Ecology report to legislature due Nov 2022:

- Review of existing BMPs that may help reduce the toxicity in roadway runoff
- Knowledge gaps impacting BMP certainty
- Next steps on managing stormwater



2021 Assignment cont'd

Project Advisory Team: WSDOT, UW-T, WSU, Ecology, and consultant team

- The universities are contracted to provide memos on status and next steps, as well as provide professional guidance on this project.
- Cross-disciplinary input is critical for success, toxicity prevention without aquatic criteria to aim at is new for stormwater BMP engineering



Pairing: BMP processes to pollutant properties

Using mostly EPA model data and the literature studies to find physical and chemical properties on:

- Tire wear particulate (TWP)
- Particulate-bound 6PPD & 6PPD-quinone
- Dissolved 6PPD & 6PPD-quinone



Physical properties and BMP presumptions

Tires/wear	Size	Specific Gravity	Will they settle in column of water?* (pooling BMPs)	Could they be filtered out?* (cartridge filters, waddles)
Tires	(3-6 feet)	>1 Heavier than water	Yes	NA
Medium tire wear pieces	(6 inches to ~1 inches")	>1 Heavier than water	Yes	Yes
Small tire wear particles	<1inch to 0.075mm	Same as water	Yes, but the smallest would need more time (minutes)	Yes, probably
Microscopic tire wear particles	Tiny (micrometer sized particles)	Unknown	Unknown time needed for settling. Field studies describe microscopic particles in stream sediments.	Unknown

* Responses in these columns are current understanding, recommendations in progress.

Chemical properties and BMP presumptions

Contaminant	Reactivity?	Water Solubility/ Affinity?	Binds to Soil?	Will infiltration work?*	Will sorption media work?*
Tire wear particles	NA	NA	NA	Yes, likely most will stay on surface, maintenance needs uncertain. Uncertain if microscopic sizes stay on top	Not likely for visible particles, but unknown for microscopic
6PPD (dissolved)	Quite; half life in air & water (hours) in soil (unsure)	Not very (2.8 mg/L); log Kow 4.68	Yes likely; log Koc 4.36	Yes, likely reacts so quickly with O ₃ or O ₂ , not expected to be persistent	Likely to bind to sorbents, uncertain half life in soil (days, months?)
6PPD-quinone (dissolved)	Moderate; more stable than 6PPD, but also transforms into other chemicals	Moderate 51.4mg/L; log Kow 3.98	Yes likely; log Koc 3.94	Yes, likely infiltrate into top layer of soil column and bind (Koc). Likely to react/decay (hours, days, weeks).	Likely to bind to sorbents, uncertain half life in soil (months)

* Responses in these columns are professional judgements made on EPA's modeled chemistry fields and need to be verified.

2021 Assignment – Wrap Up

Ecology's report to Legislature in November 2022

- A chapter on the considerations for spatial prioritization (earlier talk).
- A BMP section on possible controls of TWP, 6PPD and 6PDP-quinone.
- Appendix containing the university memos
- Appendix containing consultant's report on technical basis for BMP recommendations



2022 Assignment – Getting going

One year of funding Ecology will use momentum from current work to:

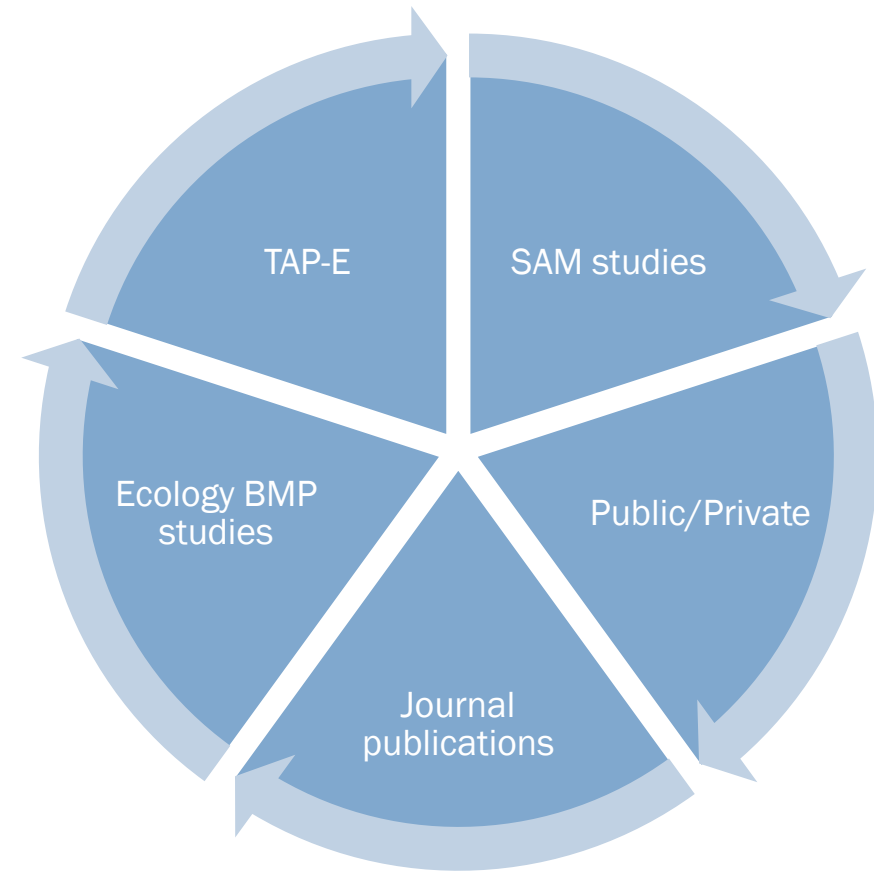
- Hire and contract for projects
- Expanding capacity with partners
- Continue to synthesize new science and engineering experience
- Develop guidance in SWMMs on what has been learned so far



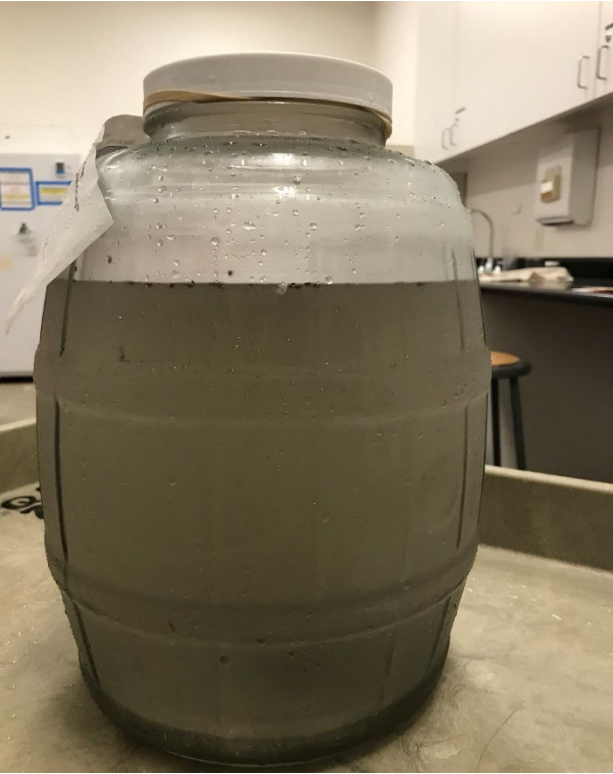
Updating and adding new information in SWMMs

Sources of information

- TAPE: Commercial and non-commercial BMPs
- SAM: MS4 permittees
- Ecology BMP studies: grants, contracts
- Journals
- Networking/
Workshops/Workgroups
- Public or Private research



Shared goals for stormwater solutions



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