# Coho Salmon and Car Tires (and Miller Creek)

Edward P. Kolodziej, Zhenyu Tian, Katherine Peter,
Nina Zhao, Ximin Hu, Mike Dodd, Jen McIntyre
+ lots of collaboration with U. Toronto, WSU-Puyallup,
And NOAA-NMFS

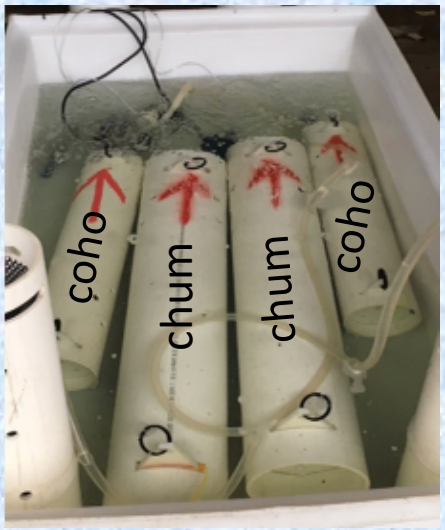
CENTER FOR URBAN WATERS

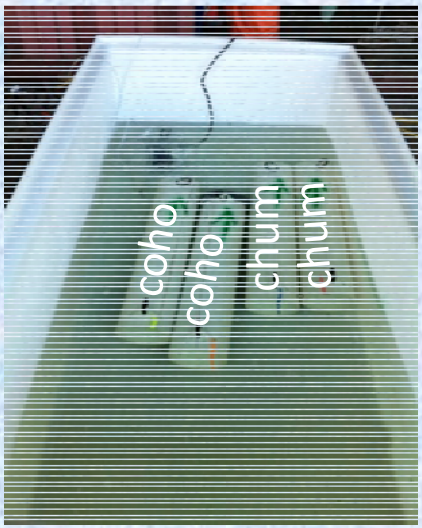
W

# 2017: Ecotoxicology Studies

**Hatchery salmon returns to the Grover's Creek Suquamish Tribal Hatchery**

**Tire Rubber Leachate**

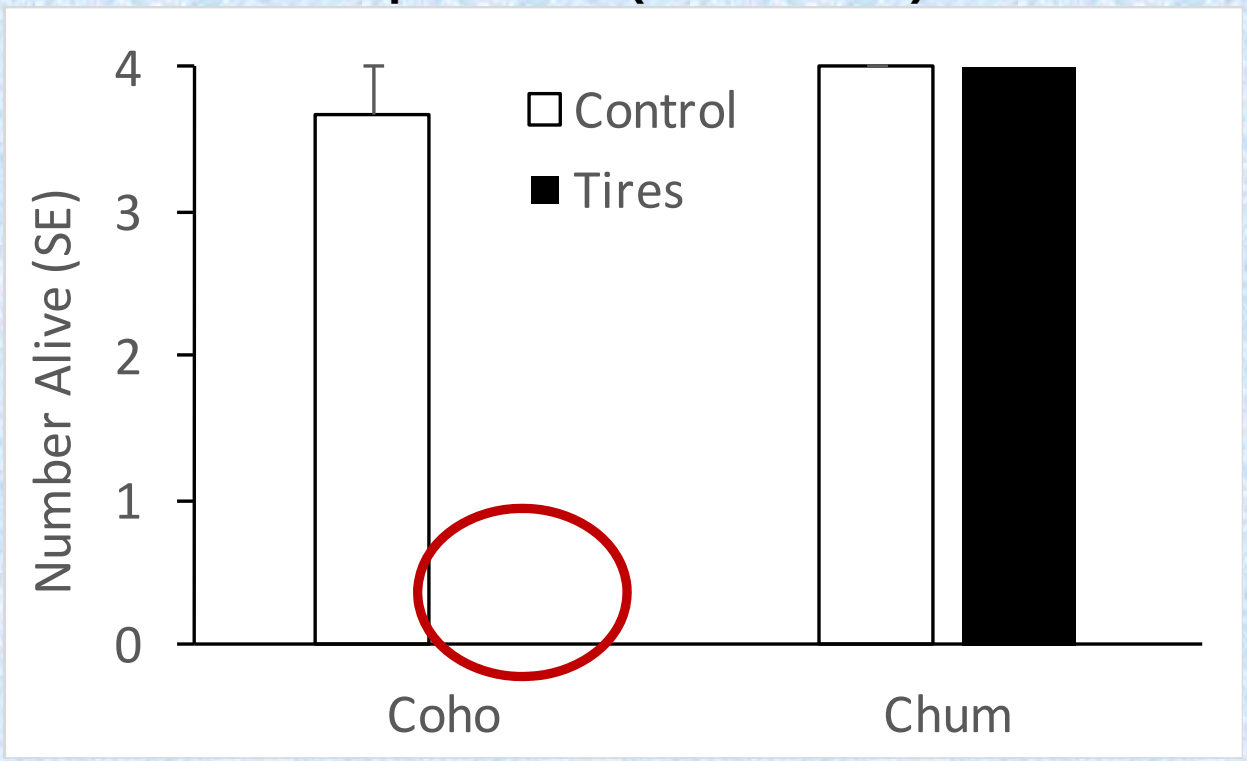


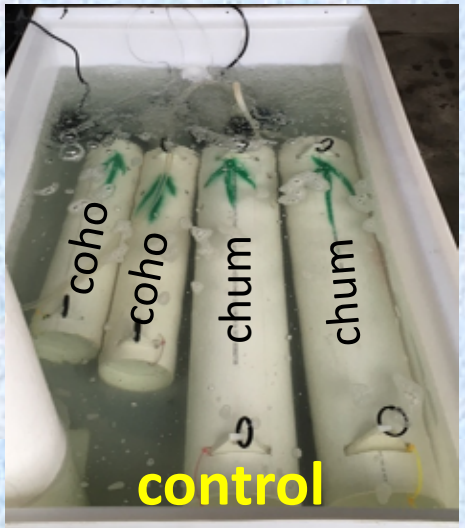



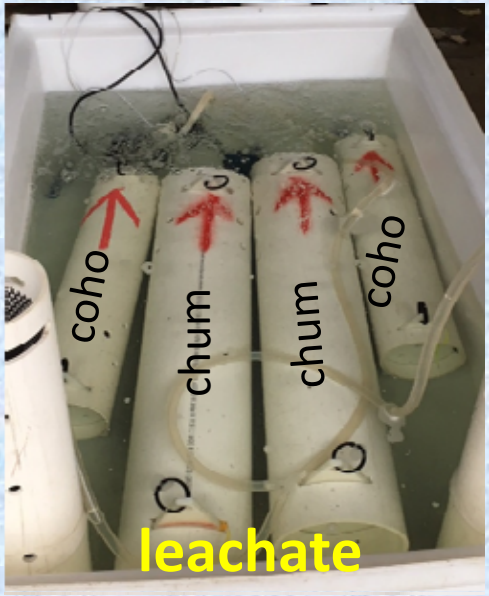

Jen McIntyre (WSU-Puyallup) and NOAA studies

# 2017: Tire Rubber is Lethally Toxic to Adult Coho

**~320 mg/L tire rubber (HRMS: more like 100 mg/L)**
**Leaching: 24 h at 8-10 ºC**
**Exposure: 24 h**
**Repeated 4X (64 fish total)**



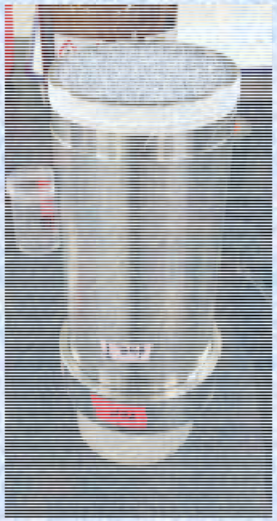

**16 of 16 exposed coho salmon died,**
**16 of 16 exposed chum salmon lived**

Jen McIntyre (WSU-Puyallup) and NOAA studies

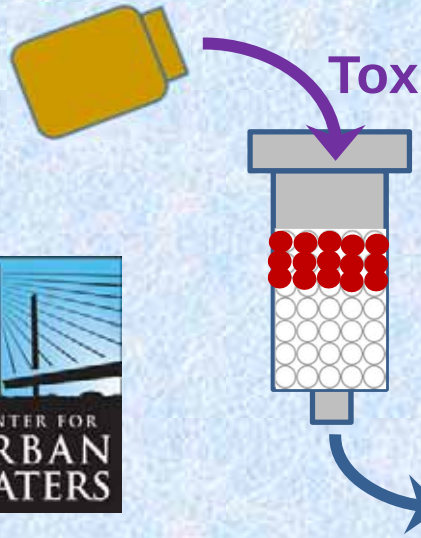
# 2017-2020: TIE/EDA Identify Toxicant(s) in Tire Rubbers

## Leach tire particles into water






## Fractionate tire leachate & expose juvenile coho



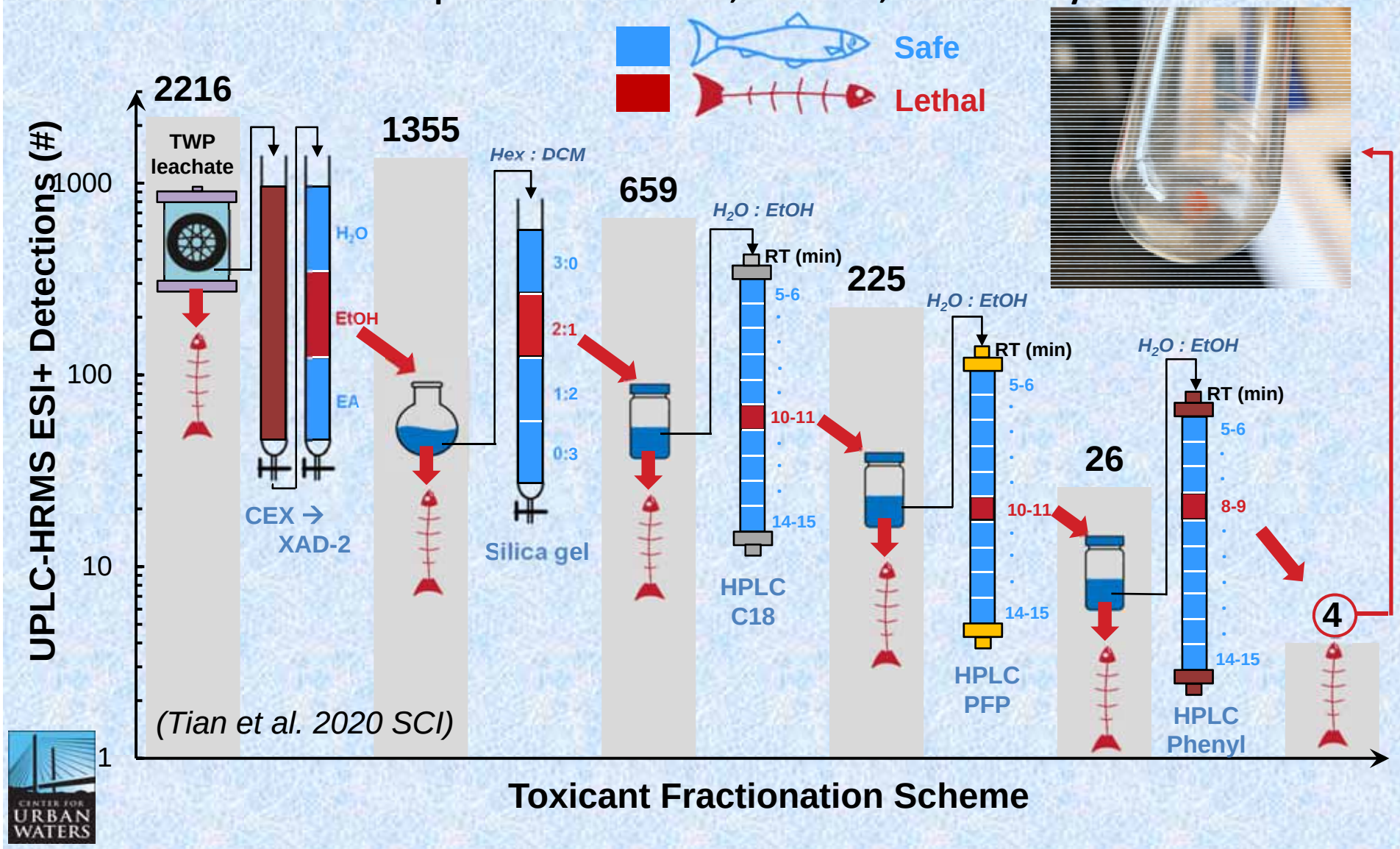

5 juvenile coho in 15-30 L, 24 h

CENTER FOR URBAN WATERS

# 2017-2019: We Isolated a Single Toxic Fraction..

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

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

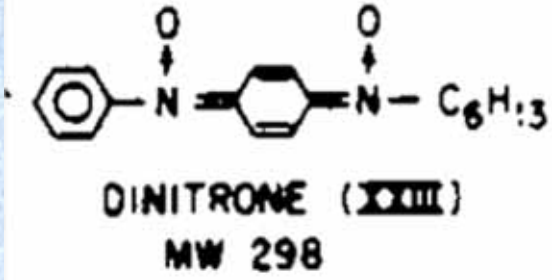


# Late 2019: Final Toxic Fraction: What Was $C_{18}H_{22}N_2O_2$??

- **$C_{18}H_{22}N_2O_2$** 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"**



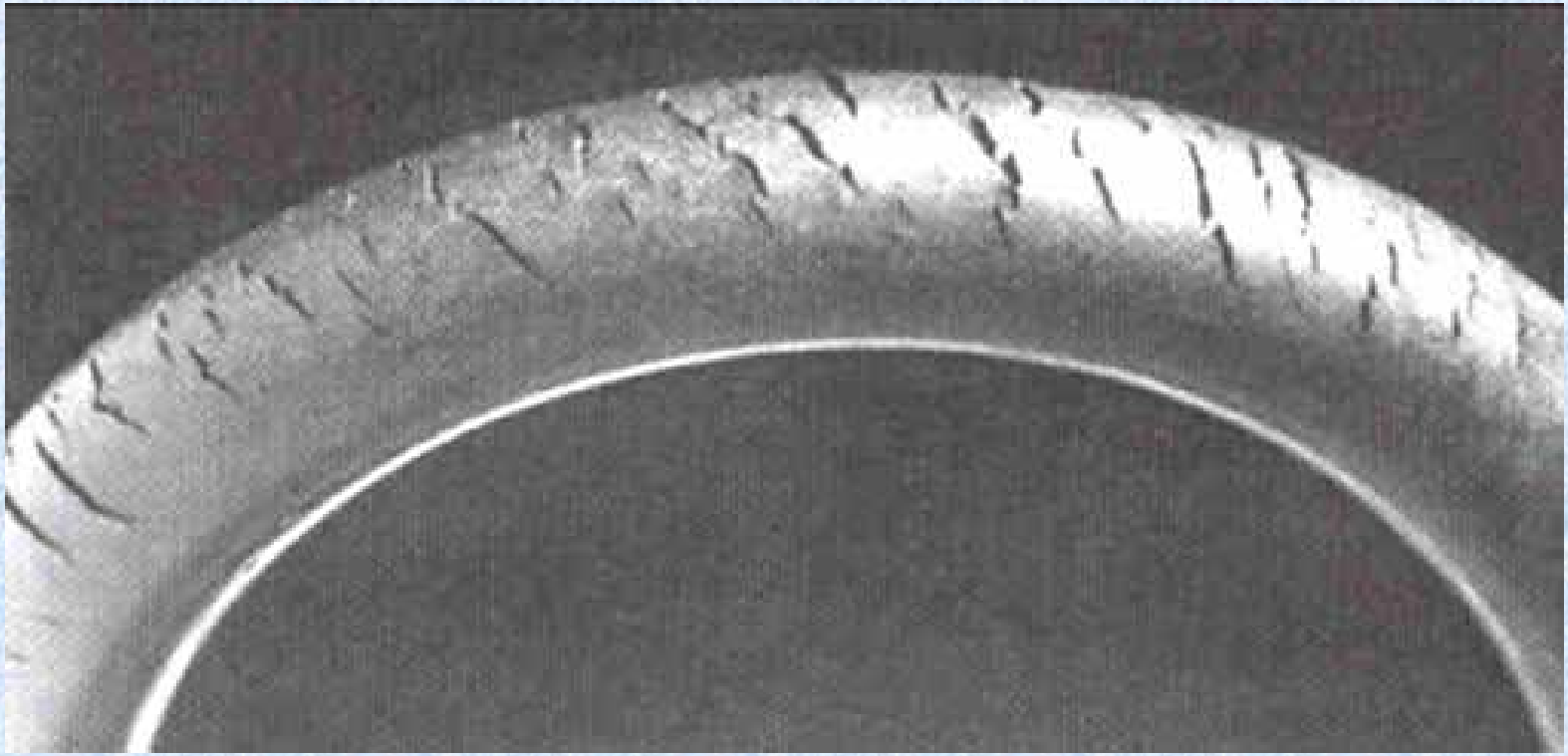
DINITRONE (XXIII)
MW 298

TABLE I
COMPOSITIONS OF OZONE-HPPD REACTION PRODUCTS

| 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**

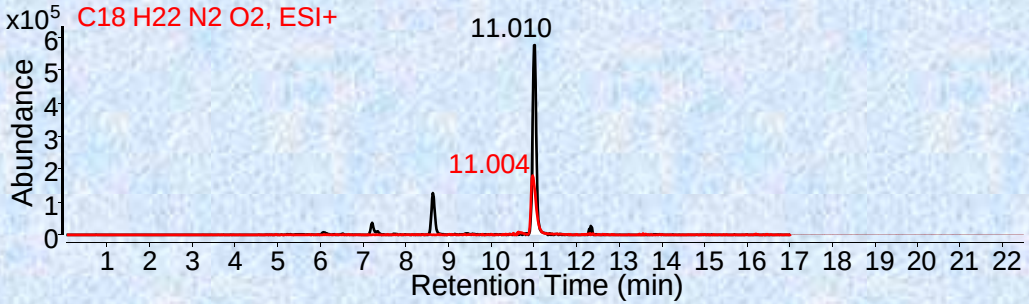


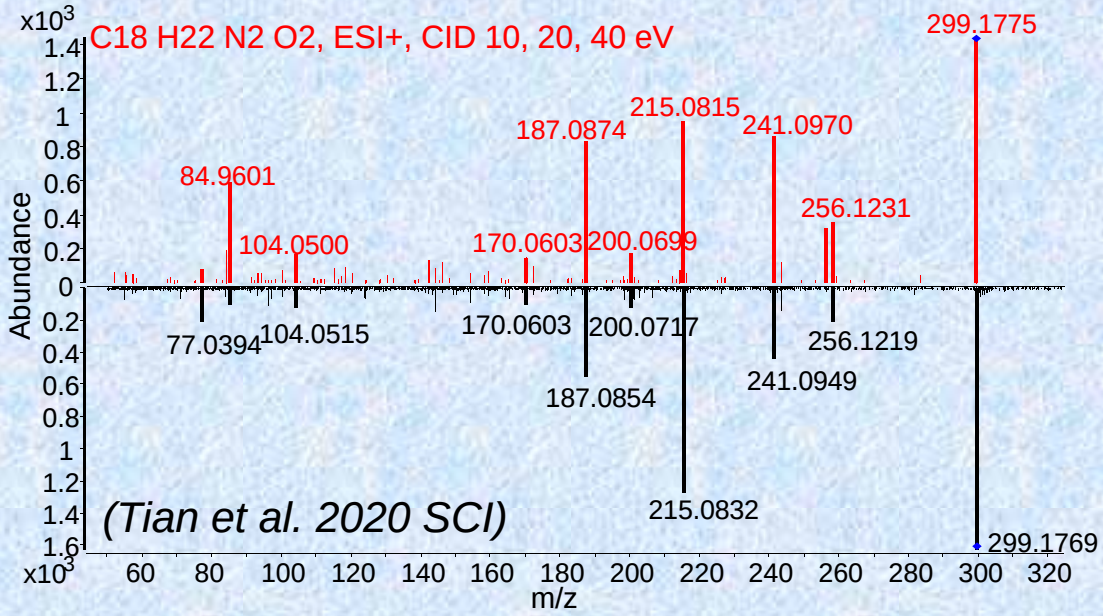
**We all own/purchase 6PPD:**
**Each car, ~100 lbs rubber, ~1 lb 6PPD**
**Heavy trucks: >2000 lbs rubber, maybe 2% 6PPD?**

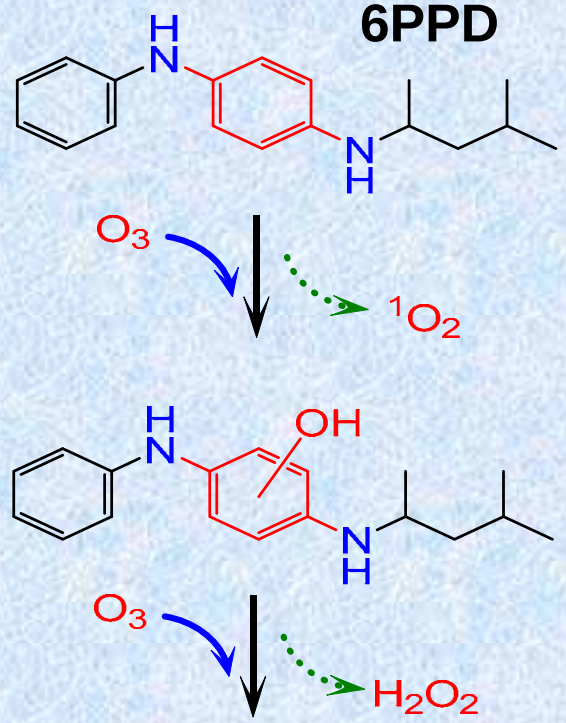
# 2019-2020: Purified $C_{18}H_{22}N_2O_2$ from Tire Leachate and Ozonation

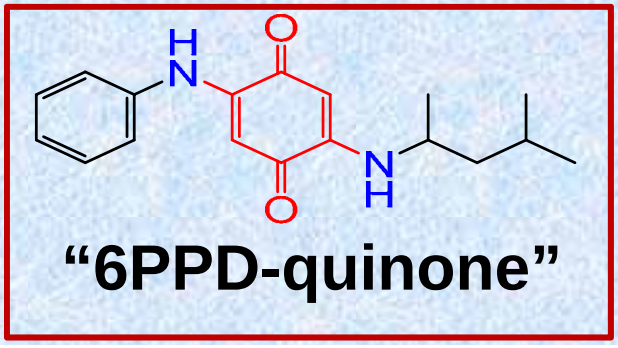
**-Andre Simpson, U. Toronto NMR Analysis:**
**Identical structures, $O_3$ synthesized ~98% pure**

Tire leachate | 6PPD ozonation



# Field Mortality

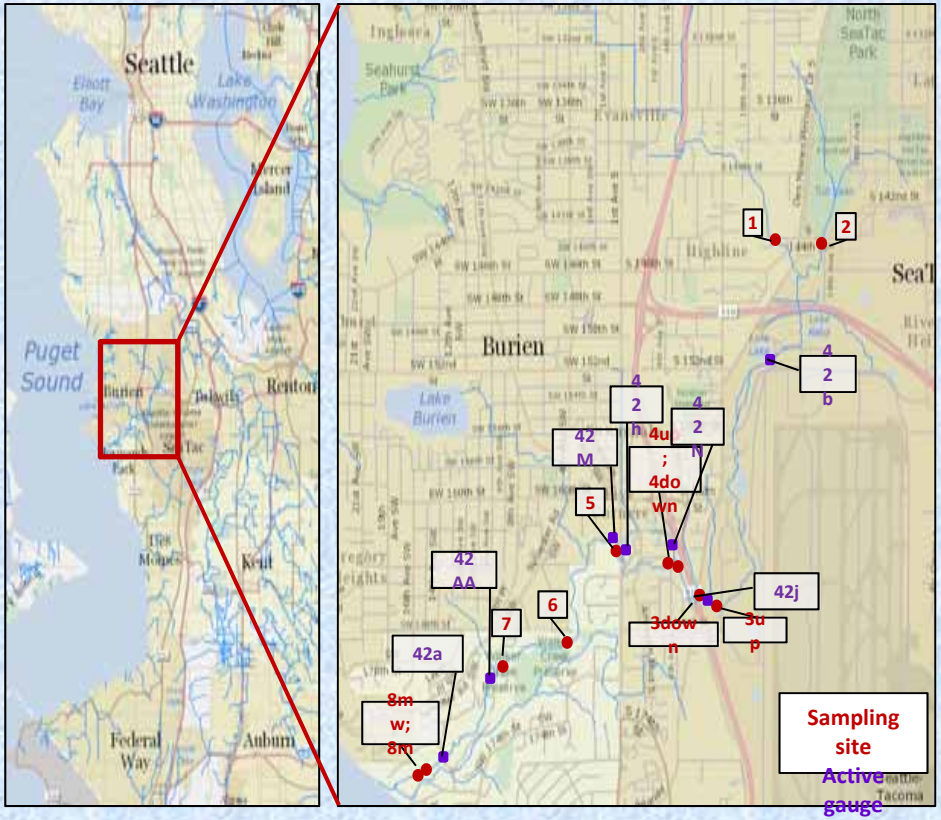
October 21, 2017
Lower Duwamish R.
(Puget Soundkeeper)

# Lab Exposure

February 17, 2020
WSU-Puyallup
(Kolodziej video)

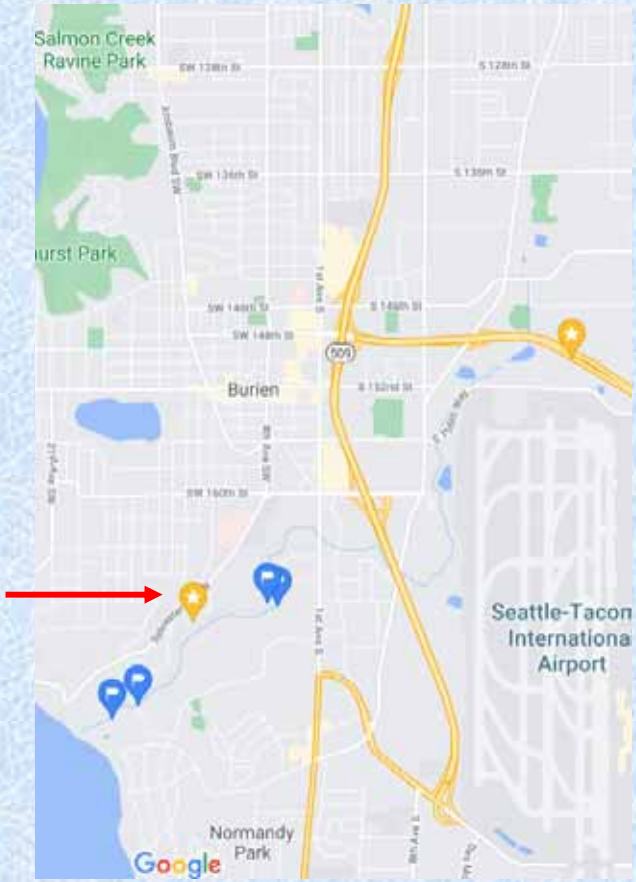
# 2021+: How Do We Protect Our Salmon??

## Where should we treat stormwater??




Miller Creek Watershed, Burien WA

# 2020-2022: Pollutant Dynamics During Storms





- **Miller Creek (documented URMS site, stream gauge data)**
- **7 storms: autumn/winter 2020 (4) and spring 2021 (3)**
- **Sampling every 30 mins, combine 2 samples (1-hour averaged)**

# Who Really Puts the Rubber On Our Roads?

Is it us?

Is it Amazon?


# Source Control: Make "Salmon Safe" Tires??

U.S. TIRE MANUFACTURERS ASSOCIATION

WASHINGTON STORMWATER CENTER
ASSISTANCE · RESEARCH · TRAINING

DTSC
Department of Toxic Substances Control

DEPARTMENT OF ECOLOGY
State of Washington

SALMON SAFE

??

**Tire companies need to take out the bad chemicals…**

# Other Rubber Products and PPD Antioxidants



CENTER FOR URBAN WATERS

## Occurrence of 6PPD TPs?

Science

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 Zhao[3], Katherine T. Peter[1,2], Melissa Gonzalez[1,2], Jill Wetzel[4], Christopher Wu[1,2], Ximin Hu[3], Jasmine Prat[4], Emma Mudrock[4], Rachel Hettinger[1,2], Allan E. Cortina[1,2], Rajshree Ghosh Biswas[5], Flávio Vinicius Crizóstomo Kock[5], Ronald Soong[5], Amy Jenne[5], Bowen Du[6], Fan Hou[3], Huan He[3], Rachel Lundeen[1,2], Alicia Gilbreath[7], Rebecca Sutton[7], Nathaniel L. Scholz[8], Jay W. Davis[9], Michael C. Dodd[3], Andre Simpson[5], Jenifer K. McIntyre[4], Edward P. Kolodziej[1,2,3]*

## 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

**Brook trout $LC_{50}$ (24 hr): 590 ng/L**
**Rainbow trout $LC_{50}$ (72 hr): 1000 ng/L**

## The Tire-Derived Chemical 6PPD-quinone Is Lethally Toxic to the White-Spotted Char *Salvelinus leucomaenis pluvius* but Not to Two Other Salmonid Species

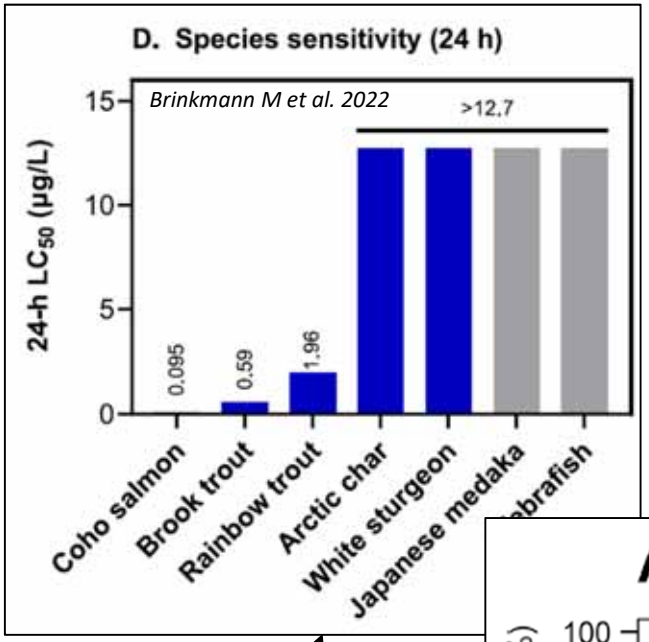
Kyoshiro Hiki* and Hiroshi Yamamoto

**White spotted char $LC_{50}$: 510 ng/L**

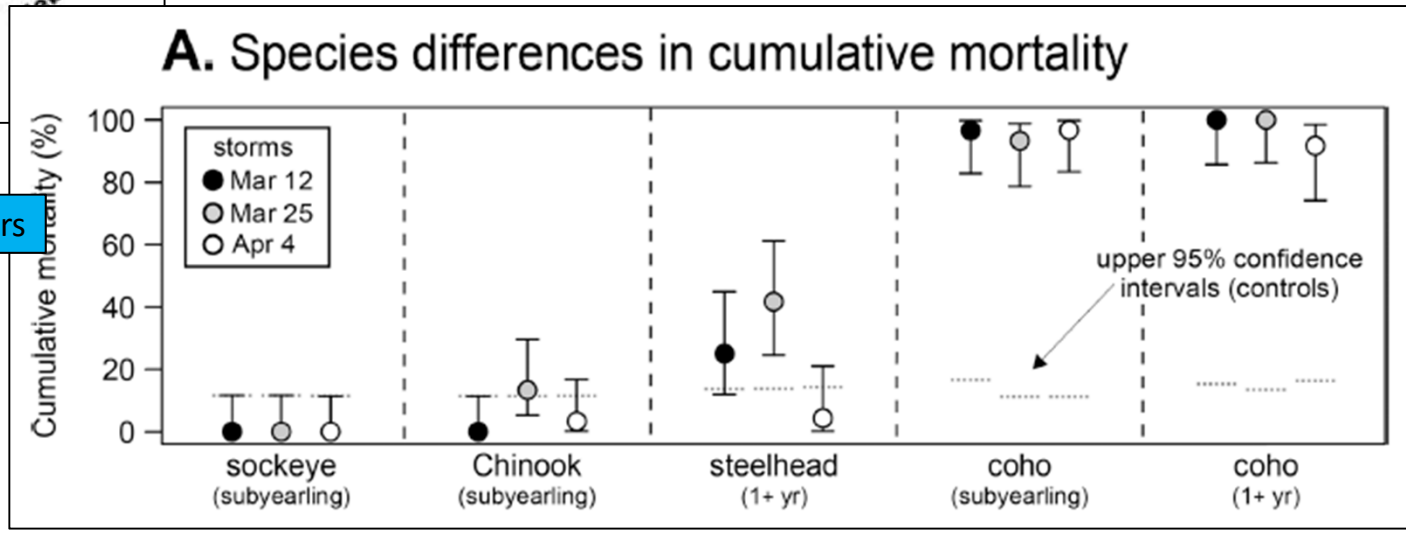
***SETAC 2022: Atlantic salmon fry??***

***Hua et al. (2022): Chronic intestinal toxicity to C. elegans***

# Relative Sensitivity of Salmonids




Pure 6PPD-q exposure for 24 hours




Stormwater exposure for 24 hours
(6PPD-q was not added or quantified)

*(Slide from Catherine Gockel, EPA R10)*

*French et al. 2022*

Science

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 Zhao[3], Katherine T. Peter[1,2], Melissa Gonzalez[1,2], Jill Wetzel[4], Christopher Wu[1,2], Ximin Hu[3], Jasmine Prat[4], Emma Mudrock[4], Rachel Hettinger[1,2], Allan E. Cortina[1,2], Rajshree Ghosh Biswas[5], Flávio Vinicius Crizóstomo Kock[5], Ronald Soong[5], Amy Jenne[5], Bowen Du[6], Fan Hou[3], Huan He[3], Rachel Lundeen[1,2], Alicia Gilbreath[7], Rebecca Sutton[7], Nathaniel L. Scholz[8], Jay W. Davis[9], Michael C. Dodd[3], Andre Simpson[5], Jenifer K. McIntyre[4], Edward P. Kolodziej[1,2,3]*

## 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*

**Juvenile coho salmon $LC_{50}$: 95 ng/L (ongoing: 70-130 ng/L)**

***USGS $LC_{50}$: 85 ng/L (J. Hansen, personal comm.)***

Table 1. Comparison of the Toxicity of 6PPD-Q to Coho Salmon with Those of the Most Toxic Chemicals for Which the U.S. Environmental Protection Agency Has Established Aquatic Life Criteria[a]

| chemical class | name | most sensitive species | $LC_{50}$ (ppb) | 95% CI | ref | CMC (ppb) | EPA document |
|---|---|---|---|---|---|---|---|
| OP | parathion | *Orconectes nais* | 0.04 | 0.01–0.2 | 25 | 0.065 | EPA 440/5-86-007 |
| quinone | 6PPD-Q | *O. kisutch* | 0.10 | 0.08–0.11 | this study | not available | not available |
| OC | mirex | *Procambaris blandingi* | 0.10 | not reported | 26 | 0.001 | EPA 440/5-86-001 |
| OP | guthion | *Gammarus fasciatus* | 0.10 | 0.073–0.014 | 25 | 0.01 | EPA 440/5-86-001 |
| OP | chlorpyrifos | *Gammarus lacustris* | 0.11 | not reported | 27 | 0.083 | EPA 440/5-86-005 |
| OC | endrin | *Perca flavescens* | 0.15 | 0.12–0.18 | 28 | 0.086 | EPA 820-B-96-001 |

Science

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 Zhao[3], Katherine T. Peter[1,2], Melissa Gonzalez[1,2], Jill Wetzel[4], Christopher Wu[1,2], Ximin Hu[3], Jasmine Prat[4], Emma Mudrock[4], Rachel Hettinger[1,2], Allan E. Cortina[1,2], Rajshree Ghosh Biswas[5], Flávio Vinicius Crizóstomo Kock[5], Ronald Soong[5], Amy Jenne[5], Bowen Du[6], Fan Hou[3], Huan He[3], Rachel Lundeen[1,2], Alicia Gilbreath[7], Rebecca Sutton[7], Nathaniel L. Scholz[8], Jay W. Davis[9], Michael C. Dodd[3], Andre Simpson[5], Jenifer K. McIntyre[4], Edward P. Kolodziej[1,2,3*]

## Occurrences of Tire Rubber-Derived Contaminants in Cold-Climate Urban Runoff

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

**6PPDQ: 80-1400 ng/L in roadway runoff**

***similar studies in China, Australia, Canada, even >10 µg/L***

**6 PPDs**
**81% of $PM_{2.5}$**

## Occurrence of Substituted *p*-Phenylenediamine Antioxidants in Dusts

Wei Huang, Yumeng Shi, Jialing Huang, Chengliang Deng, Shuqin Tang, Xiaotu Liu, and Da Chen*

**5 PPDQs, more stable**

## 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*

**Pathways to human exposure**

## Widespread *N*-(1,3-Dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine Quinone in Size-Fractioned Atmospheric Particles and Dust of Different Indoor Environments

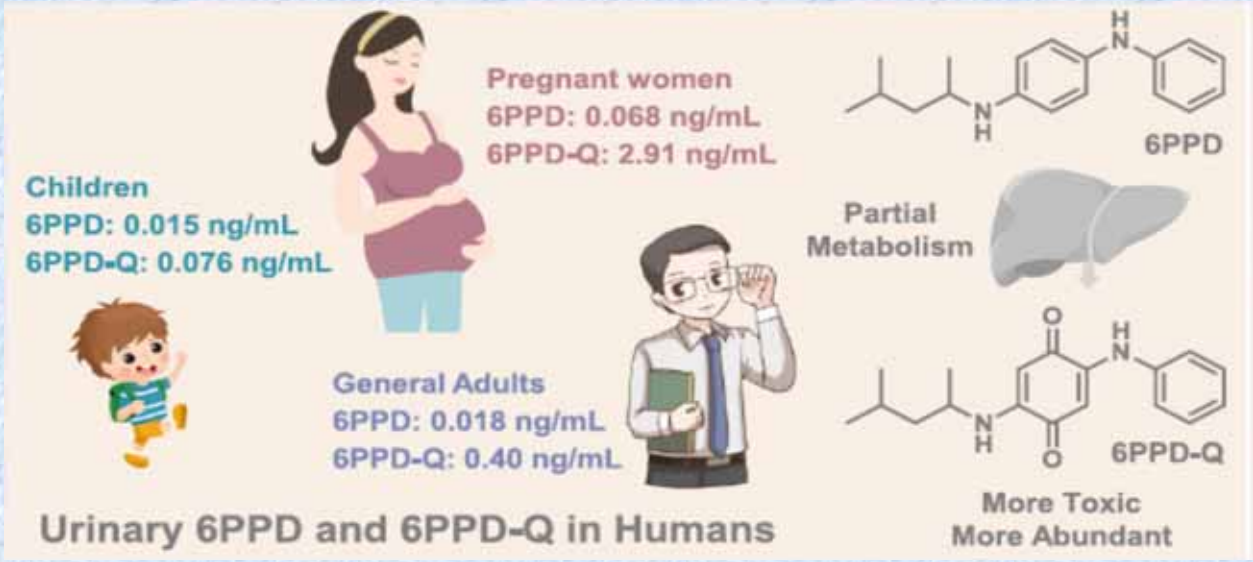
Ying-Jie Zhang,‡ Ting-Ting Xu,‡ Dong-Min Ye, Ze-Zhao Lin, Fei Wang, and Ying Guo*

Science

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 Zhao[3], Katherine T. Peter[1,2], Melissa Gonzalez[1,2], Jill Wetzel[4], Christopher Wu[1,2], Ximin Hu[3], Jasmine Prat[4], Emma Mudrock[4], Rachel Hettinger[1,2], Allan E. Cortina[1,2], Rajshree Ghosh Biswas[5], Flávio Vinicius Crizóstomo Kock[5], Ronald Soong[5], Amy Jenne[5], Bowen Du[6], Fan Hou[3], Huan He[3], Rachel Lundeen[1,2], Alicia Gilbreath[7], Rebecca Sutton[7], Nathaniel L. Scholz[8], Jay W. Davis[9], Michael C. Dodd[3], Andre Simpson[5], Jenifer K. McIntyre[4], Edward P. Kolodziej[1,2,3]*




**60-100% detection frequency**

## First Report on the Occurrence of *N*-(1,3-Dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China

Bibai Du, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng*

**6PPD Poem by:**
**Amalie Flynn**
**“Pattern of Consumption”**

**RUN / 54**
There is a die-off
Coho salmon ready to spawn
In streams that are stretching
Out from Puget Sound.
How salmon circle surface water
Gasp for air and die.
And it is 6PPD
A chemical preservative or tire
Dust
Running off into waters these
Waters where salmon used to
Run.

https://patternofconsumption.com/2022/02/23/54/

# Acknowledgements and Thanks To:

## The CUW Research Team!


Alex, Allan, Zhenyu, Rachel H., Rui, Ting, Nina, Melissa, Rachel L., and Kathy

+

Kathy Peter

# Acknowledgements and Thanks To:


- **Collaborators, Funders, & Citizen Science Teams**
  - NOAA NWFSC – Nat Scholz, James Cameron, Jessica Lundin (and many others)
  - WSU-Puyallup Stormwater Center – Jen McIntyre, John Stark (and many others)
  - Andre Simpson et al. (U. Toronto)
  - Suquamish and Puyallup Tribes
  - US Fish & Wildlife Service – Jay Davis, Ken King
  - WSDOT – Alex Nguyen, Jana Crawford
  - FHWA – Cindy Callahan
  - National Science Foundation
  - EPA-National Estuary Program
  - WA Department of Ecology
  - Miller Walker Community Salmon Investigation, Puget Soundkeeper, Thornton Creek Alliance

# Thank You!!

**Miller Creek is ground zero for understanding coho mortality and changing all of our vehicle tires..**

**You did this!!**

CENTER FOR URBAN WATERS

W