Car Tires & Salmon

State of the Science: 6PPD-Q

Dr. Jenifer McIntyre
WA State University | School of the Environment
Puyallup Research & Extension Center | WA Stormwater Center

Premature mortality of coho: Weight-of-evidence ⇒stormwater

Longfellow Creek 2003 Des Moines Creek 2004 Longfellow Creek 2012

OPEN ACCESS Freely available online

(2011, 6(8):e28013)

PLoS one

Recurrent Die-Offs of Adult Coho Salmon Returning to Spawn in Puget Sound Lowland Urban Streams

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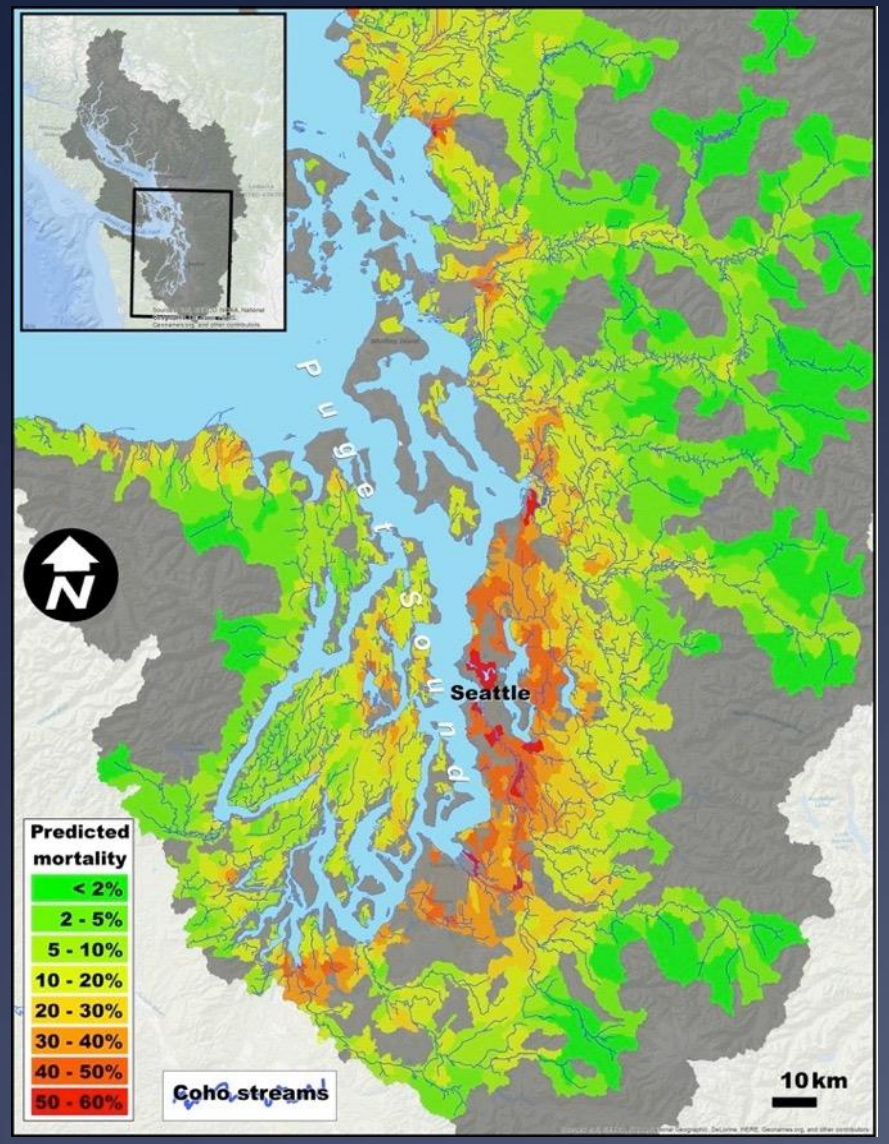
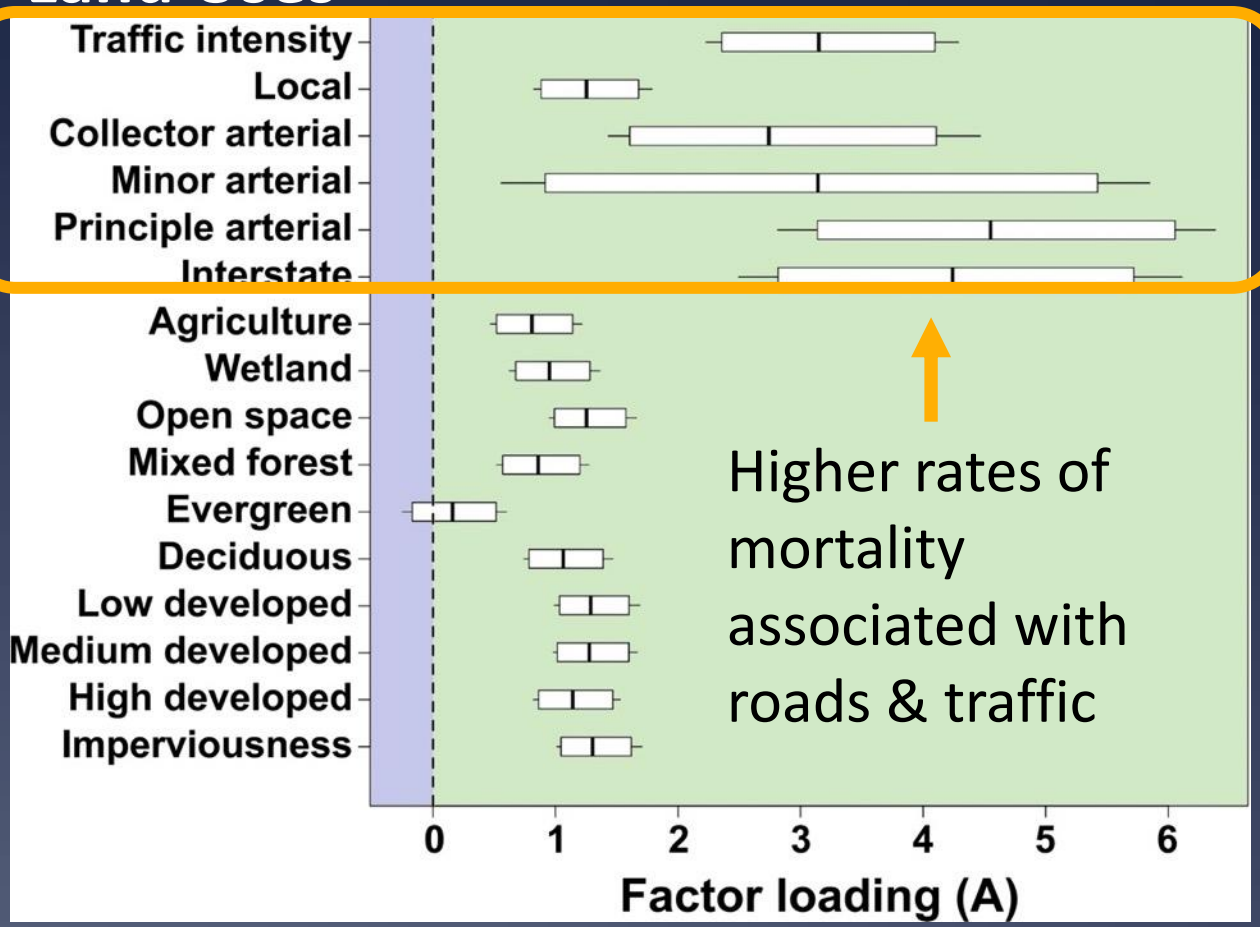
1 Northwest Fisheries Science Center, NOAA Fisheries, Seattle, Washington, United States of America, 2 Department of Natural Resources and Parks, King County, Seattle, Washington, United States of America, 3 Wild Fish Conservancy, Duvall, Washington, United States of America, 4 Seattle Public Utilities, City of Seattle, Seattle,

Coho mortality rates associated with roads & traffic



Land Uses



Increasing Mortality →

Feist et al. 2017. Ecol Applications

Urban road runoff is sufficient to kill coho salmon

Spromberg et al. 2016

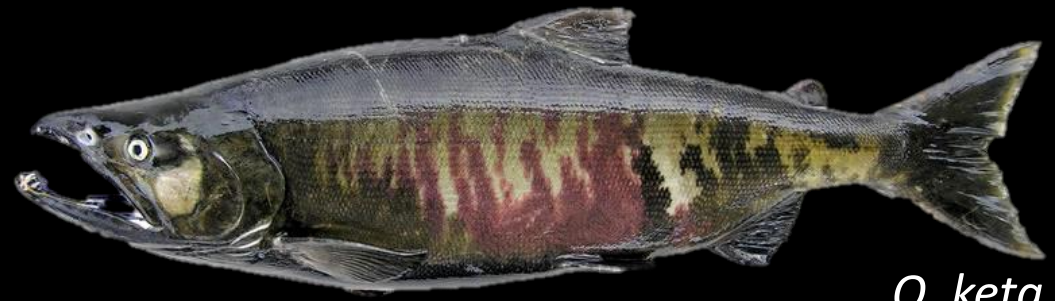
McIntyre et al. In Prep

Chow et al. 2019

All free-swimming life stages susceptible

Sensitivity to stormwater varies among species

O. kisutch



O. keta

McIntyre et al. 2018. Environ. Pollution

O. mykiss

O. nerka

O. kisutch

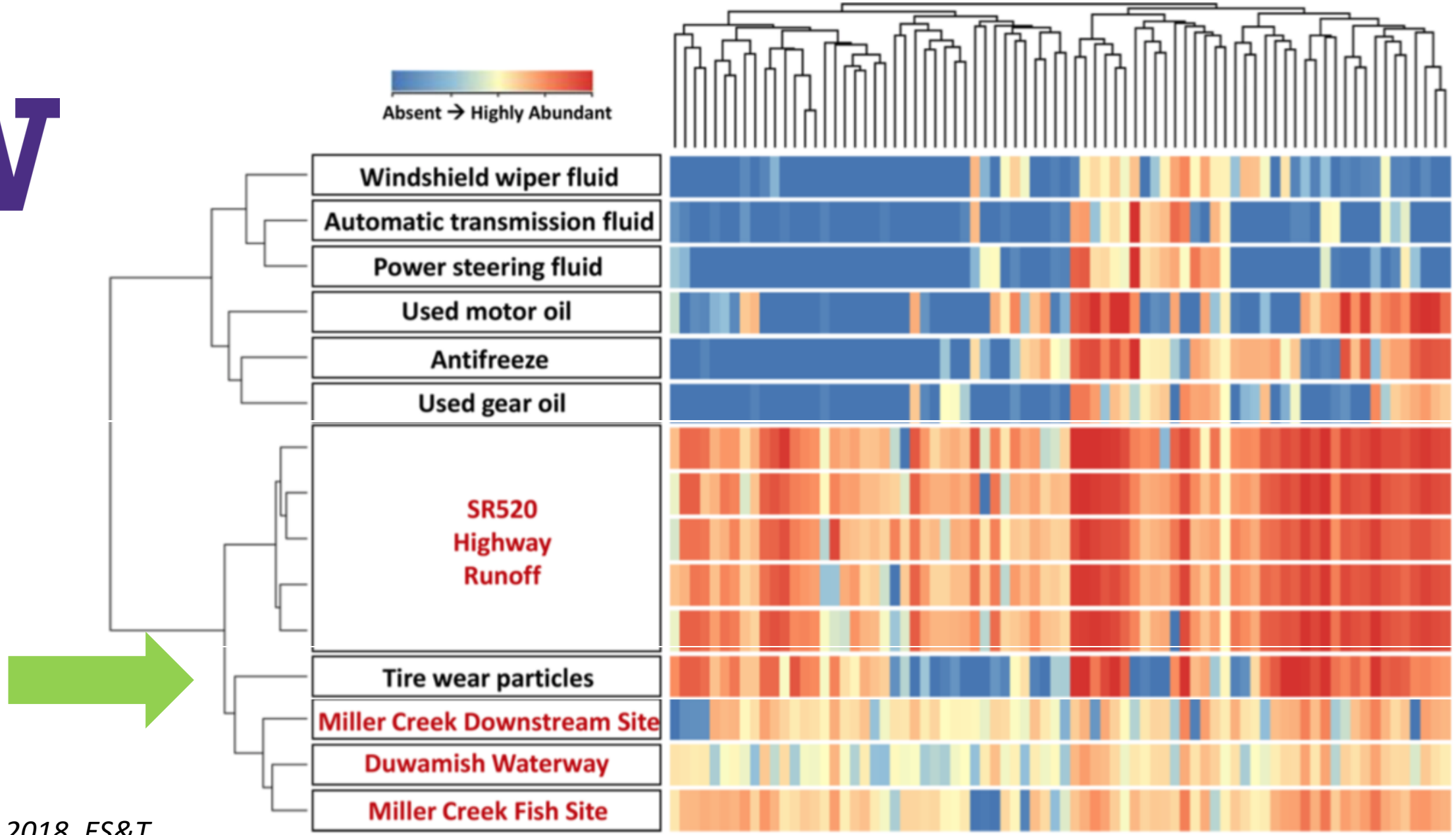
Chow et al. 2019. Aquat. Tox.

O. tshawytscha

French et al. In Prep.

Coho > Steelhead > Chinook > Sockeye = Chum

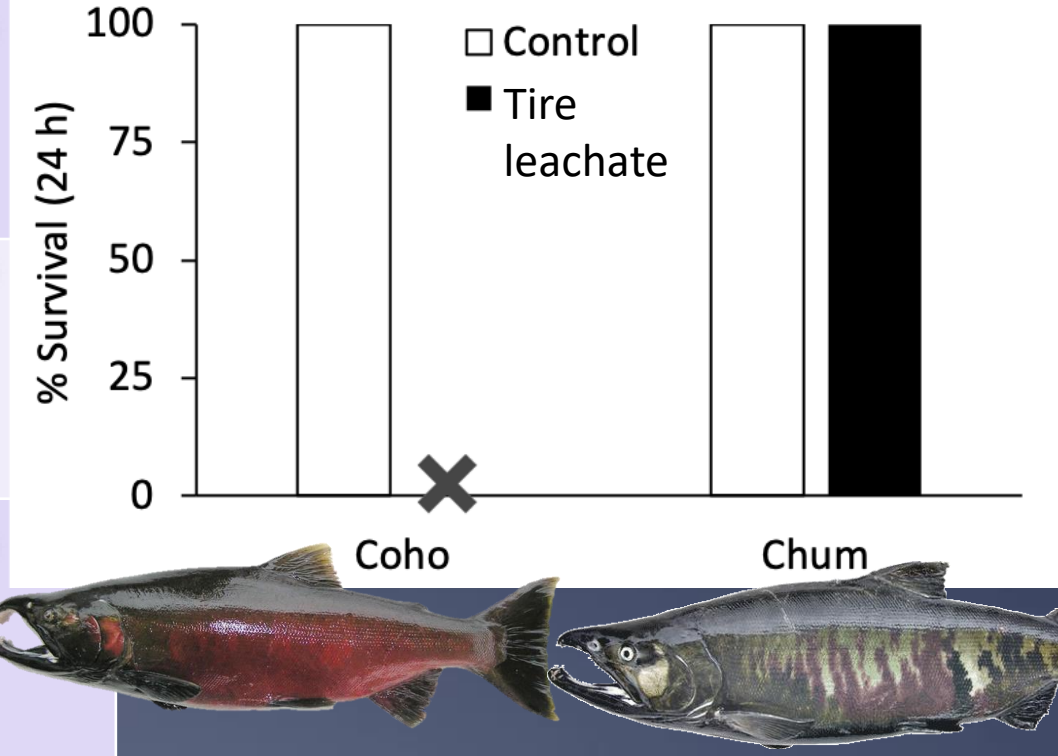
Tires a likely source of the chemicals that kill coho



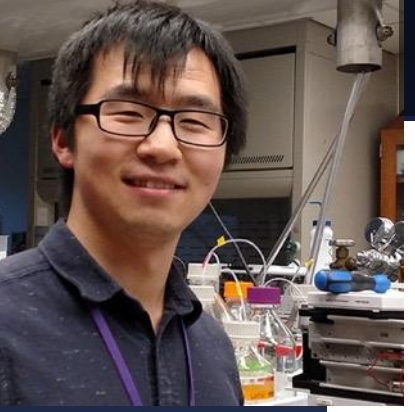
Peter et al. 2018. ES&T

Tire leachate is sufficient to kill coho

Toxic Endpoint	Stormwater	Tire Leachate
Acutely lethal to coho salmon	✓ Spromberg et al. 2016.	✓
Pathophysiology: high HCT, reduced plasma ions & pH	✓ McIntyre et al. 2018	✓
Does not impact chum salmon	✓ McIntyre et al. 2018	✓

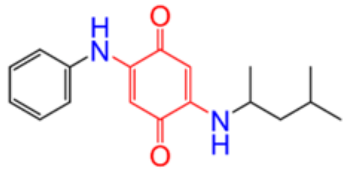


McIntyre et al. 2021



Zhenyu Tian

6PPD-quinone discovered !



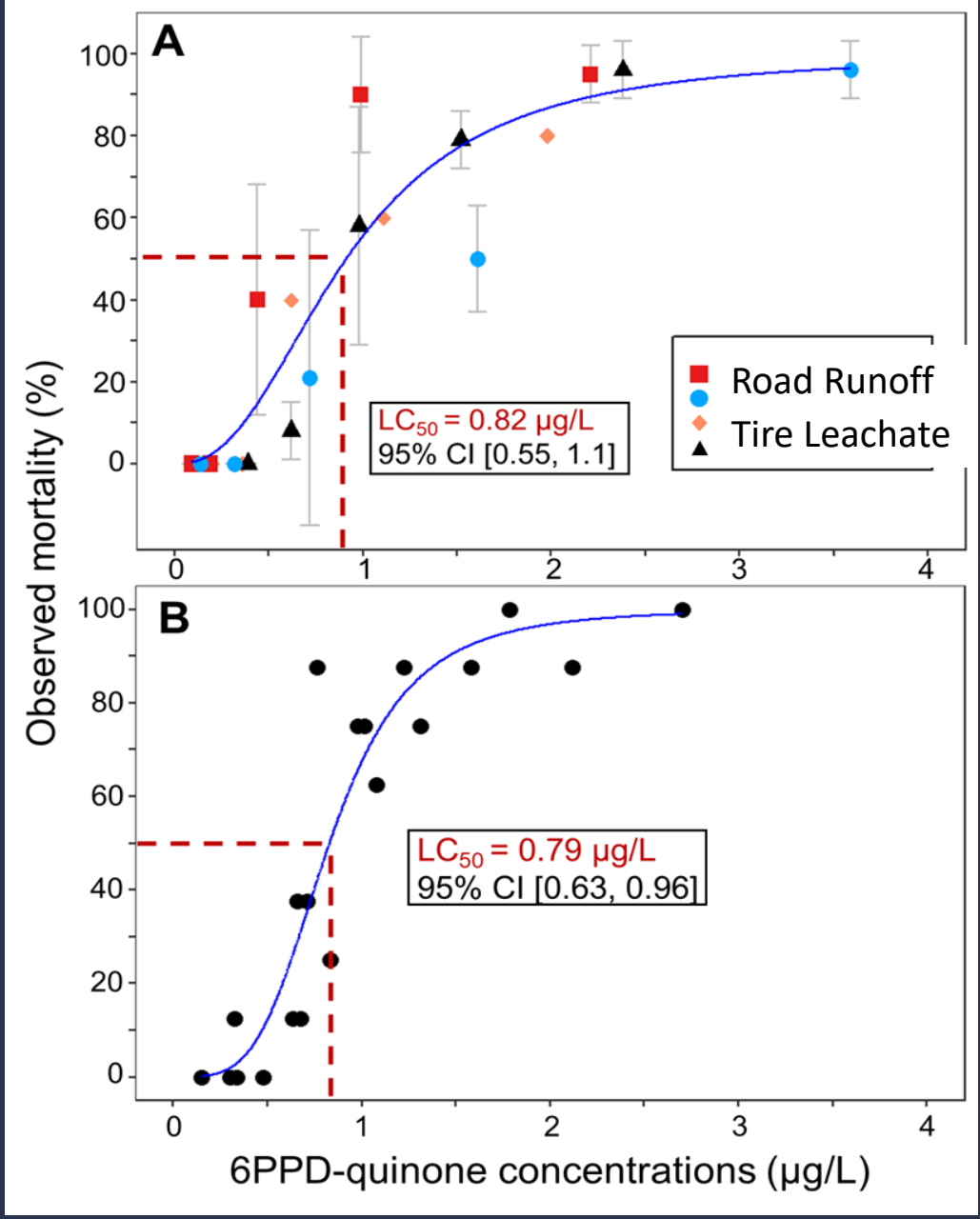
6PPD-quinone

$C_{18}H_{22}N_2O_2$

CENTER FOR URBAN WATERS

Tian et al. 2021. Science

6PPD-quinone toxic alone and in complex mixtures



Dilutions of roadway runoff and tire particle leachate

Toxicity explained by

Purified 6PPD-quinone

6PPD-quinone: Primary causal toxicant

Tian et al. 2021. Science

Environmental Relevance of 6PPD-quinone

- 6PPD-Q is derived from 6PPD – an antiozonant in tires
- Ozone (O_3) is a secondary air pollutant, highly reactive
- Ambient O_3 is continually interacting with tire surface (up to ~20 um)
- 6PPD in tires migrates slowly to tire surface to protect tire polymers from O_3
- Ozone transforms 6PPD into 6PPD-quinone (brown color of tires)
- Can leach into water directly from tire surface or from worn tread particles


6PPD-Q
Toxicology
Update
6PPD-Q
Chemistry
Update
6PPD-Q
Solutions
Update


6PPD-Q
Toxicology
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Chemistry
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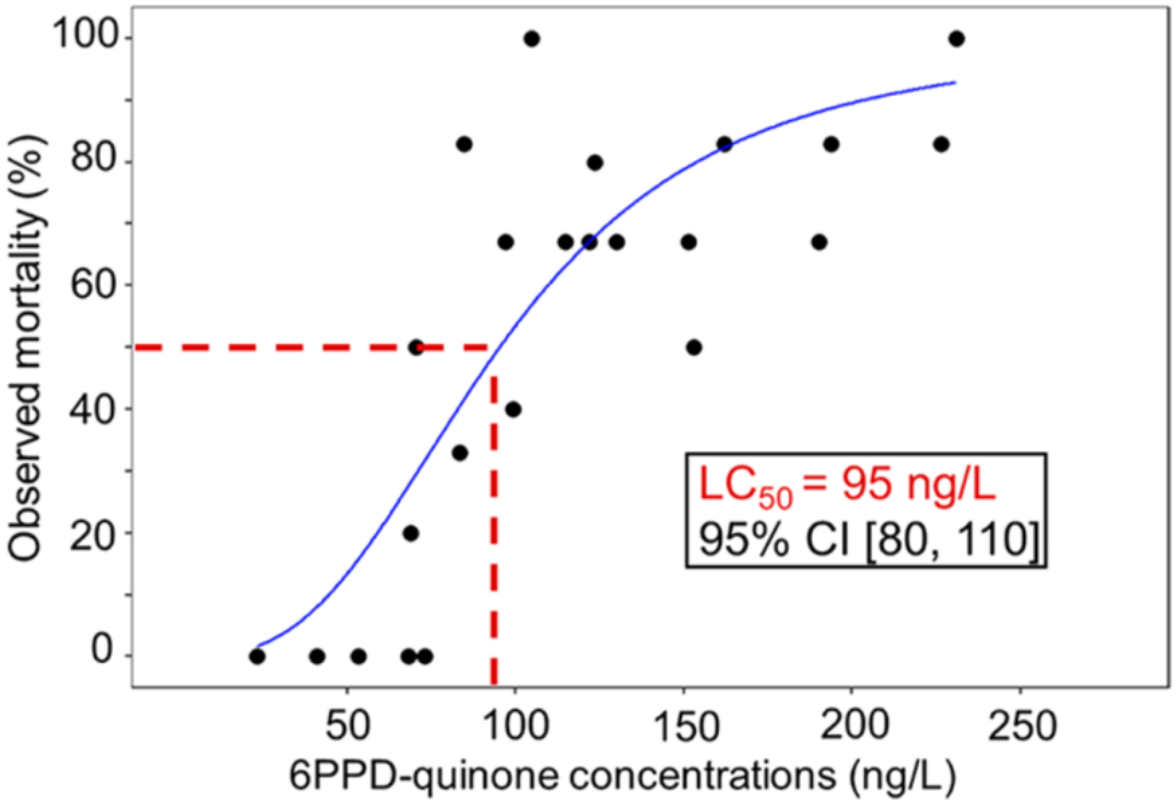
6PPD-Q
Solutions
Update
Aquatic Toxicity
Mode of Action

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 ngL

6PPD-quinone toxicity for other species

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

Toxicity of 6PPD-quinone vs other chemicals

(Tian et al. 2022 ES&T Letters)

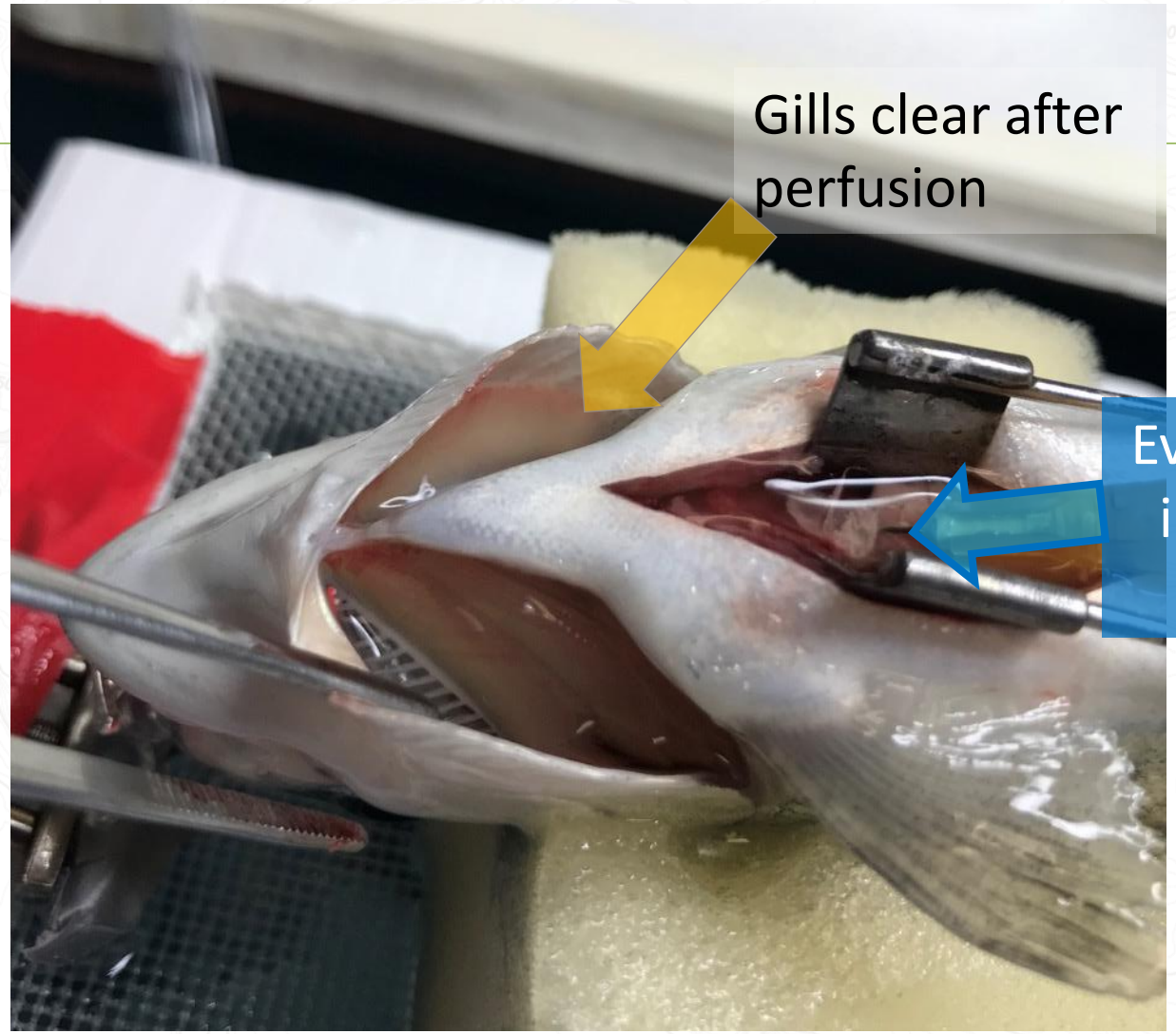
chemical class	name	most sensitive species	LC_{50} (ppb)	95% CI
OP	parathion	*Orconectes nais*	0.04	0.01–0.2
quinone	6PPD-Q	*O. kisutch*	0.10	0.08–0.11
OC	mirex	*Procambaris blandingi*	0.10	not reported
OP	guthion	*Gammarus fasciatus*	0.10	0.073–0.014
OP	chlorpyrifos	*Gammarus lacustris*	0.11	not reported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

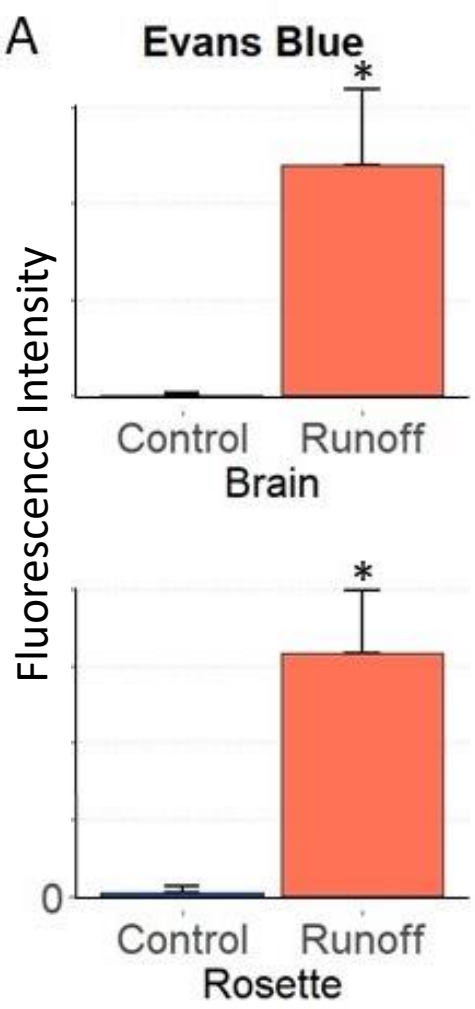
Stephanie Blair
Ph.D. candidate
WSU SOE

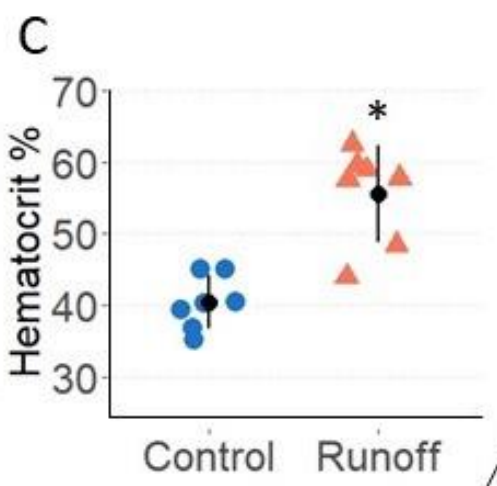
- Runoff exposure to equilibrium loss
- Injected fluorescent dye into fish heart, circulate
- Rinsed all blood from fish
- Measured fluorescence of dye that leaked from vascular system

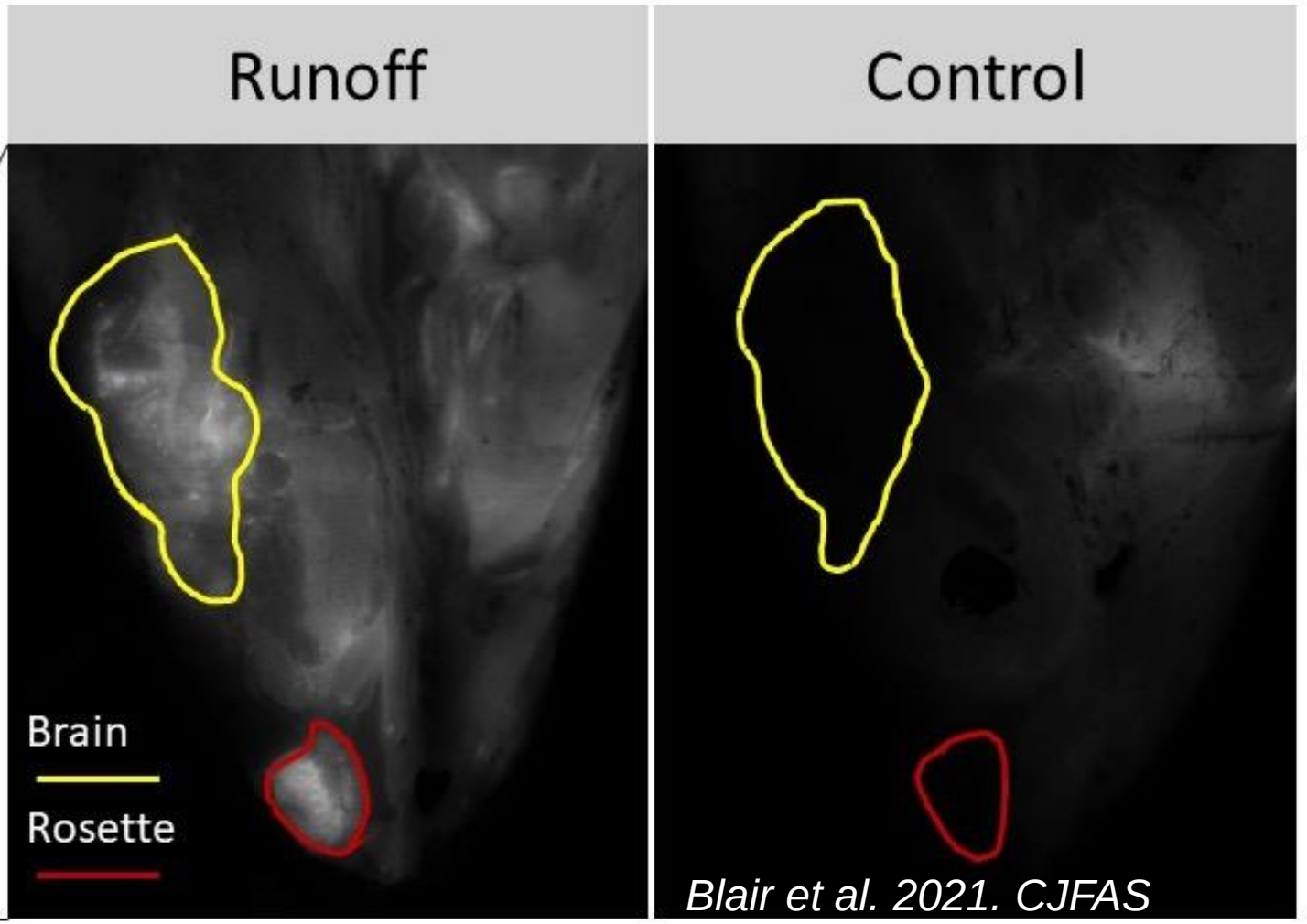


Blair et al. 2021. CJFAS

Blood brain barrier of coho becomes leaky



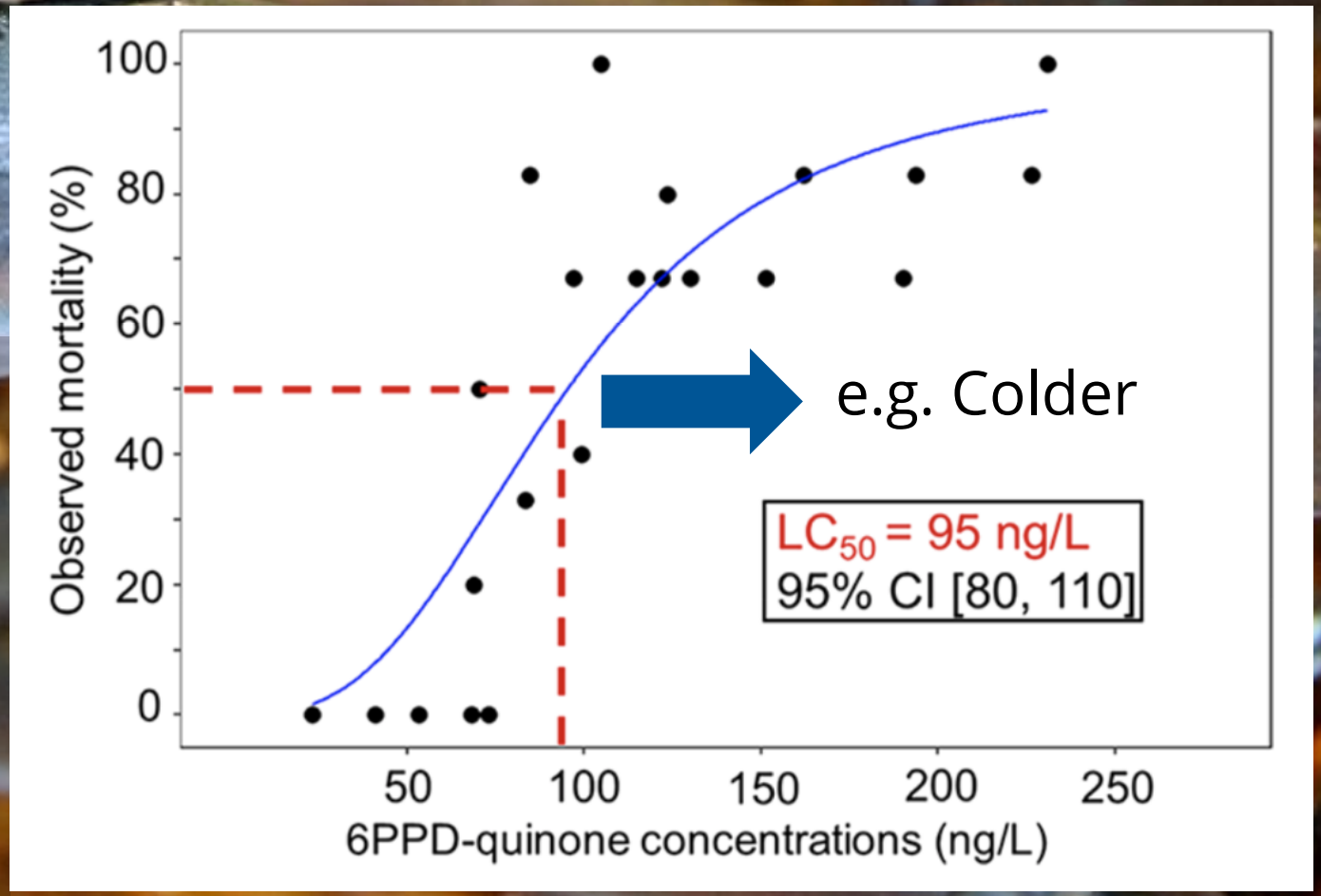




Hemoconcentration linked to plasma leaking from vascular system

6PPD-quinone toxicity: Environmental variables

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




6PPD-Q
Toxicology
Update
6PPD-Q
Chemistry
Update
6PPD-Q
Solutions
Update
Global detections
Transformations

Global Detections of 6PPD-Q

Canada, Germany, China, Australia

- Runoff, snow, receiving waters,

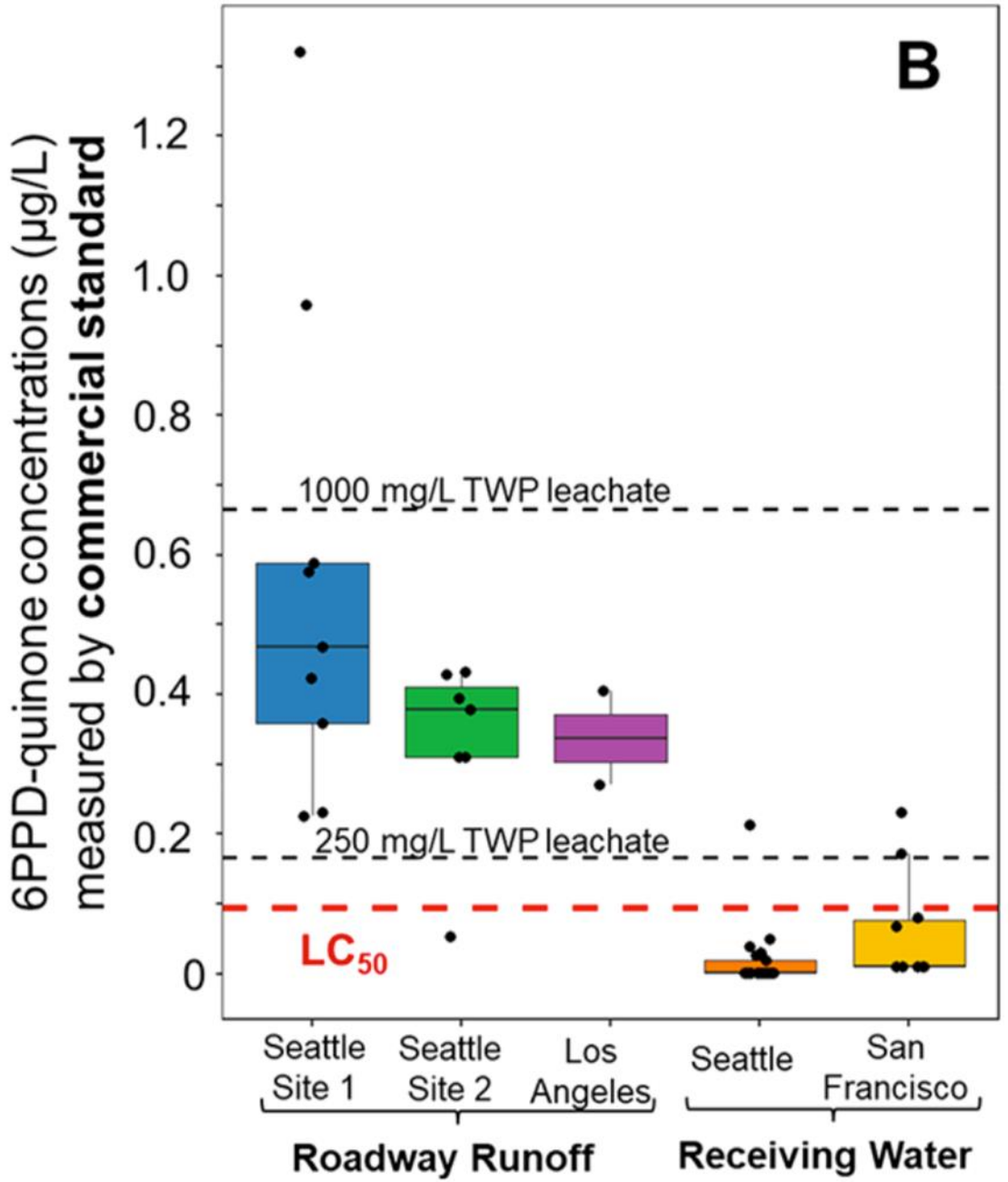
(Challis, Monahan, Johannessen, Rauert)

- Roadside soils, dust

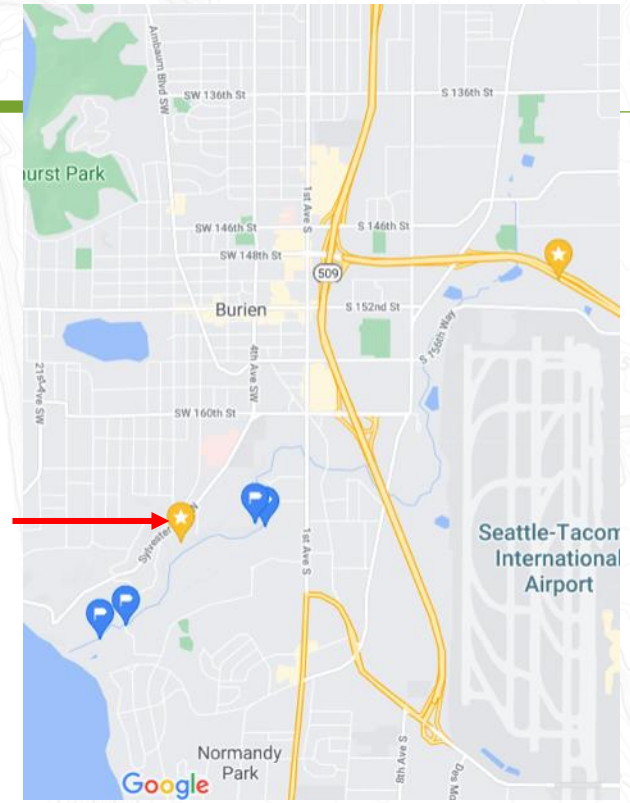
(Klockner, Huang, Zhang)

Consistent with our reported values for runoff and receiving waters

Tian et al. 2022. ES&T Letters

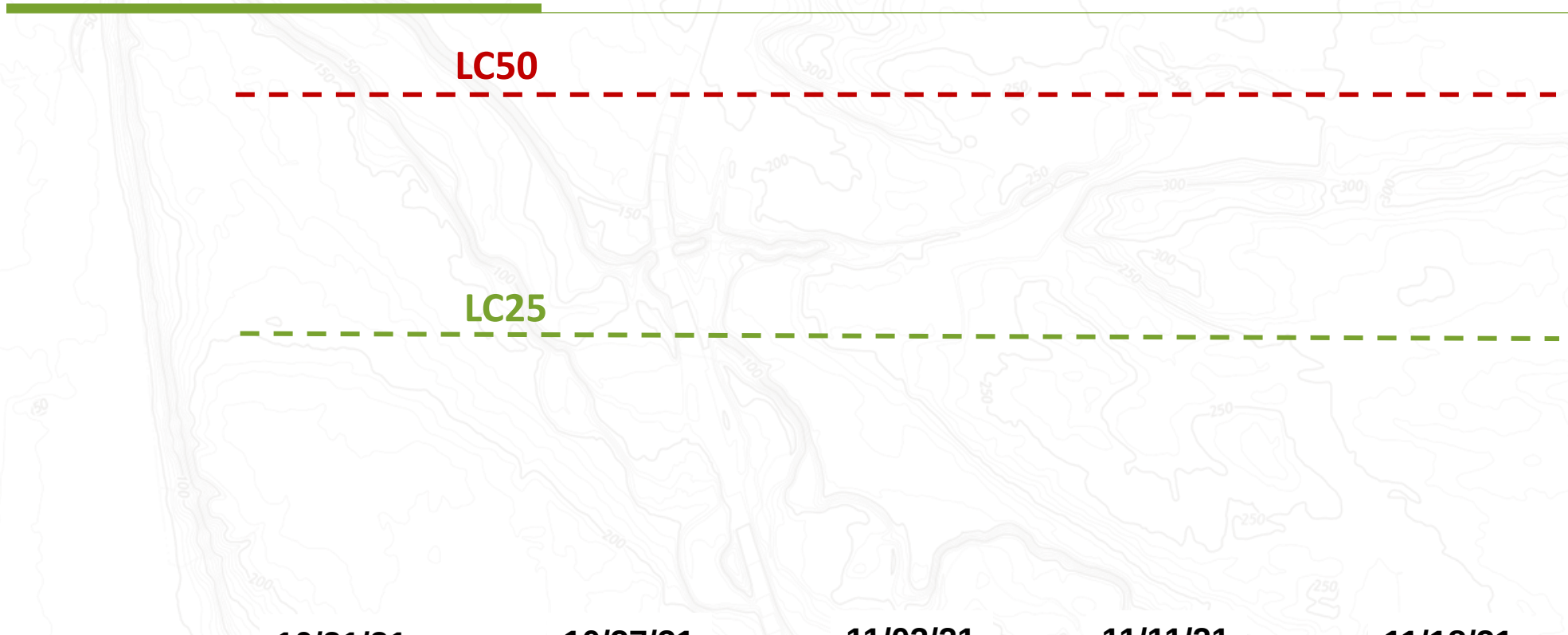


What concentrations and duration of 6PPD-Q?



Sampled every 30 min across 5 storms

Peak 6PPD-Q concentrations during 5 storm events



Most events would kill significant proportions of fish

How long is 6PPD-Q elevated during a storm?

Miller Creek, WA

LC25

LC25

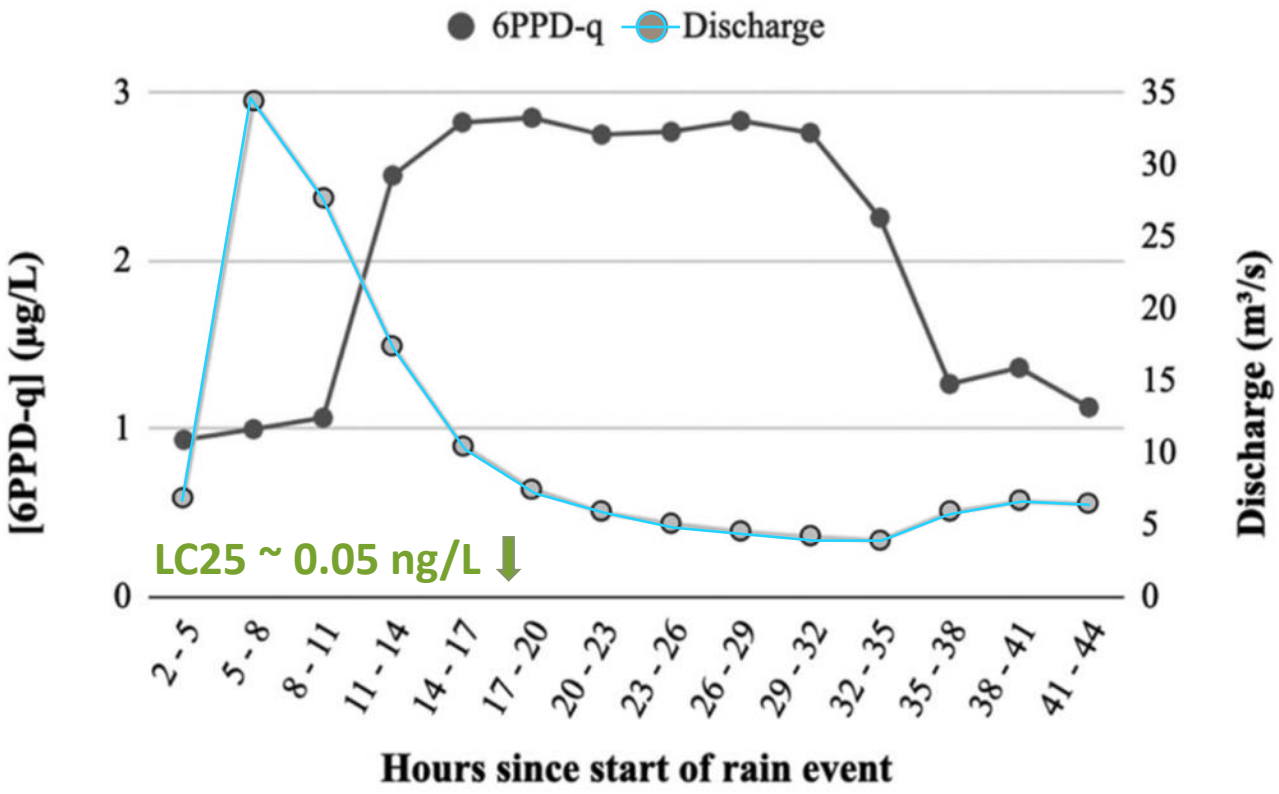
6PPD-Q: lethal levels for several hours

6PPD-Q peaks within hydrograph

How long is 6PPD-Q elevated during a storm?

Don River, Toronto

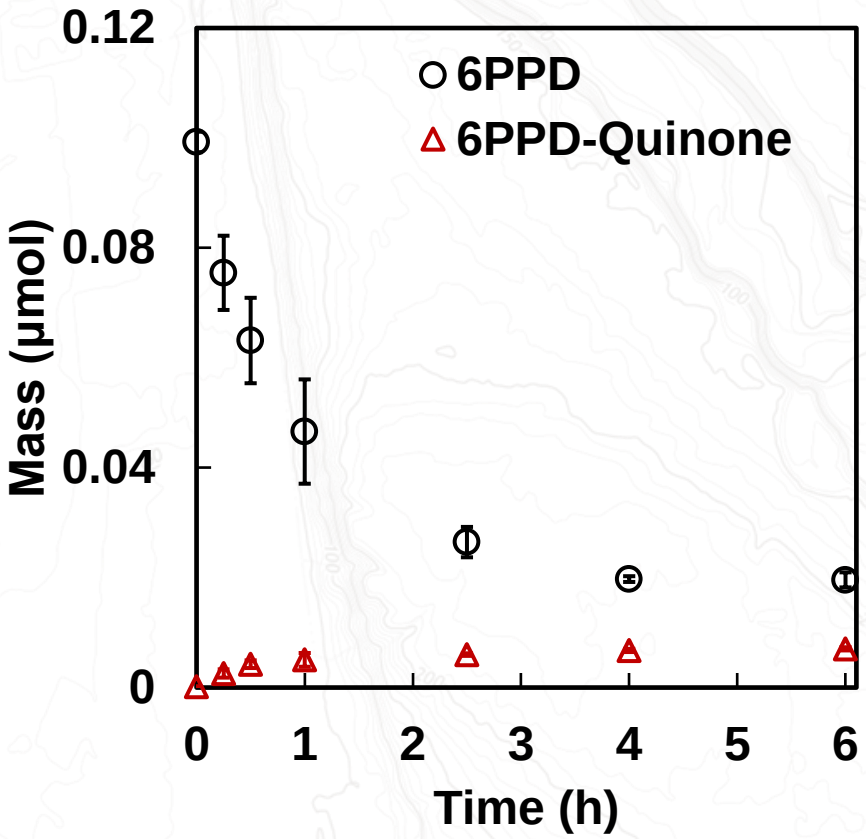
Lethal levels of 6PPD-Q through entire storm (48 h)

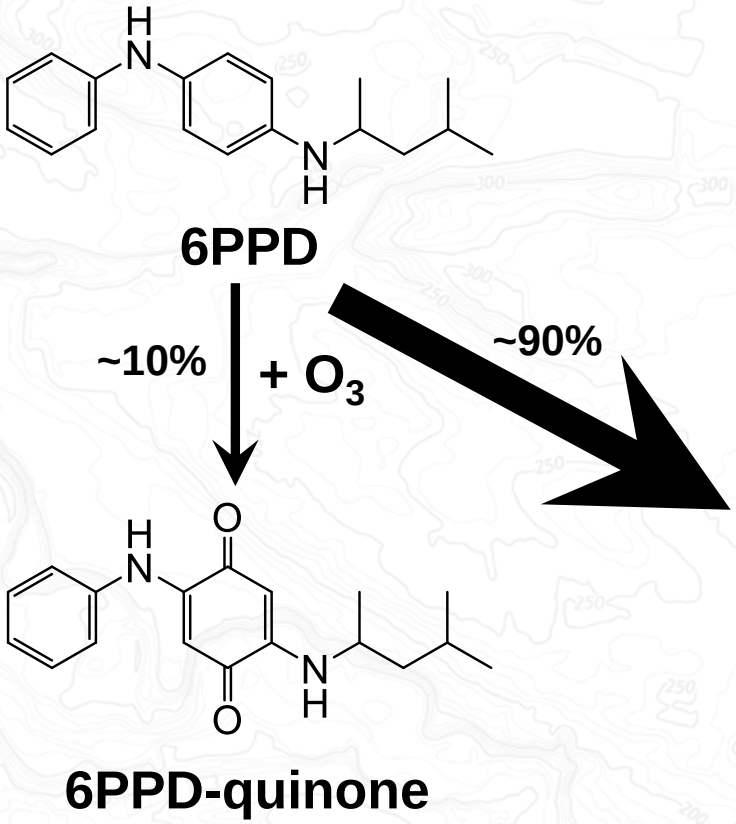


Johannessen et al. 2021. Arch. Environ. Contam. Toxicol.

6PPD-Q elevated beyond hydrograph

Additional transformation products of 6PPD

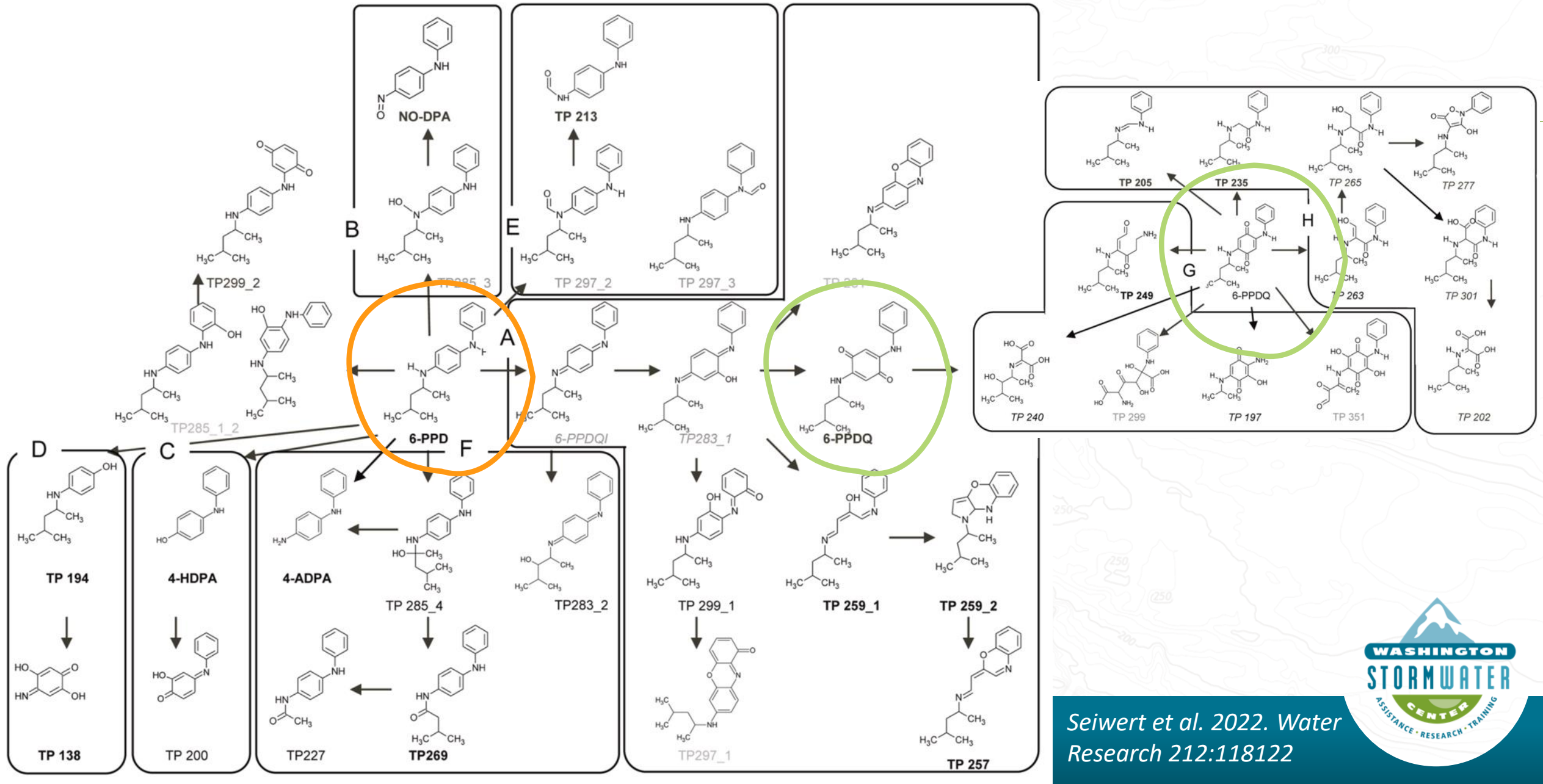




Other TPs??
Discharge to environment??

Hu et al. 2022. ES&T Letters

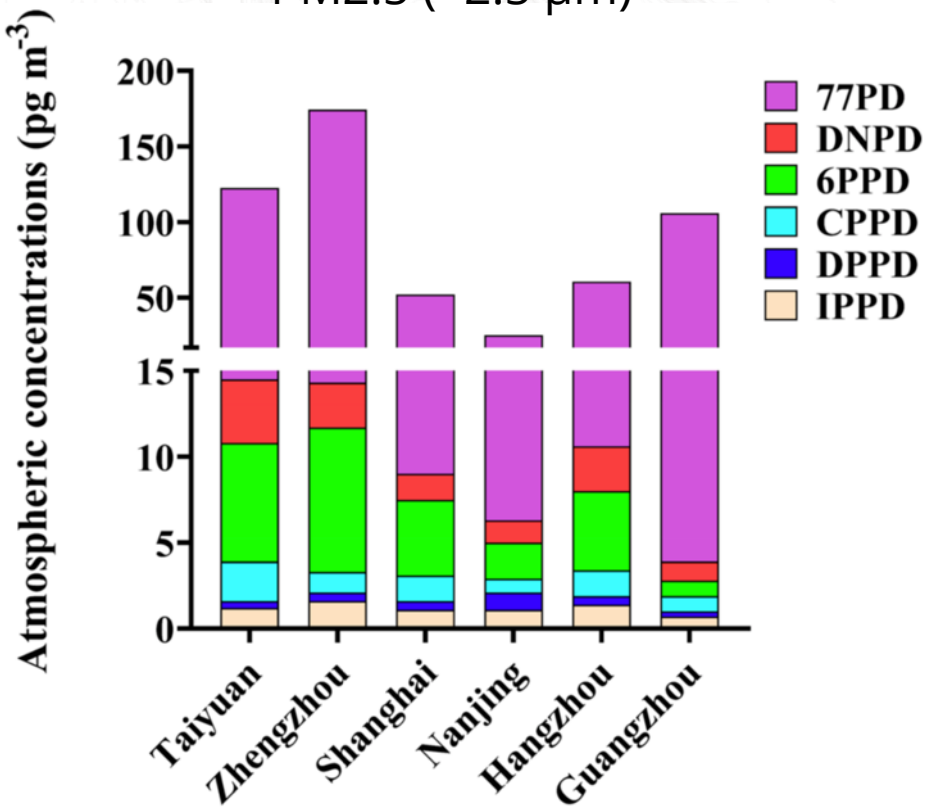
Transformation pathways of 6PPD and 6PPD-Q



Seiwert et al. 2022. Water Research 212:118122

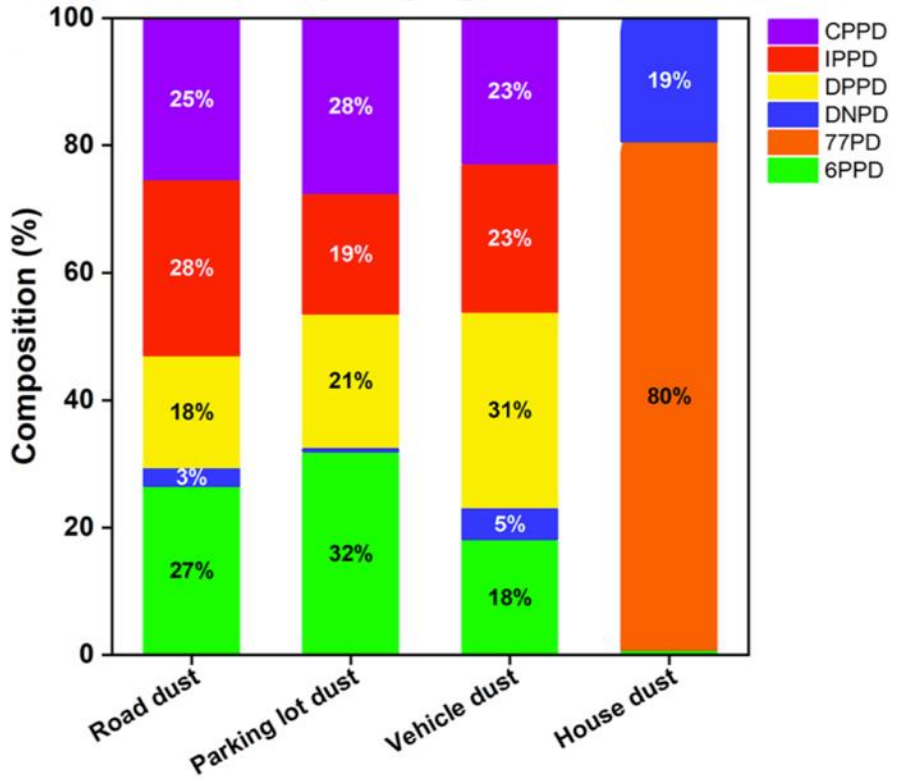
Additional (P)PDs Detected in Air/Dust/Soil

PM2.5 (<2.5 μm)



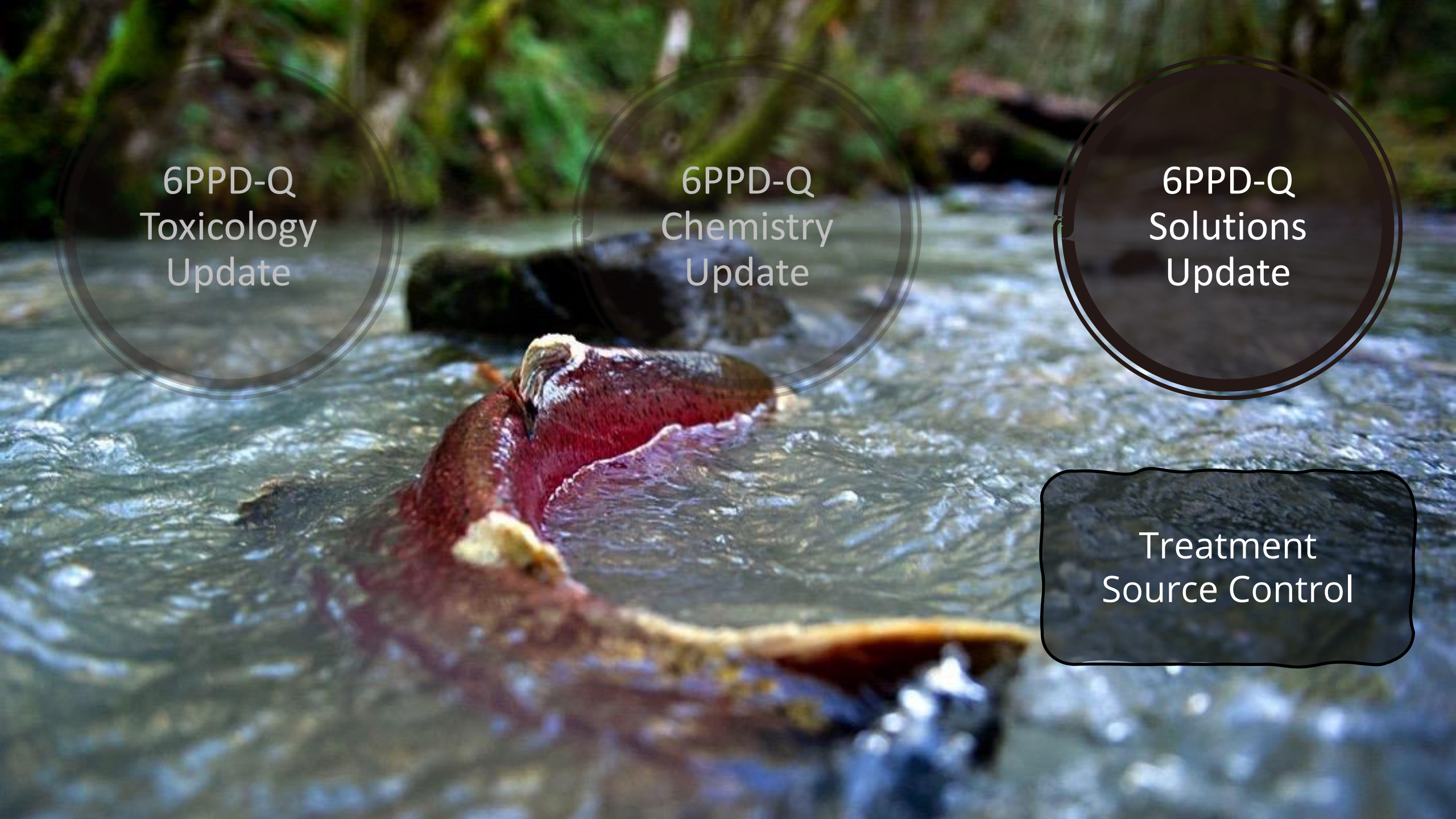
Zhang et al. 2022. ES&T

Particles = 25-250 μm



Huang et al. 2022. ES&T Letters

77PD is most abundant in ambient air & dust (household/building)


6PPD-Q
Toxicology
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Solutions
Update
Treatment
Source Control

Treatment: Green Stormwater Infrastructure

Bioretention treatment of stormwater prevents toxicity

Well water (4 hr)

All 4 fish alive at 24 hr

Unfiltered stormwater (4 hr)

0 of 4 fish alive at 24 hr

Filtered stormwater (4 hr)

All 4 fish alive at 24 hr

Prevents acute mortality in spawners, juveniles, and alevin

Spromberg et al. 2016. J. Applied Ecology Videos: https://besjournals.onlinelibrary.wiley.com/doi/full/10.1111/1365-2664.12534

Biofiltration Performance: Roadside Treatments

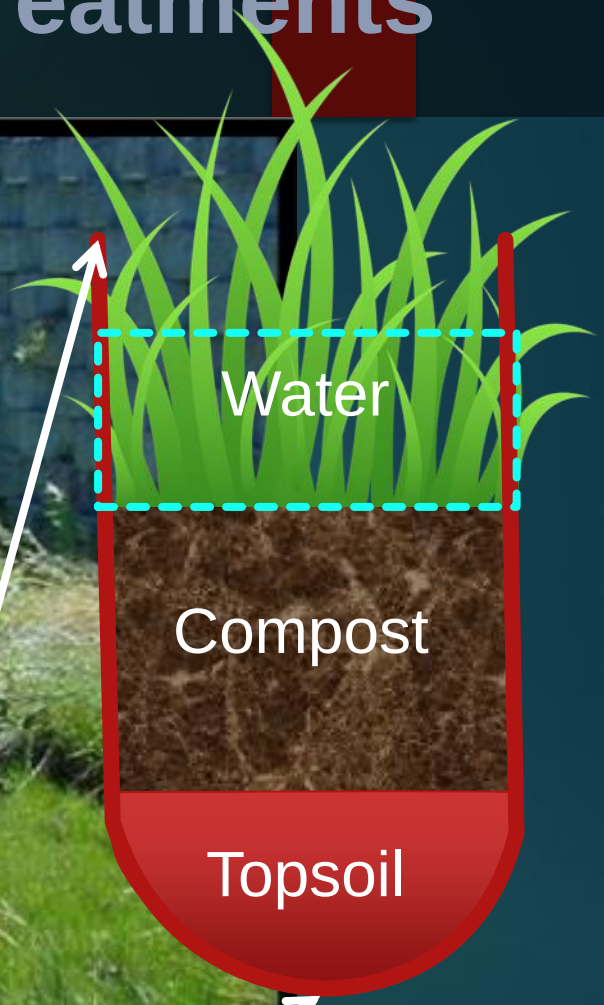
WSU
Ben Leonard
Ph.D. student
SOE

UW
Ed Kolodziej
+ 2 postdocs

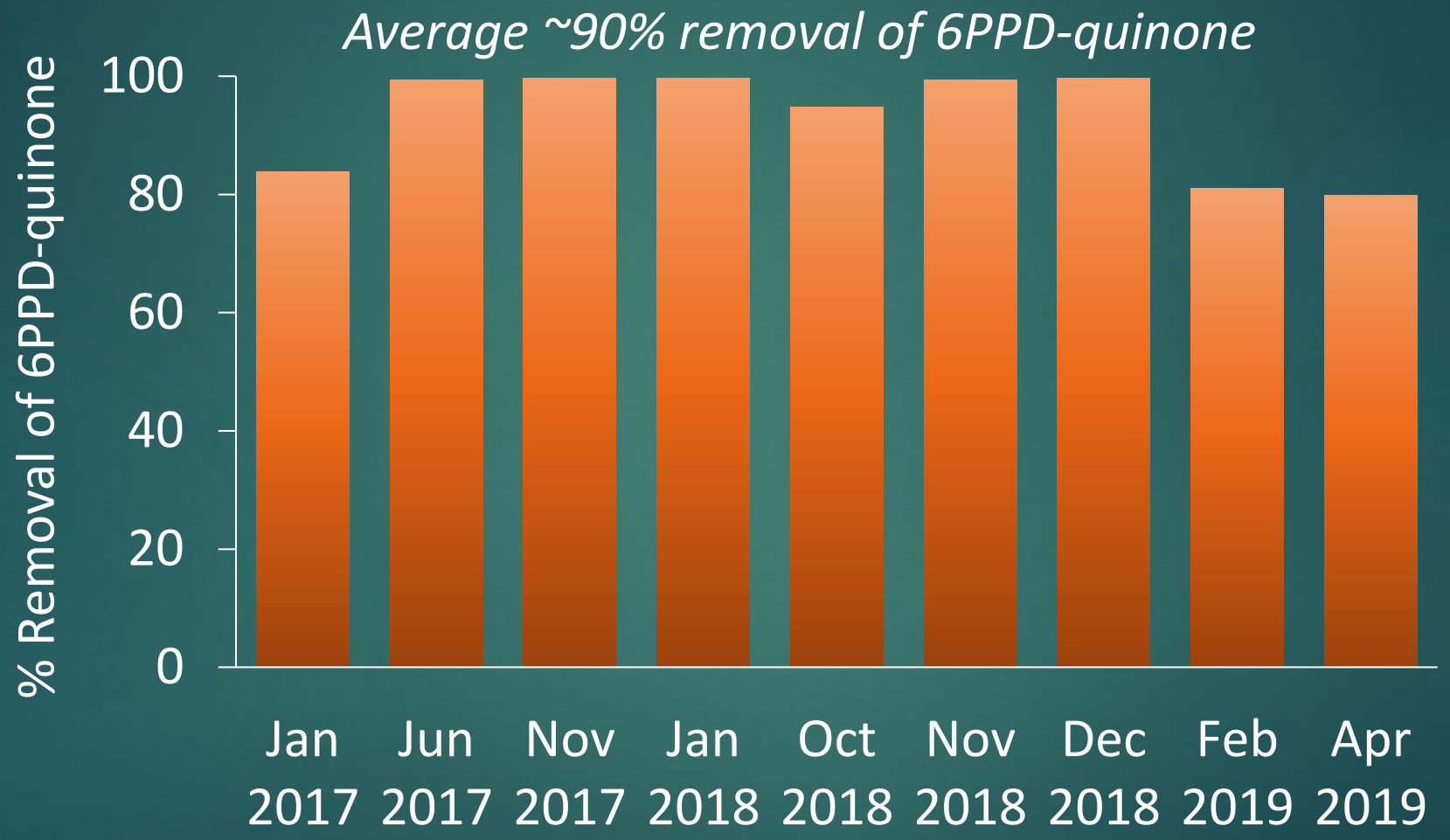
FHWA

WSDOT

Washington State DOT
Compost-Amended Bioswale

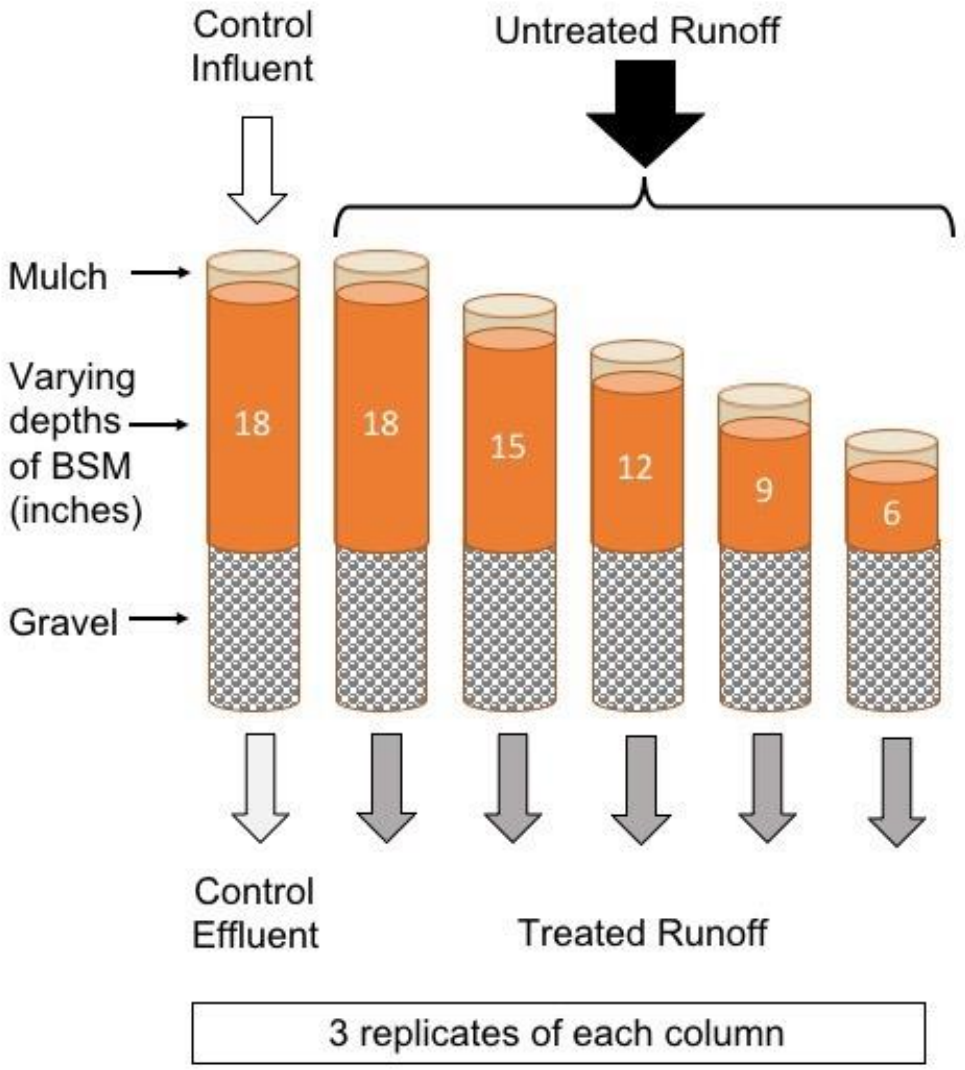


SR 518 CABS treatment of roadway runoff



Tian, Du, Peter, Leonard, et al. In Prep

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:

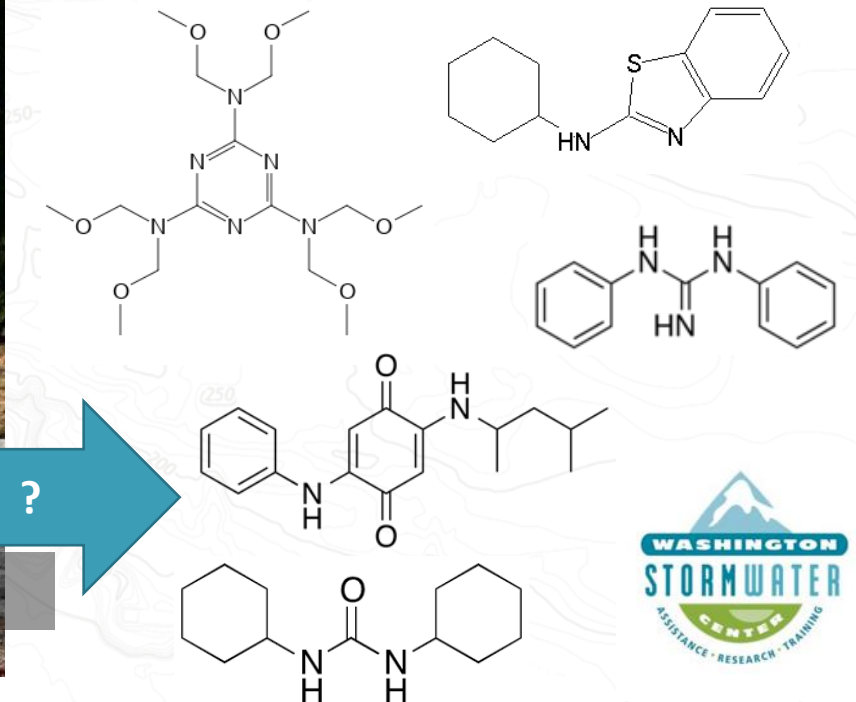
- Dosing with collected runoff
- 10 water years across 2-yr study
- Assess chemical and biological performance at end of every water year

Lane Maguire
M.S. 2021

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

Chelsea Mitchell (WSU PhD candidate)
Anand Jayakaran

?



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Mitigation: Source Control

Ongoing conversation about safer alternatives to 6PPD

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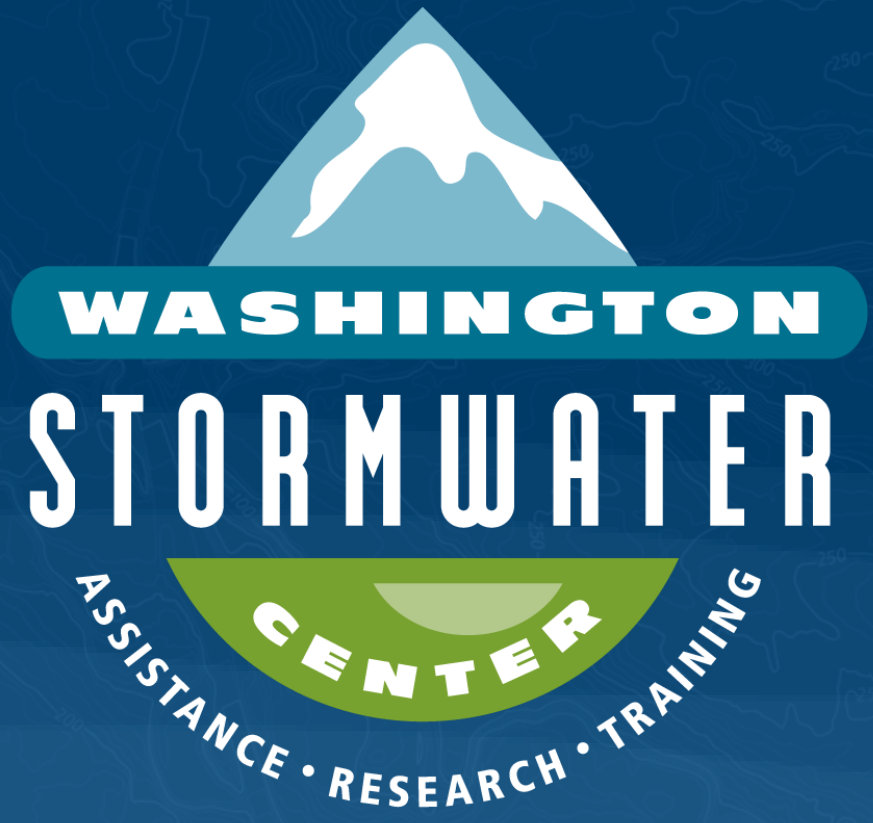
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