

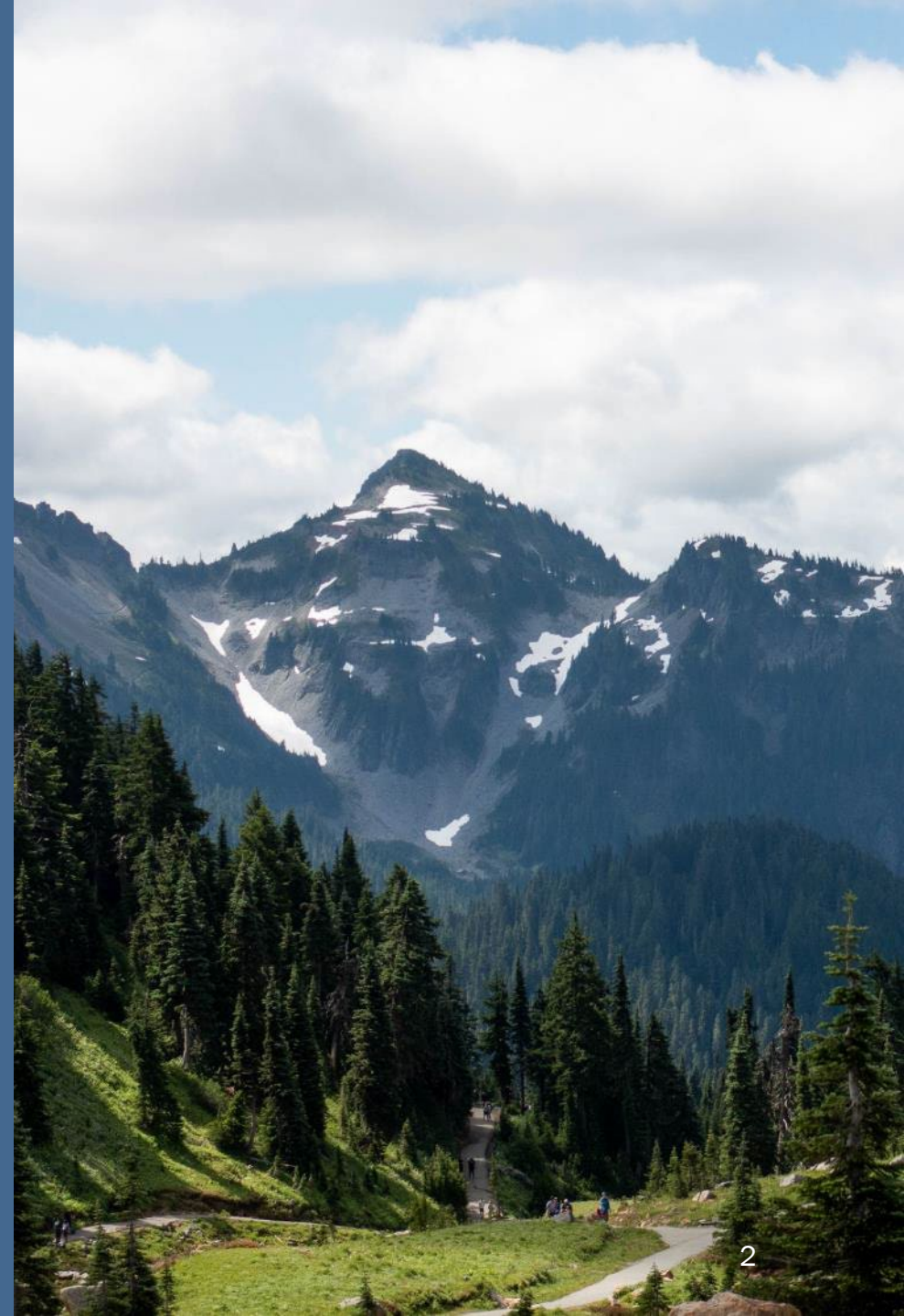


# 6PPD and 6PPD-quinone: Finding Solutions

Presented to: Spokane River Forum  
April 26, 2023

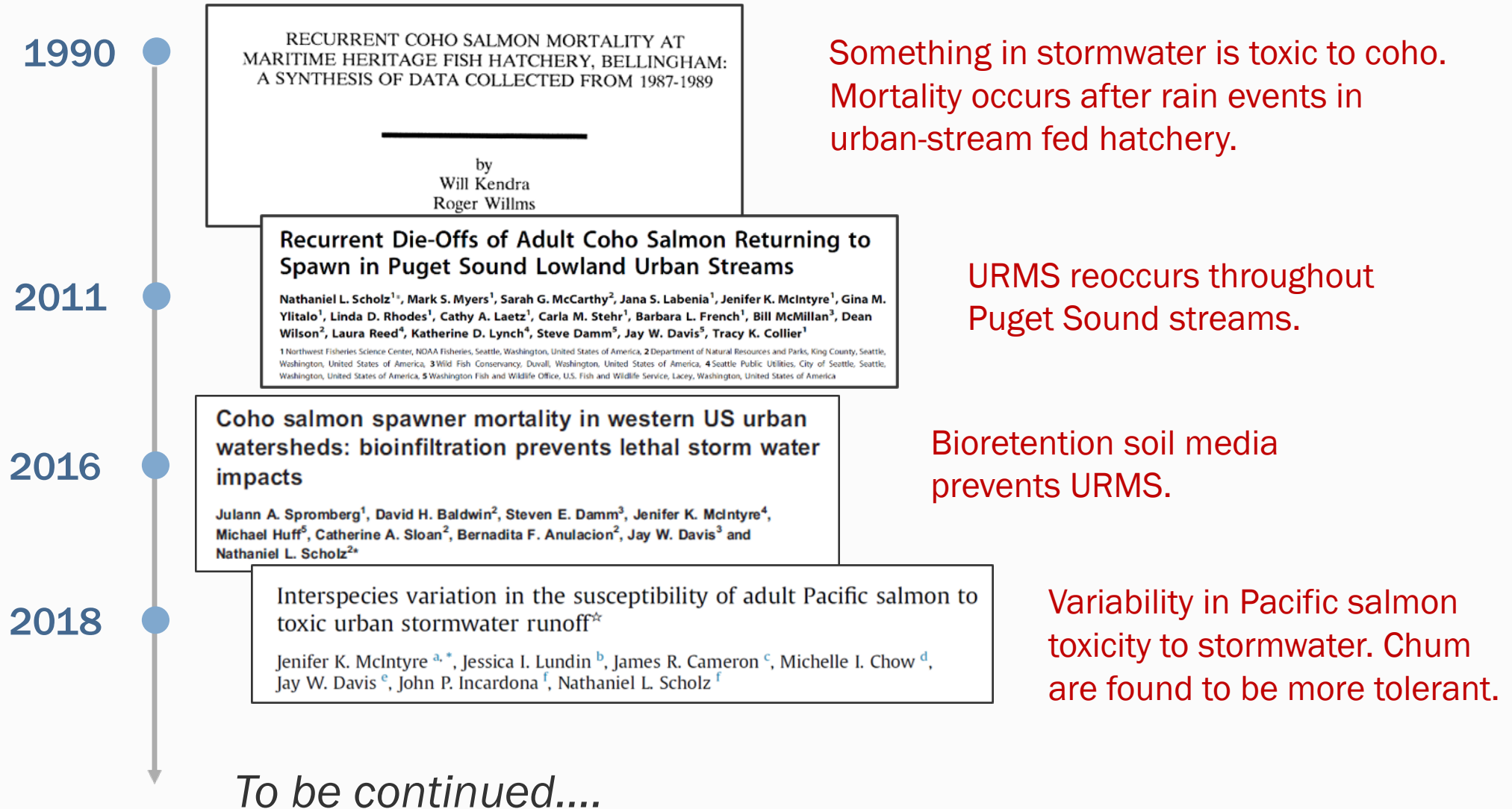


# Identification of the Problem



# Urban Runoff Mortality Syndrome (URMS) Timeline

URMS was first documented in the 1980s



# URMS Reoccurs in Puget Sound Streams

- Up to 100% of coho salmon died before they could spawn in an urban creek
- Female carcasses showed >90% egg retention
- Symptoms: disorientation, swimming on side, gasping
- Hypothesized cause as road runoff

Scholz et al. 2011

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



# Where else is mortality occurring in coho?

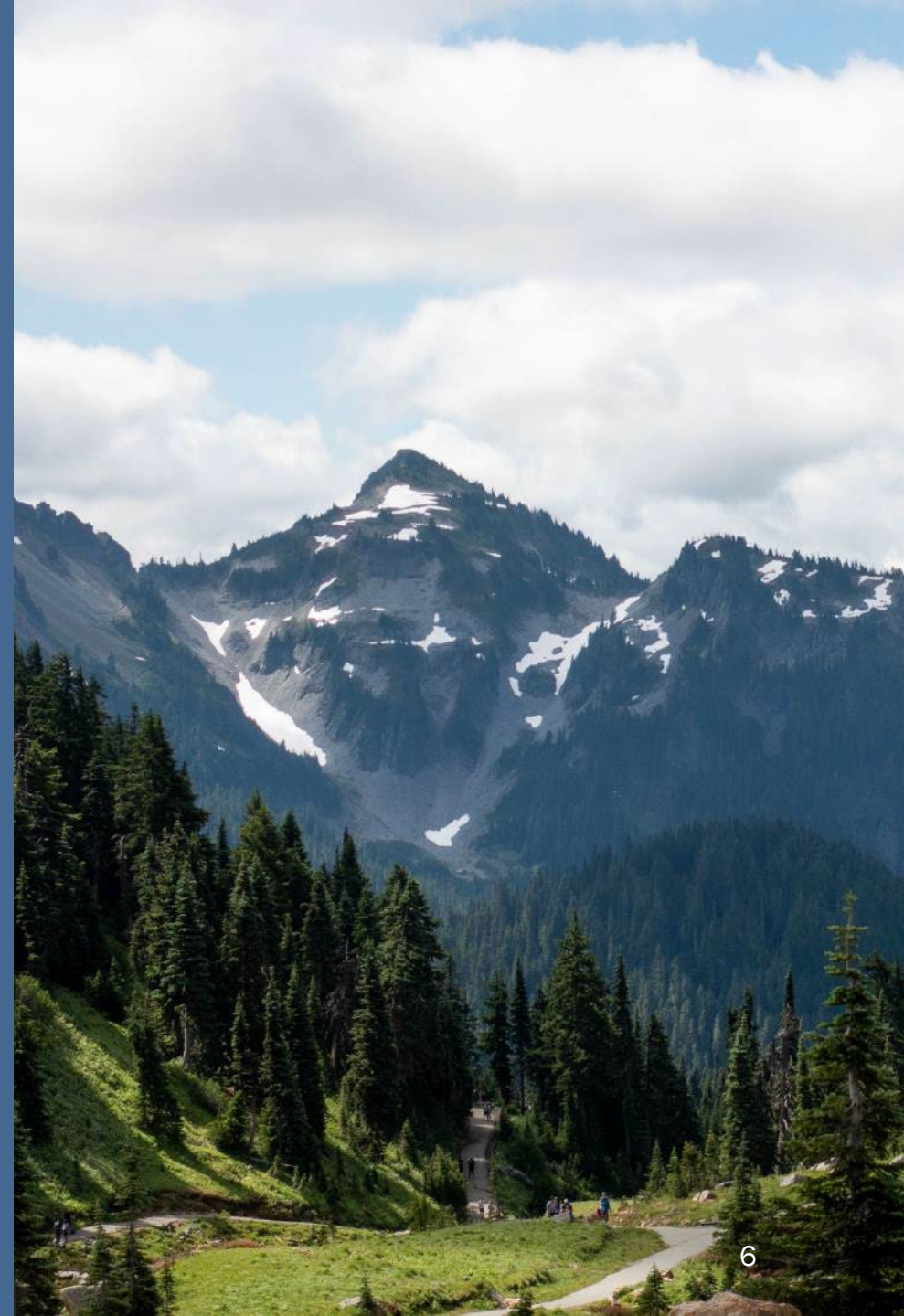
- **2019: Chow et al.**
  - Juveniles (fry) mortality confirmed
  - Symptomatic fish transferred to clean water did not recover
- **In Prep: McIntyre et al.**
  - Alevin (first free swimming stage) mortality confirmed



Photo: Coho salmon in the alevin life stage. McIntyre et al. In Prep



# Identification of the Cause



# URMS Timeline continued...

## Contaminant research using HRMS started in 2018

2018

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

Katherine T. Peter,<sup>\*,†,‡,Ⓞ</sup> Zhenyu Tian,<sup>†,‡,Ⓞ</sup> Christopher Wu,<sup>‡</sup> Peter Lin,<sup>‡</sup> Sarah White,<sup>‡</sup> Bowen Du,<sup>||</sup> Jenifer K. McIntyre,<sup>⊥</sup> Nathaniel L. Scholz,<sup>#</sup> and Edward P. Kolodziej<sup>†,‡,§</sup>

Analytical advancements allow researchers to detect cocktail of chemicals in stormwater.

2020

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

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

The chemical culprit is discovered among 2,000 chemicals!

6PPD-quinone

# 6PPD in Tires

- Chemical anti-degradant that prevents tire rubber from cracking when exposed to ozone
- Tire industry started using in 1960s
- Improves performance and longevity
- Makes up 1-3% of tire composition
- Assumed to be used in all tires

With 6PPD



Without 6PPD



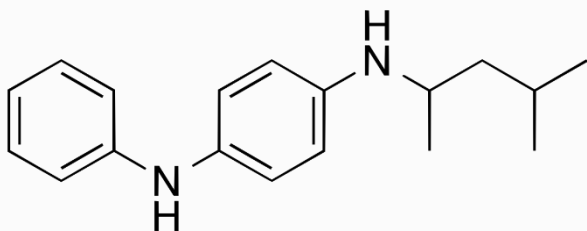
Photo credit: U.S. Tires Manufacturer's Association



# 6PPD-quinone

## 6PPD

*N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine



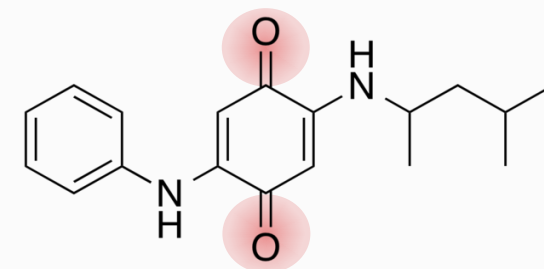
ozone in the  
environment



## 6PPD-quinone

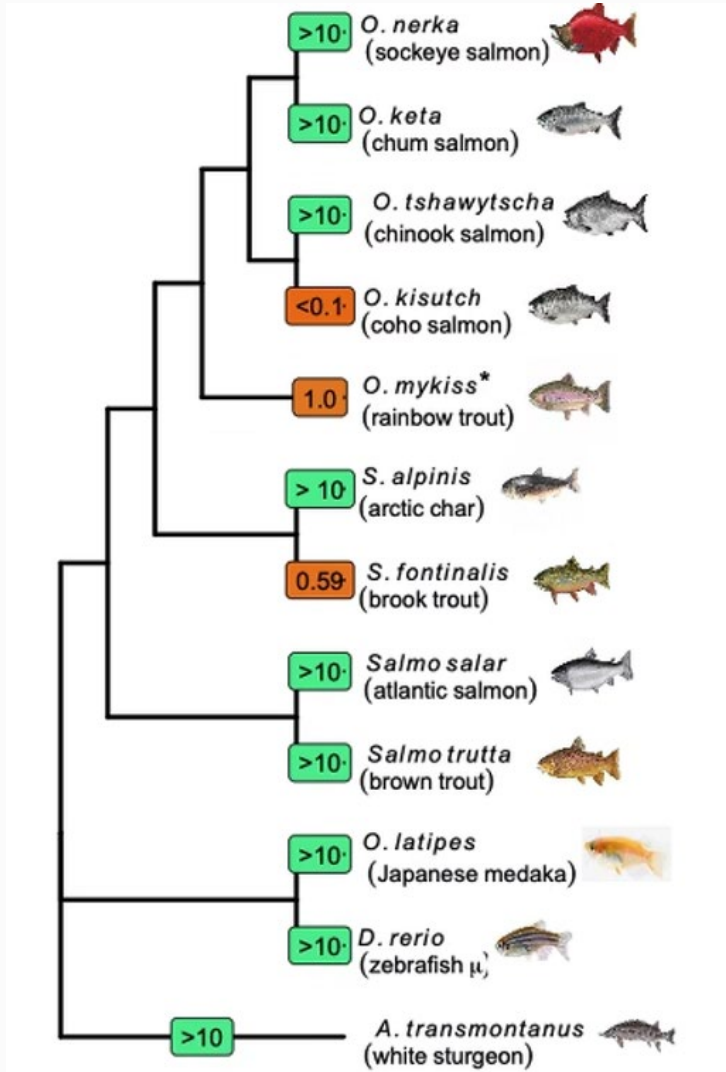
*N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine-*quinone*

Discovered in 2020\*



tire wear  
particles

# Toxicity to Fish

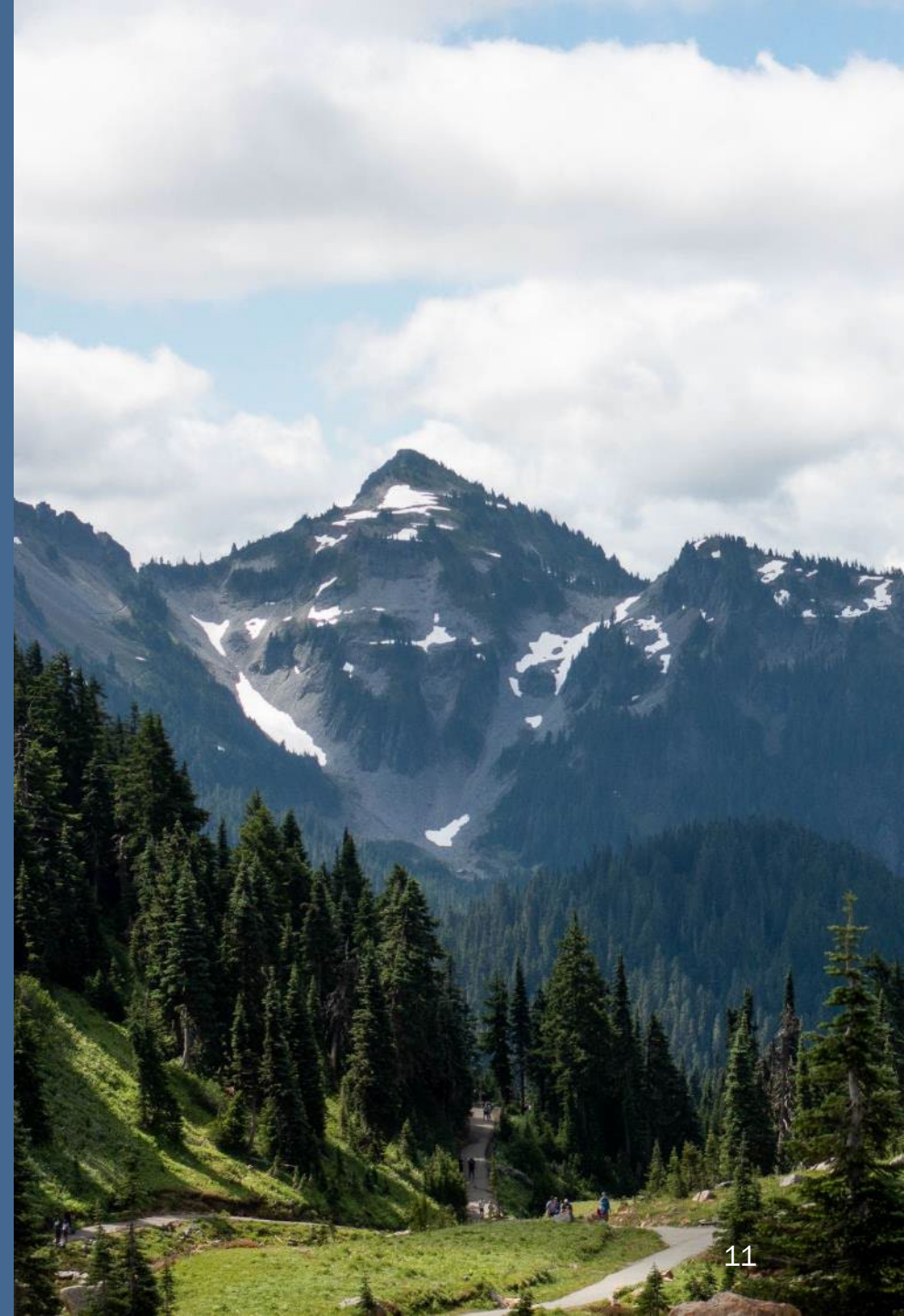


Common Name	LC-50 ( $\mu\text{g/L}$ )
Coho salmon	< 0.10
White-spotted char	0.51
Steelhead/rainbow trout	0.60
Brook trout	0.59 – 1.00
Chinook salmon	> 10.00
Sockeye and chum salmon	> 10.00
Zebrafish	> 10.00
Arctic char and white sturgeon	No mortality even at 14.20 $\mu\text{g/L}$

Photo: John Hansen, US Geological Survey  
 Data: McIntyre et al., 2022 Memo for 6PPD Proviso,  
 Brinkmann et al., 2022



# Finding a Solution



# Ecology's 3-Part Approach



AND



AND



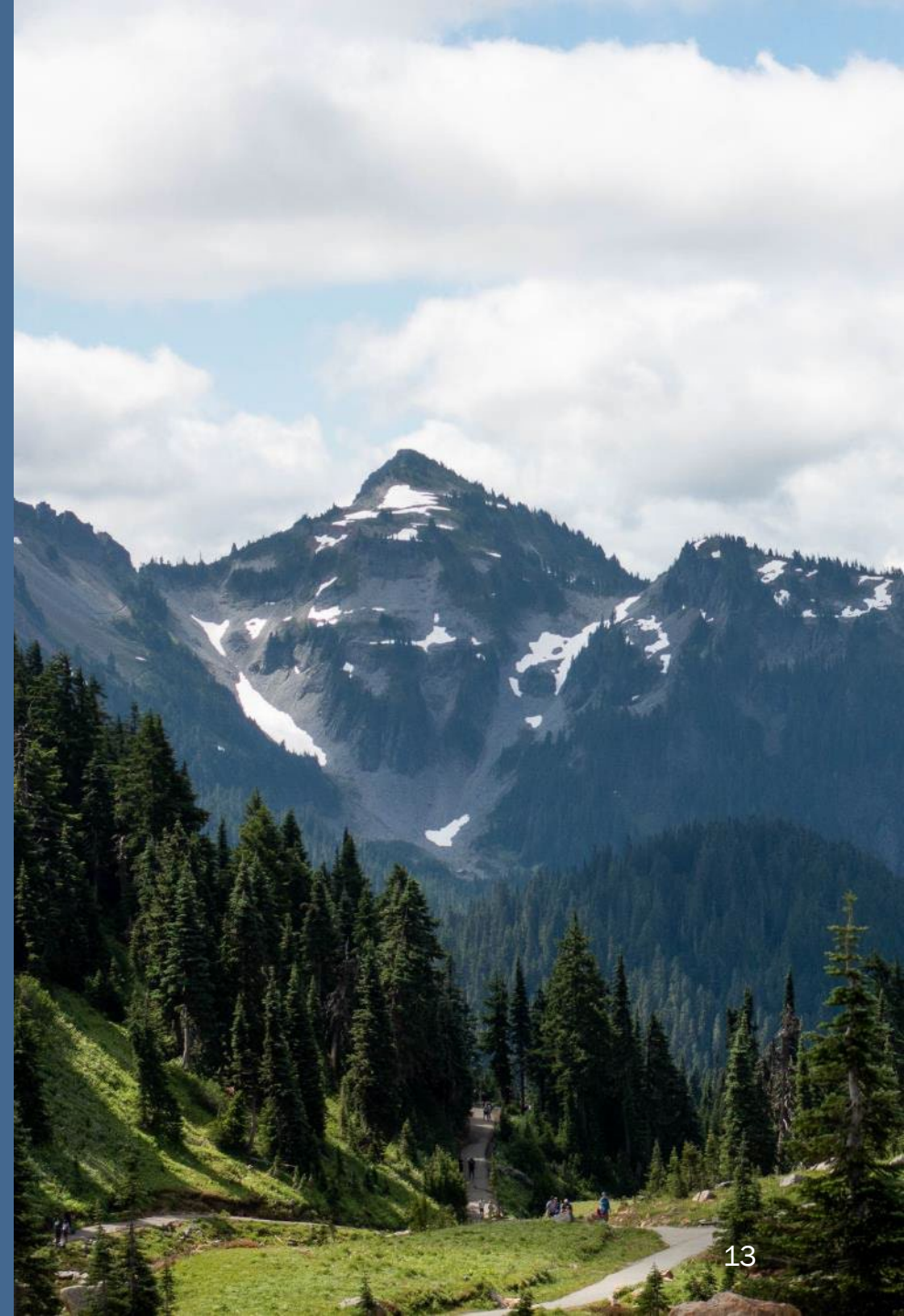
Reducing sources of  
6PPD & evaluating  
alternatives

Assessing  
6PPD-quinone  
in the environment

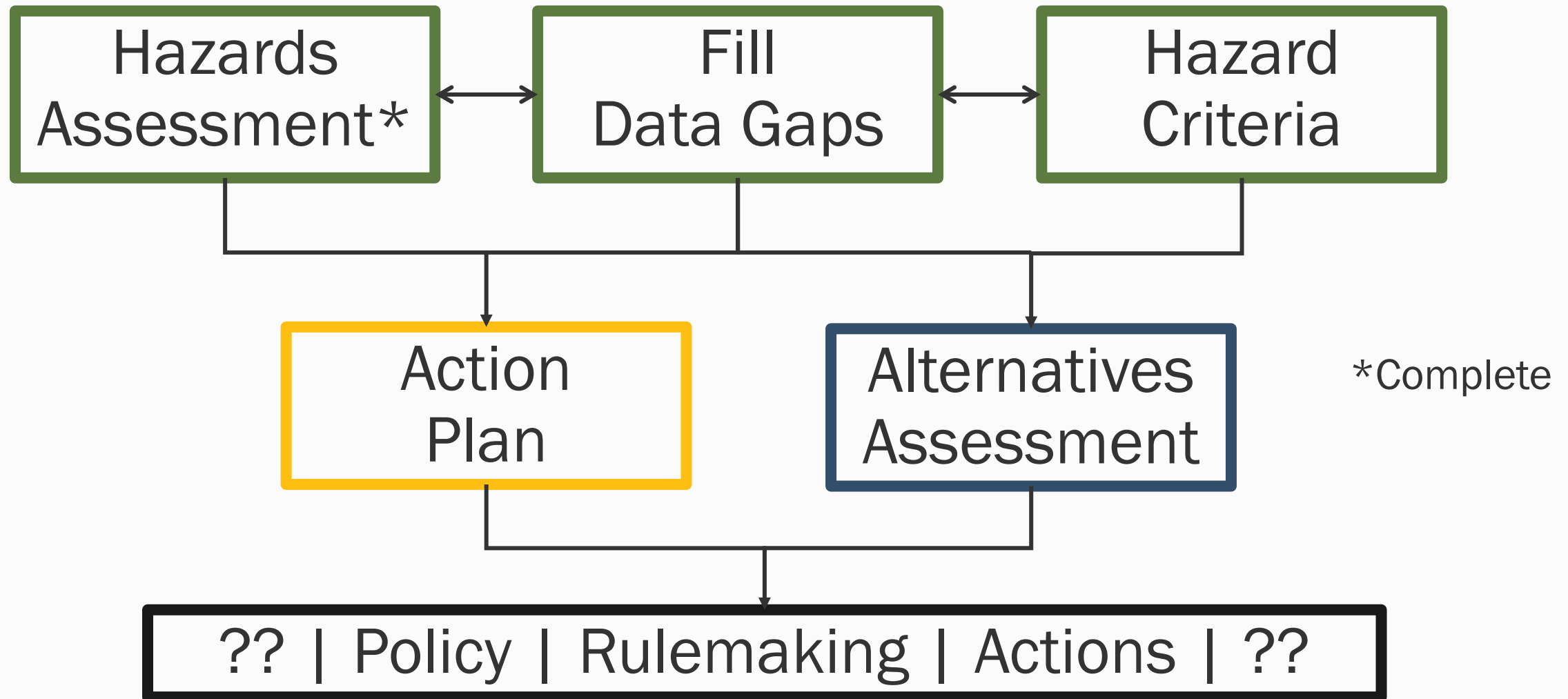
Stormwater Best  
Management  
Practices (BMPs)



# Source Reduction

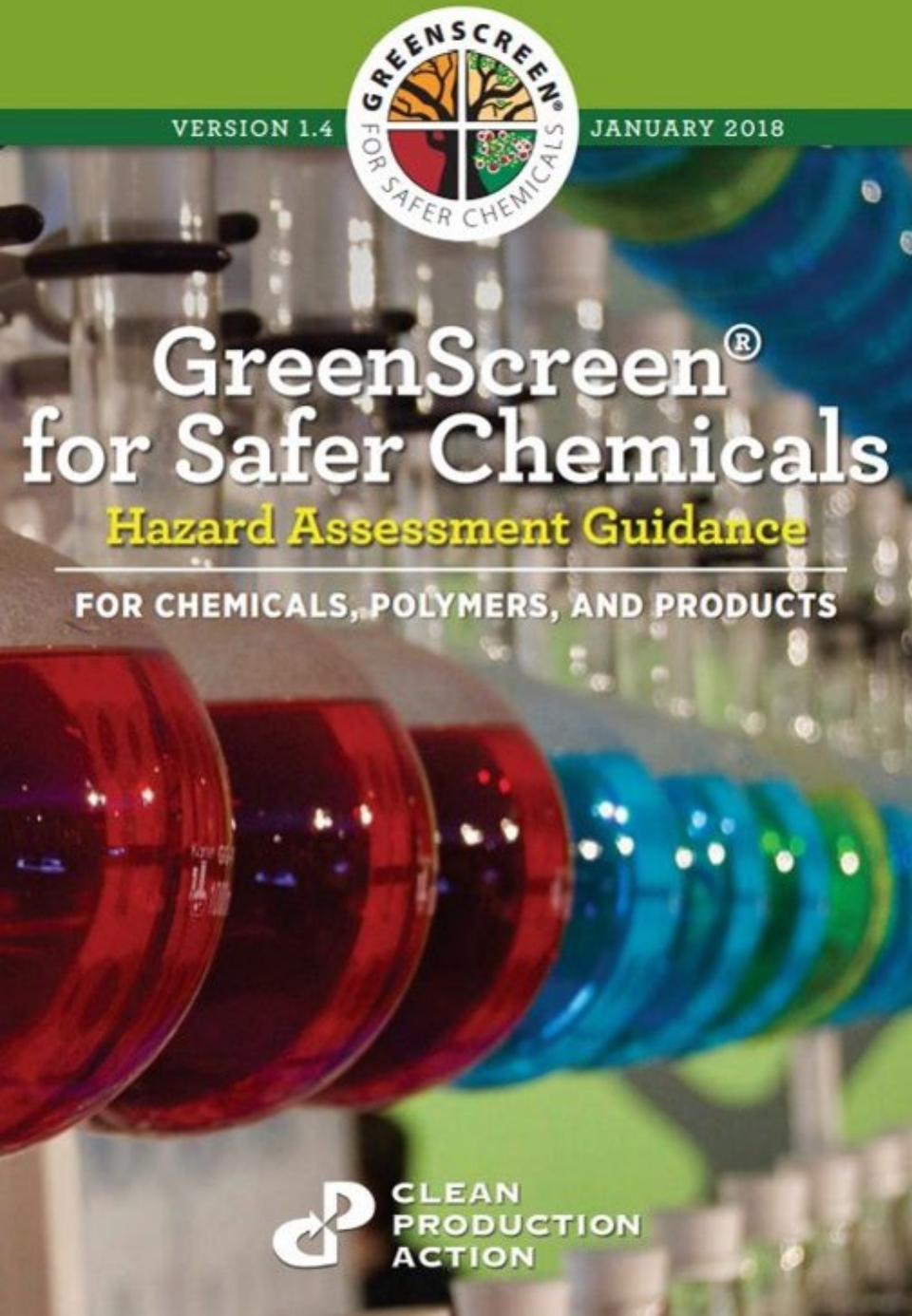


# Source Reduction Road Map



# Hazards Assessment

- [Completed in November 2021](#)
- Chemicals assessed were selected based on whether they had promise as an anti-degradant in tires, according to:
  - Reviews of journal articles and government reports
  - Communications with manufacturers and California Department of Toxic Substances Control



# Hazards Assessment - Results

Chemical	GreenScreen® Benchmark Score
6PPD (#793-24-8)	BM-1
77PD (#3081-14-9)	BM-2
CCPD (#4175-38-6)	BM-1
IPPD (#101-72-4)	BM-1
7PPD (#3081-01-4)	BM-1
TMQ (#26780-96-1)	BM-2
6QDI (#52870-46-9)	BM-1
NBC (#13927-77-0)	BM-1
Ethoxyquin (#91-53-2)	BM-2
Dilauryl thiodipropionate (#123-28-4)	BM-3 with data gap

BM-1: Avoid - Chemical of High Concern

BM-2: Use - but search for safer substitutes

BM-3: Use - but still opportunity for improvement



# Current/Ongoing Research

- Learn more about 6PPD and 6PPD-q to develop standard for comparison to other chemicals
  - Toxicity of 6PPD on coho salmon to other tire chemicals
  - Environmental condition (like water pH) impacts to toxicity
  - Toxicity of 6PPD on rainbow trout and potentially other aquatic species
  - Analyze toxicity of selected alternative chemicals
- Measure the presence of 6PPD, 6PPD-q, and other chemicals present in passenger car, light truck, and commercial truck tires

# Hazard Criteria

- Specific data requirements and standards to assess chemical safety
- Ecology is currently developing the criteria for assessing 6PPD alternatives
- Alternative will require data on carcinogenicity, reproductive toxicity, mutagenicity, acute/chronic toxicity, and other parameters



# Alternatives Assessment

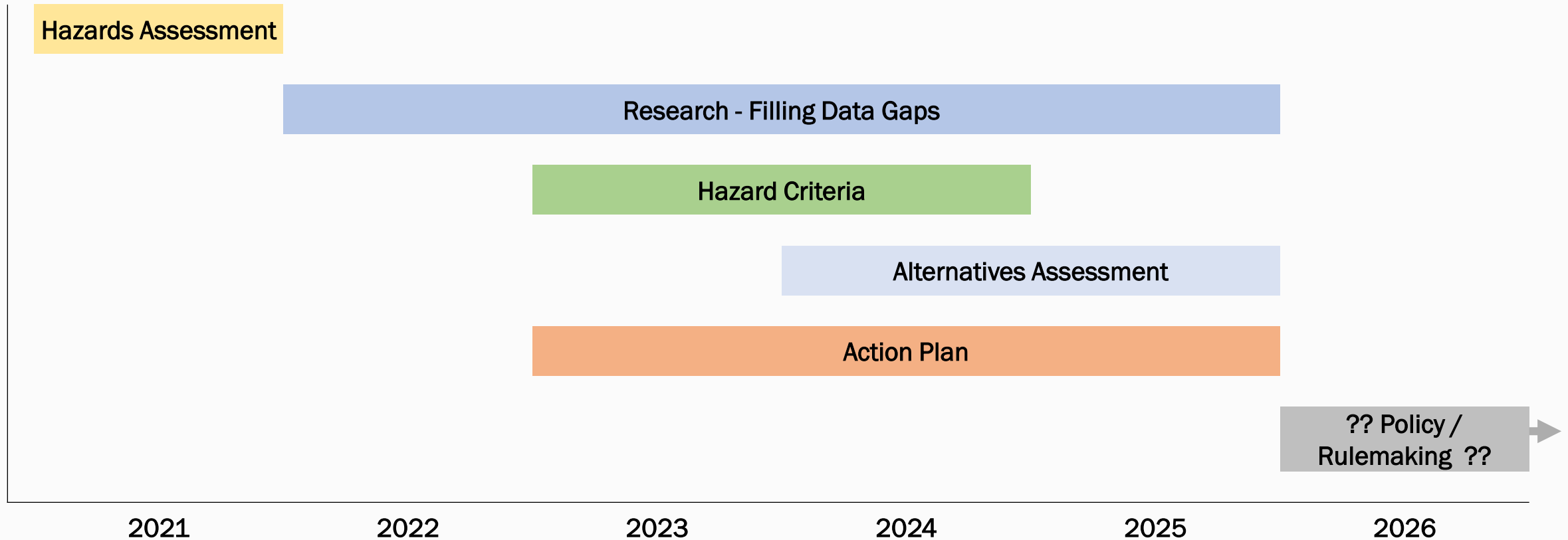
- Will begin once data gaps are filled in and hazard criteria is finalized
- Identify, compare, and select safer alternatives to 6PPD
  - Review requirements for toxicity, performance, availability, and cost
  - “If the department finds safer alternatives exist, include recommended regulatory, policy, or legislative actions to advance safer alternatives.”

# 6PPD Action Plan

- Problem review and EJ review
- Follow the public process and economic analysis of WAC 173-333
- Consider tire performance and safety
- Provide actionable recommendations, including regulatory, policy, or legislative
- **Advisory Committee – contact [tanya.williams@ecy.wa.gov](mailto:tanya.williams@ecy.wa.gov)**



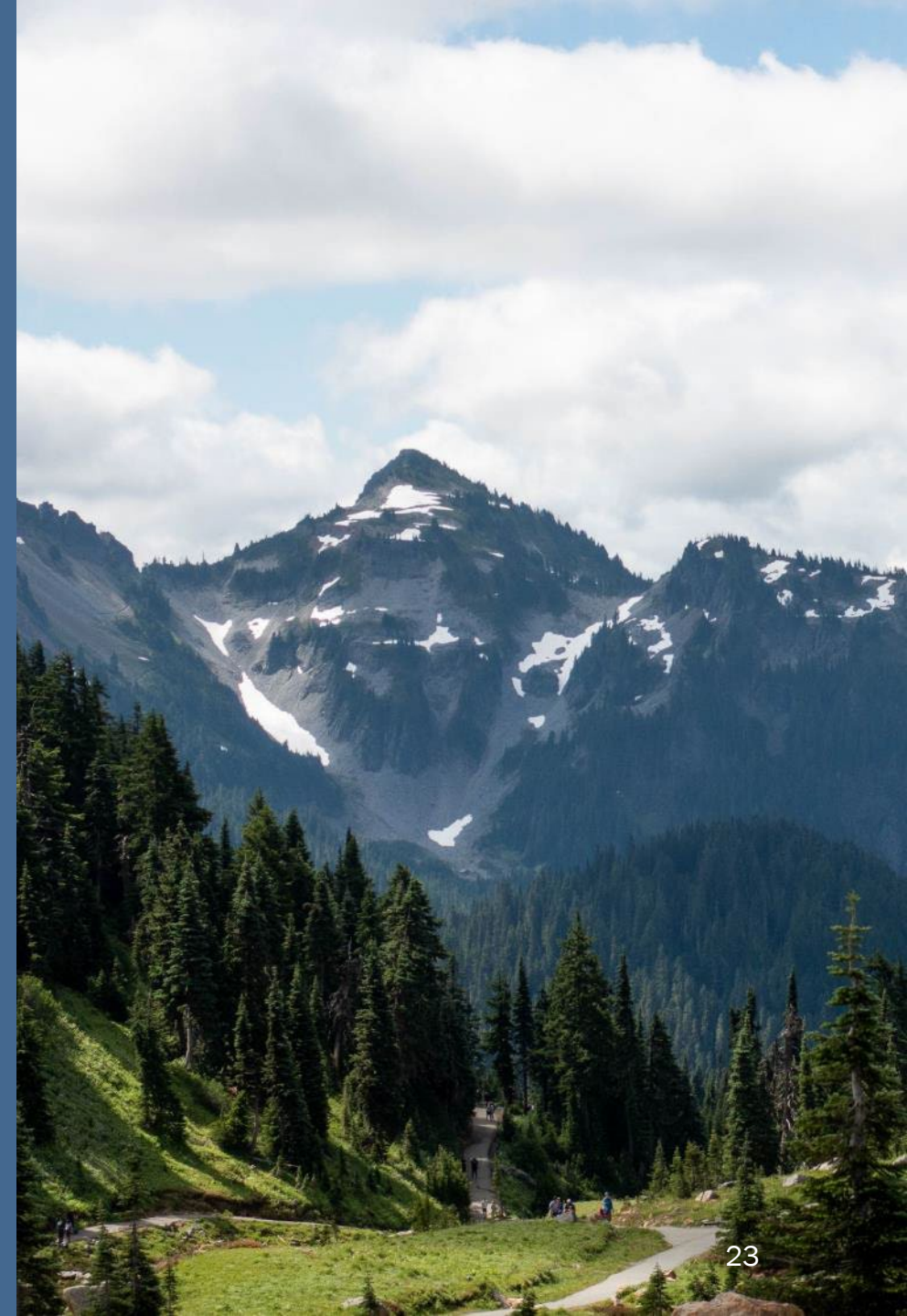
# Estimated Timeline



Schedule dependent on legislative funding and progress/outcome of research.



# Analytical Methods, Mapping, & Monitoring



# Mapping & Monitoring

## 1. GIS

Map existing data layers and coordinate with technical advisors to highlight potential sources and vulnerable areas.

## 2. Contaminant reconnaissance sampling

Conduct initial contaminant screening studies. These short term, exploratory studies help inform where to focus initial mitigation efforts.

## 3. Baseline Data

Baseline data collection

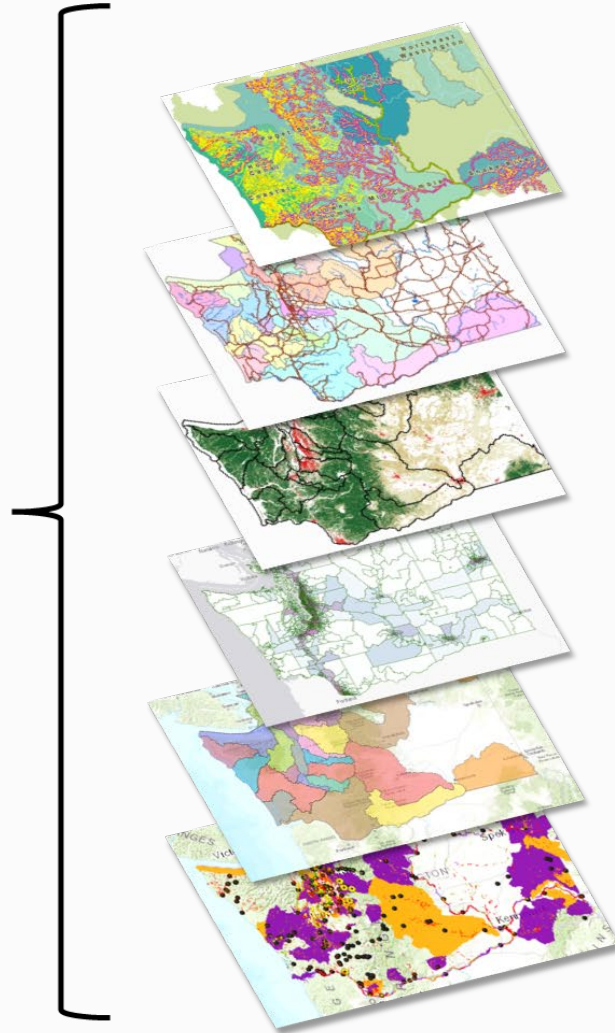
## 4. Source Identification

Identify hotspots of contamination

## 5. Watershed Scale Effectiveness Monitoring

Monitoring changes of 6PPD-quinone in watersheds.

**GOAL:  
Overlay  
GIS layers  
to support  
coordination  
and planning**



**Salmon and Habitat Distribution**

**Transportation – Traffic Counts, Bridges**

**Land Cover and Land use - % Impervious Surface**

**Health Disparities**

**Salmon Recovery Community**

**Water Quality Assessments**



# Assessing Vulnerable Areas

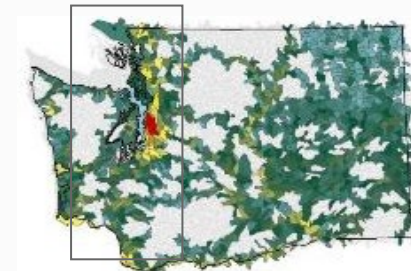
## Factors thought to influence concentrations of 6PPD-q in streams:

- Level of traffic (source)
- Impervious surfaces (land cover)
- Precipitation (transport)
- How 6PPD-q binds to other particles (TSS transport)
- Dilution factor (big river vs. small river)
- Flow rates, conveyance, and control

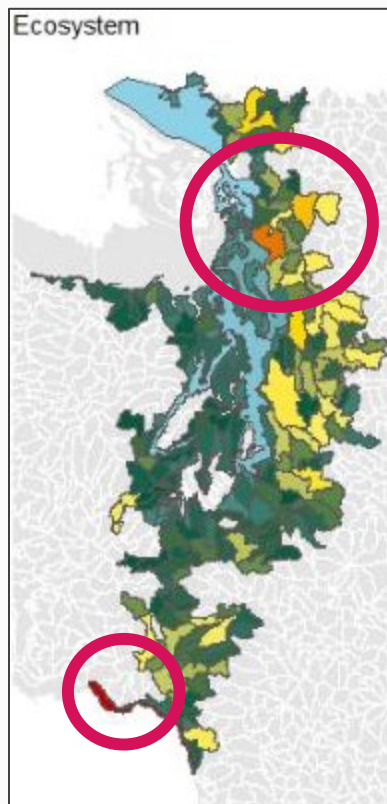
Photo by NOAA Fisheries



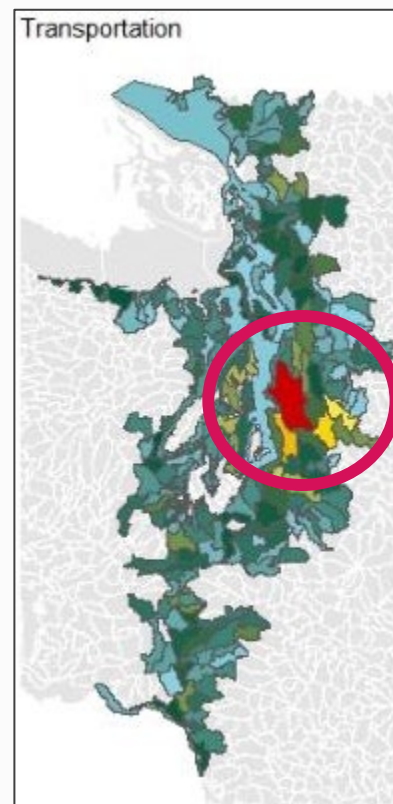
# Indicators of Vulnerability & Exposure



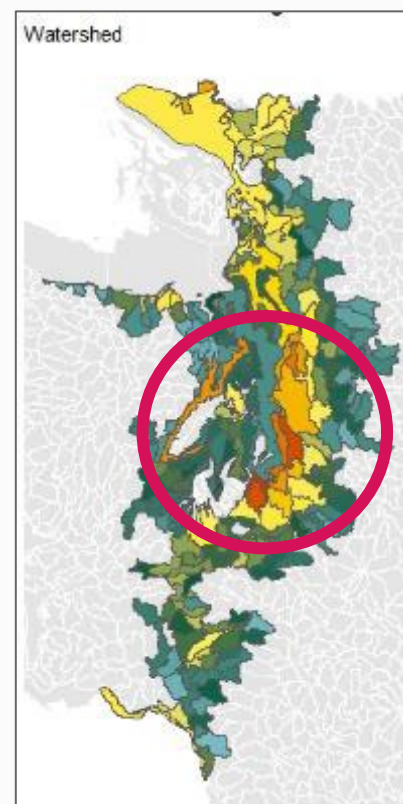
Vulnerable Areas



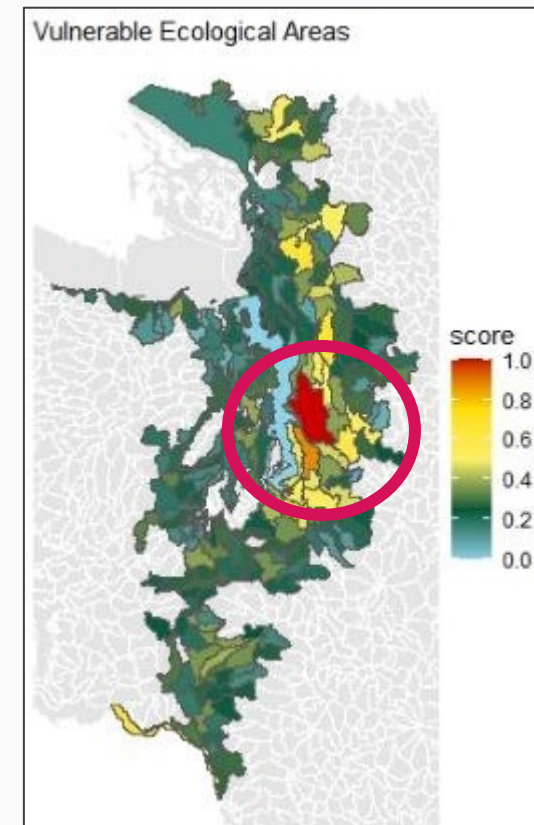
**Ecosystem**  
*e.g. Salmon*



**Transportation**  
*e.g. Cars*

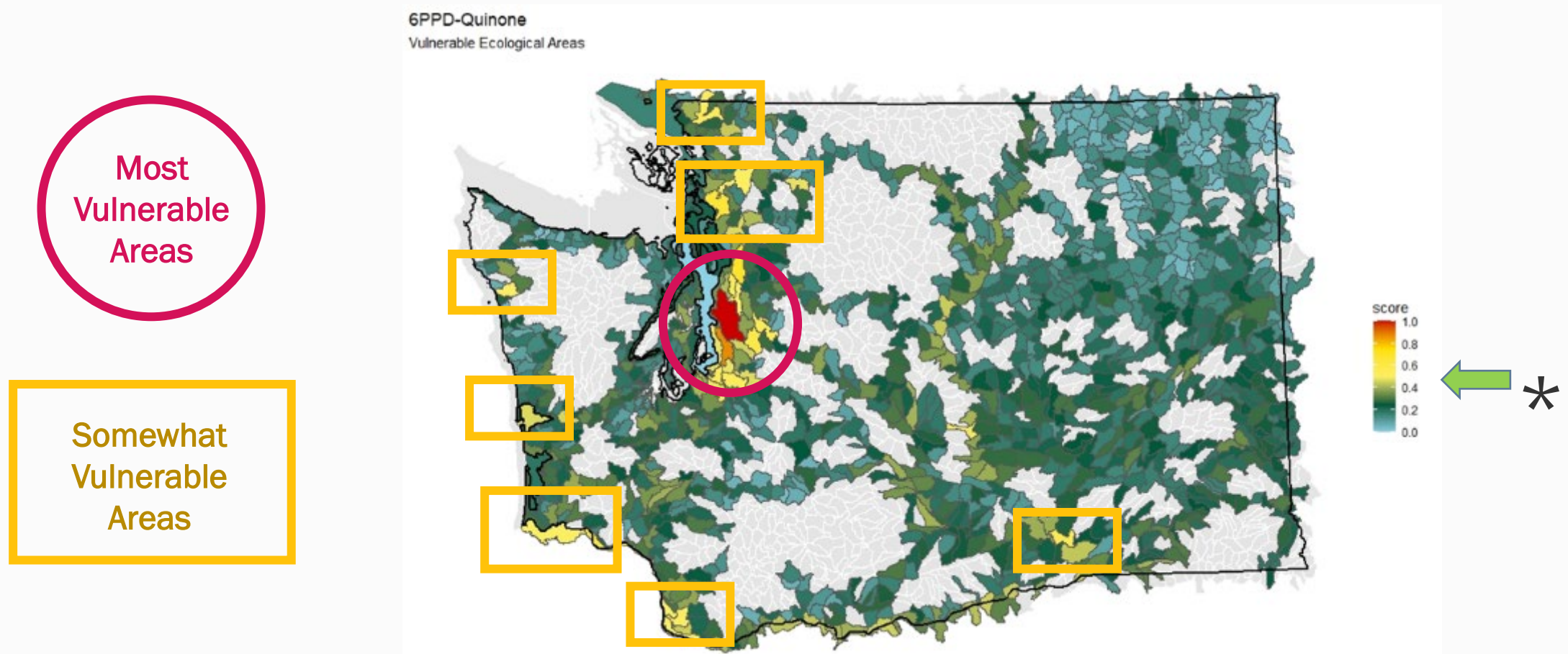


**Watershed**  
*e.g. Land Use*



**TOTAL VULNERABILITY**

# Scope and Scale of the Tire Contaminant Problem



\*Scoring strengthens understanding of problem and helps direct further studies

# Analytical & Sampling Methods

- Developing a laboratory method for measuring the concentration of 6PPD-q in water
- 6PPD-q Chemical Quantitation Accreditation
  - As of April 20, 2023, no lab accredited
- Method for sediment, tissue
- Test alternative field sampling methods
- Add related chemicals and additional tire chemicals



# Monitoring Vulnerable Areas

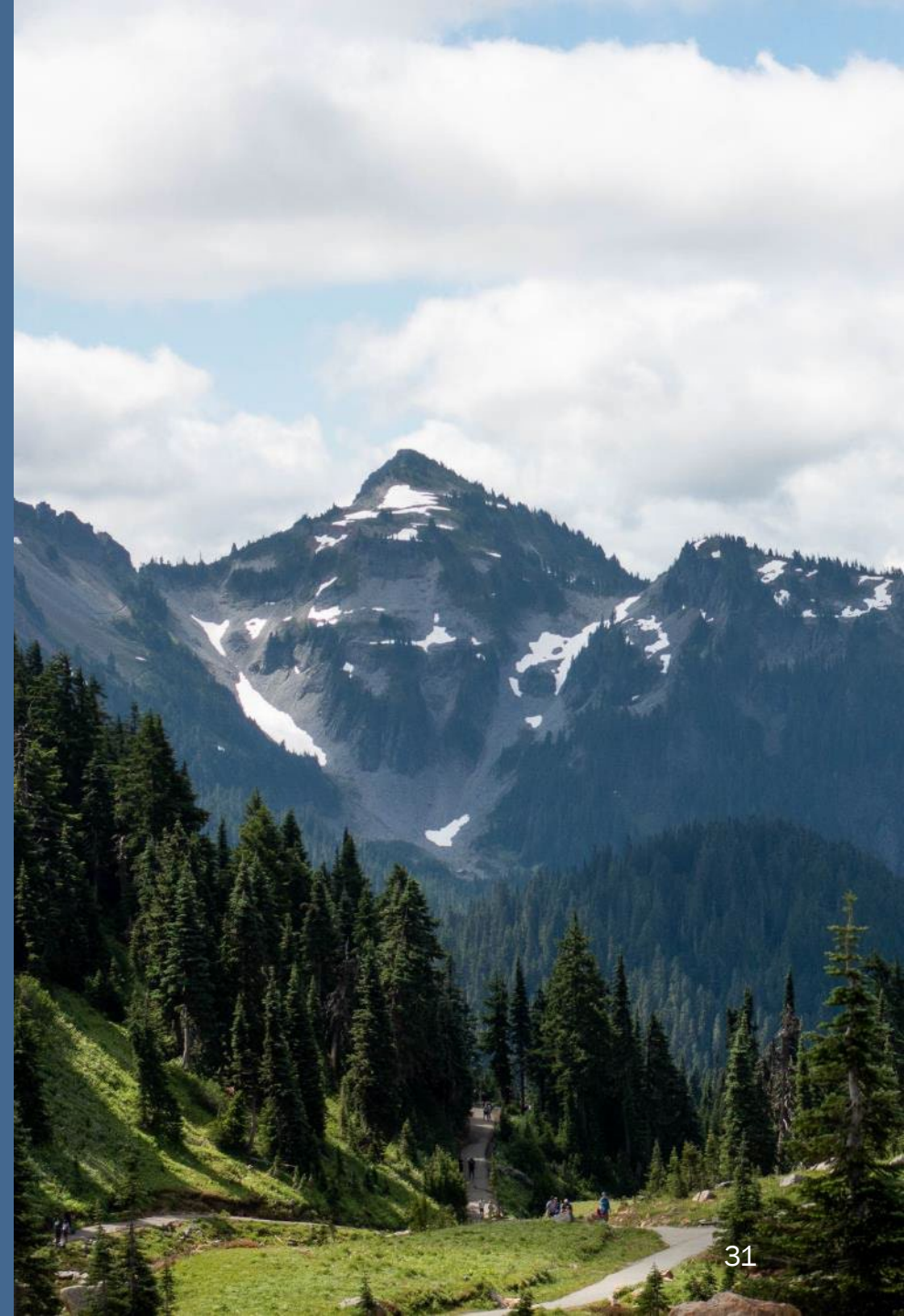
- Funding research to fill in the many data gaps
- Conducting field studies to further develop methods for evaluating 6PPD-q exposure in salmon-bearing streams
  - Stream reconnaissance
  - Device study to compare active and passive sampling methods

Photo by Rhea Smith, Ecology





# Stormwater Best Management Practices (BMPs)



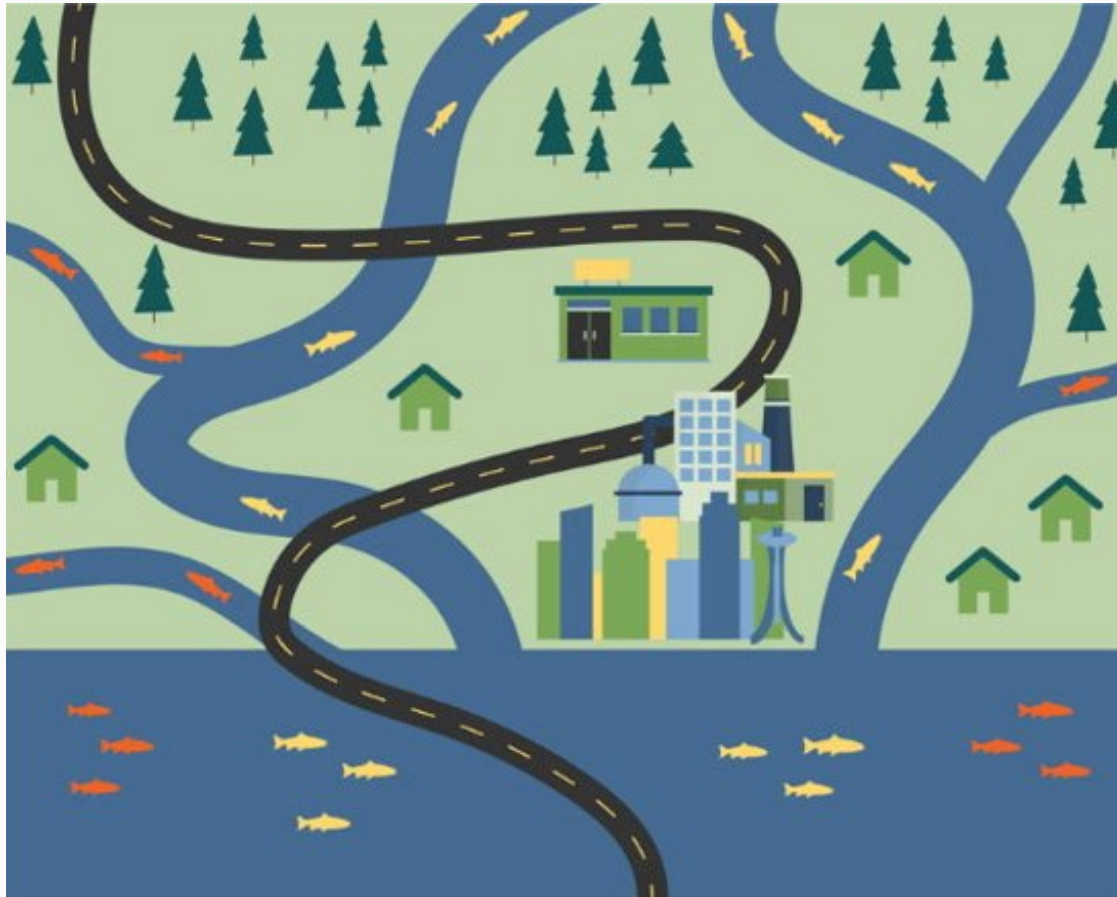


Photo: Mugdha Flores and Rhea Smith,  
WA Department of Ecology

# Stormwater BMPs & Water Quality Strategies

- Increasing grant funding capacity
- Updating guidance for regulations
- BMPs research: \$1.5 million/year for 4 years from the legislature
  - Anticipated to start July 2023

## Best Management Practices (BMPs)

- BMPs help **prevent** or **reduce** pollutants in Washington's waterways - 2019 Stormwater Management Manual for Western WA
- We've researched how effective current BMPs are at addressing 6PPD/q and [published a report](#) on:
  - Source Control BMPs
  - Flow Control BMPs
  - Runoff Treatment BMPs



# Source Control BMPs

Prevent stormwater contaminants from entering municipal separate storm sewer systems (MS4s)

Examples: Roofing to prevent mixing or street sweeping to capture trash and sediment



# Flow Control BMPs

Slow runoff and reduces runoff volume through on-site management of water

Examples: Detention ponds, vaults, infiltration basins, and bioretention



# Runoff Treatment BMPs

Reduce concentrations of targeted pollutants through means of physical filtration and chemical sorption

Examples: Trash racks, sorbent media, bioretention soil mix



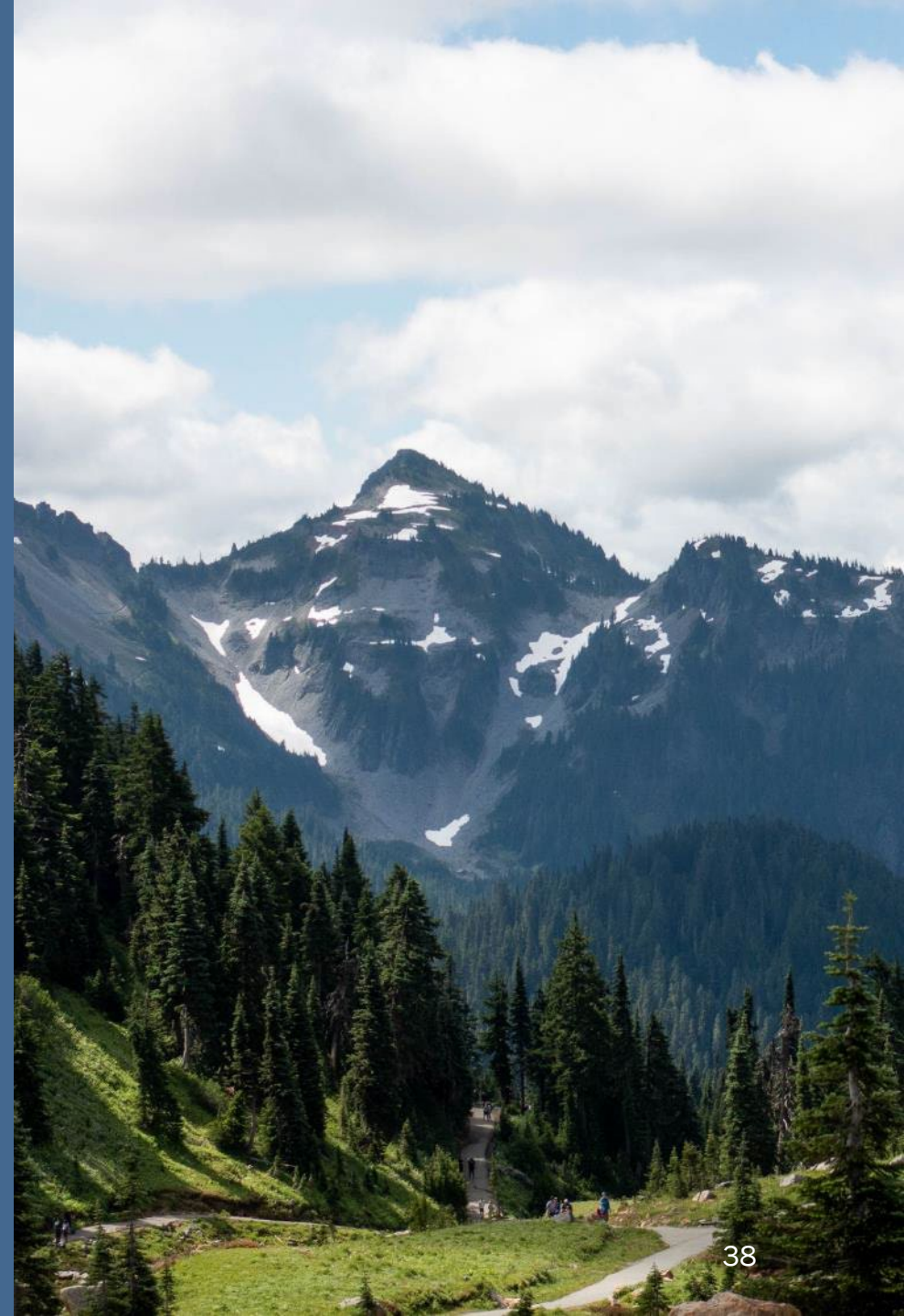
# Current 6PPD/q BMPs Projects

- WSU-Puyallup – longevity of bioretention media
- Redmond – street sweeping effectiveness
- Osborn & Evergreen StormH2O Consulting – Particle size study
- UW-Tacoma – soils and sorbents effectiveness
- King County – High Performance Bioretention Soil Mix (HPBSM) testing
- King County Environmental Lab – stormwater highway & residential characterization study
- Herrera – testing influent and effluent with TAPE devices for removal of 6PPD-q





# Engagement Opportunities



# ITRC Tire Anti-Degradants (6PPD) Team



Click the picture to learn more.

- Federal, State, and Tribal Governments, industry, academia, nonprofit, and consultants
- 2 years – initial work scope
- Synthesizing knowledge to create training and educational materials
- Identify data gaps

# Upcoming 6PPD Public Events

- **6PPD Webinar**: June 21, 1-3pm
  - Contributing agencies: Ecology, WSDOT, PSP, DOH, WDFW
  - Materials posted online for viewing one month before the live webinar
  - Live webinar: Panelists from agencies, Q&A
- **Hazard Criteria**
  - Public Review and Comment

# Questions & Discussion



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To request an ADA accommodation, contact Ecology by phone at 360-407-6831 or email at [ecyadacoordinator@ecy.wa.gov](mailto:ecyadacoordinator@ecy.wa.gov). For Washington Relay Service or TTY call 711 or 877-833-6341. Visit [Ecology's website](#) for more information.

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