DEPARTMENT OF ECOLOGY
State of Washington

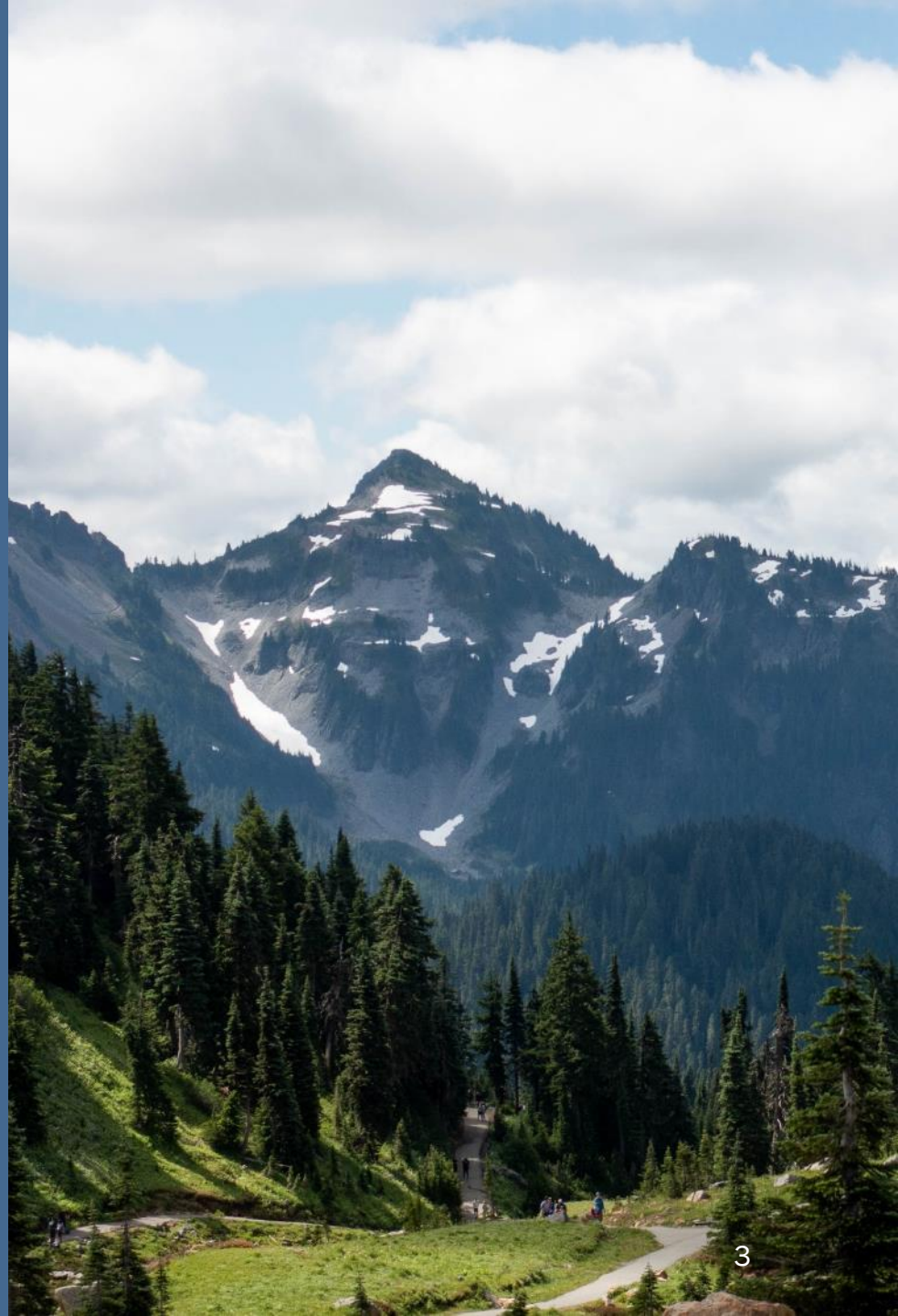
6PPD and 6PPD-quinone: Finding a Solution

Presented to: Alaska Department of Transportation
March 1, 2023

Agenda

- Identification of the Problem
- Identification of the Cause
- Finding a Solution
  - Source Reduction
  - Mapping, Monitoring, and Analytical Methods
  - Stormwater Best Management Practices
- Questions and Discussion

Identification of the Problem



Urban Runoff Mortality Syndrome Timeline

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URMS was first documented in the 1980's

1990

RECURRENT COHO SALMON MORTALITY AT MARITIME HERITAGE FISH HATCHERY, BELLINGHAM: A SYNTHESIS OF DATA COLLECTED FROM 1987-1989

by
Will Kendra
Roger Willms

Something in stormwater is toxic to coho; Mortality occurs after rain events in urban-stream fed hatchery

2011

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

Nathaniel L. Scholz[1]*, Mark S. Myers[1], Sarah G. McCarthy[2], Jana S. Labenia[1], Jenifer K. McIntyre[1], Gina M. Ylitalo[1], Linda D. Rhodes[1], Cathy A. Laetz[1], Carla M. Stehr[1], Barbara L. French[1], Bill McMillan[3], Dean Wilson[2], Laura Reed[4], Katherine D. Lynch[4], Steve Damm[5], Jay W. Davis[5], Tracy K. Collier[1]

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, Washington, United States of America, 5 Washington Fish and Wildlife Office, U.S. Fish and Wildlife Service, Lacey, Washington, United States of America

URMS reoccurs throughout the Puget Sound streams

2016

Coho salmon spawner mortality in western US urban watersheds: bioinfiltration prevents lethal storm water impacts

Julann A. Spromberg[1], David H. Baldwin[2], Steven E. Damm[3], Jenifer K. McIntyre[4], Michael Huff[5], Catherine A. Sloan[2], Bernadita F. Anulacion[2], Jay W. Davis[3] and Nathaniel L. Scholz[2]*

Bioretention soil media prevents URMS

2018

Interspecies variation in the susceptibility of adult Pacific salmon to toxic urban stormwater runoff☆

Jenifer K. McIntyre [a, *], Jessica I. Lundin [b], James R. Cameron [c], Michelle I. Chow [d], Jay W. Davis [e], John P. Incardona [f], Nathaniel L. Scholz [f]

Variability in Pacific salmon toxicity to stormwater; Chum are found to be more tolerant

To be continued....

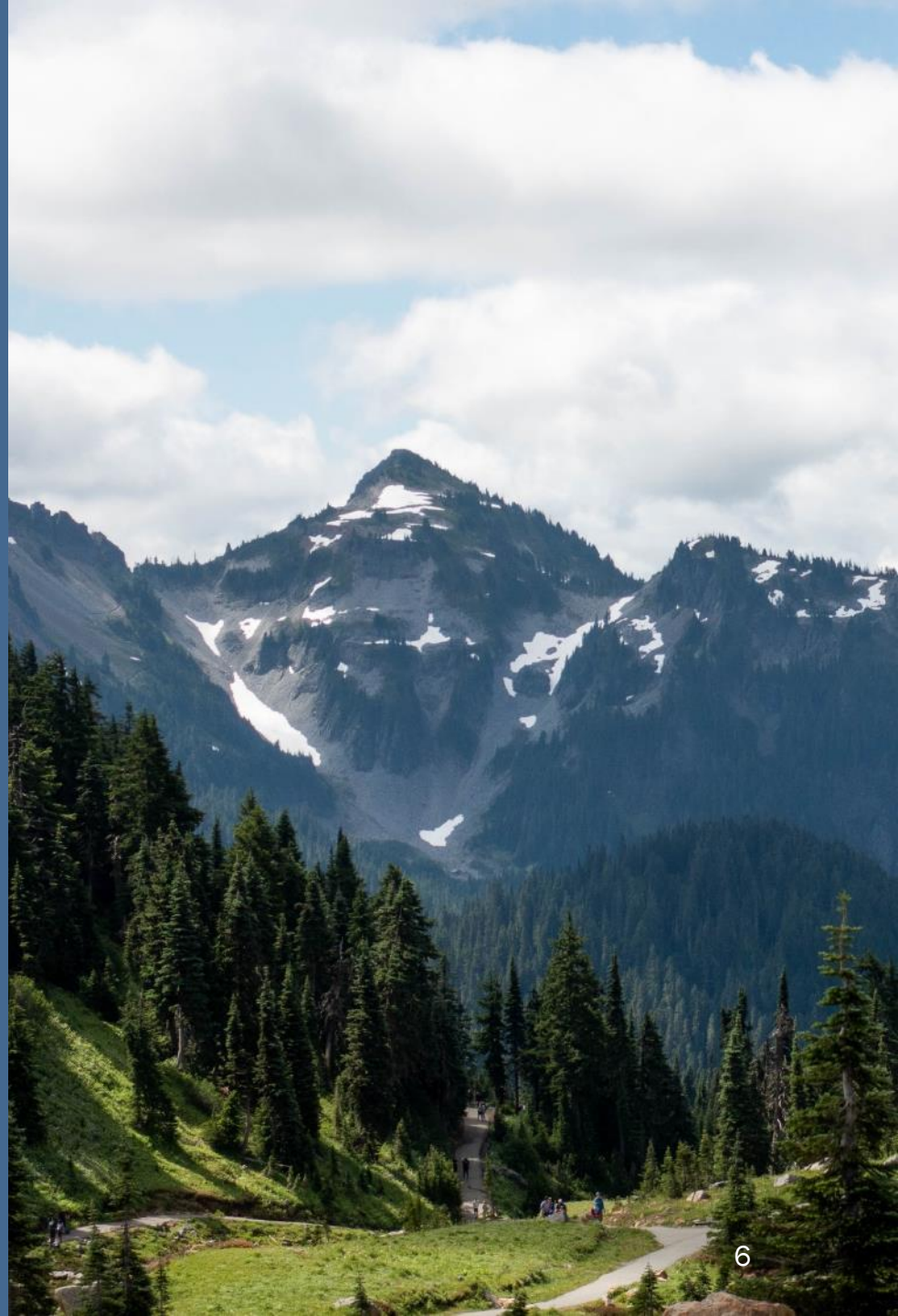
Urban Runoff Mortality Syndrome (URMS)

- Up to 100% of coho salmon died before they could spawn in an urban creek.[3]
- Female carcasses showed >90% egg retention.[3]
- Symptoms: disorientation, swimming on side, gasping, and pre-spawn mortality.[3]
- Effects all free-swimming life stages: alevin, juveniles, adult spawners.[1,2,4]
- Hypothesized cause as road runoff.[3]

Data:
[1]Chow et al. 2019
[2]McIntyre et al. In Prep
[3]Scholz et al. 2011
[4]Spromberg et al. 2016

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

Identification of the Cause



URMS Timeline continued…

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

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[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*]

The chemical culprit is discovered among 2,000 chemicals!

Discovery of the Cause

- Began research project in 2018
- UW - Center for Urban Waters
- Tire wear particle leachate
- High-Resolution Mass Spectrometry
- 2,216 toxicants
- Fractionation processes based on chemical characteristics
- Discovered 6PPD-quinone
- Published in Science in 2022

Peter et al. 2018
Tian et al. 2022

6PPD in Tires

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

With 6PPD Without 6PPD

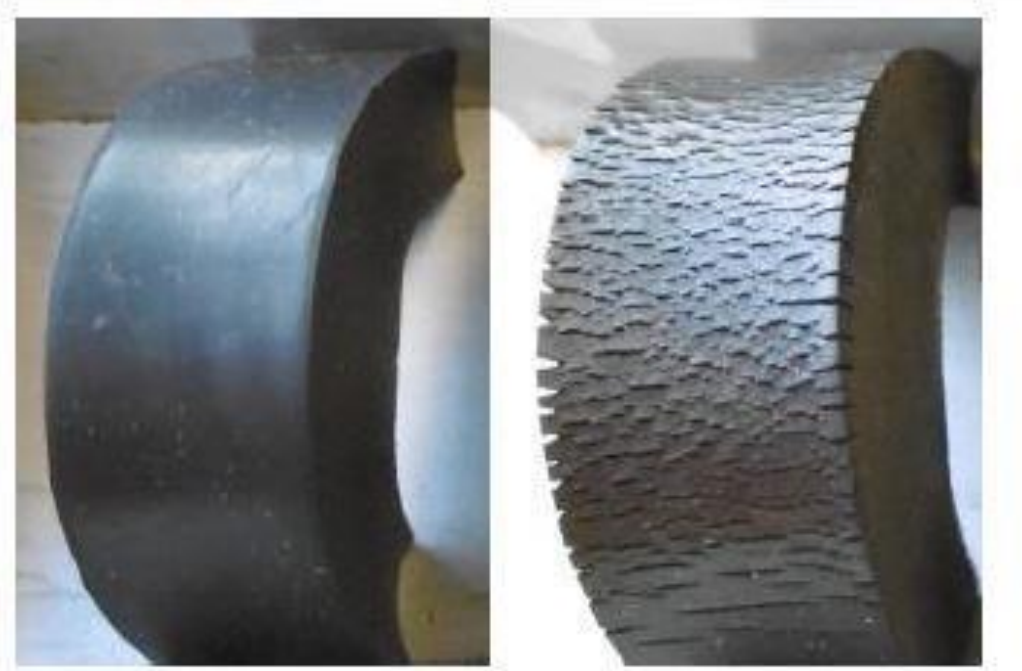

Photo credit: U.S. Tires Manufacturer's Association

6PPD-quinone

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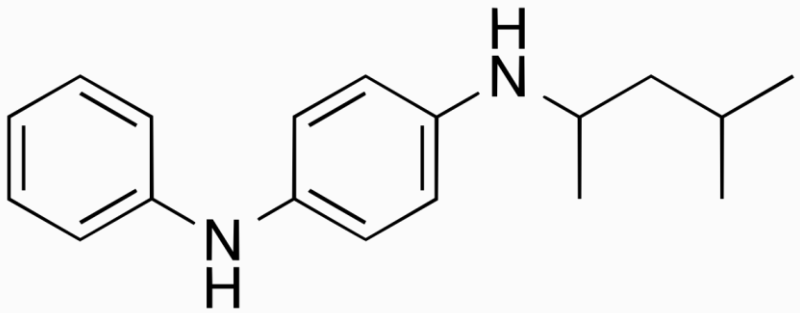
6PPD

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

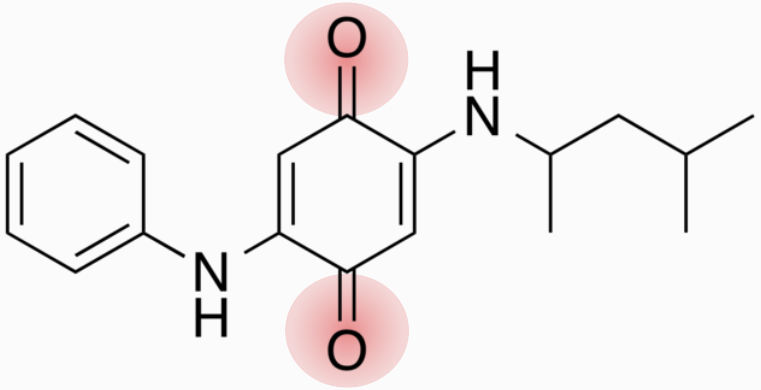


ozone in the environment

6PPD-quinone

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

Discovered in 2020*



Tian et al. 2020, 2022

Toxicity to Fish

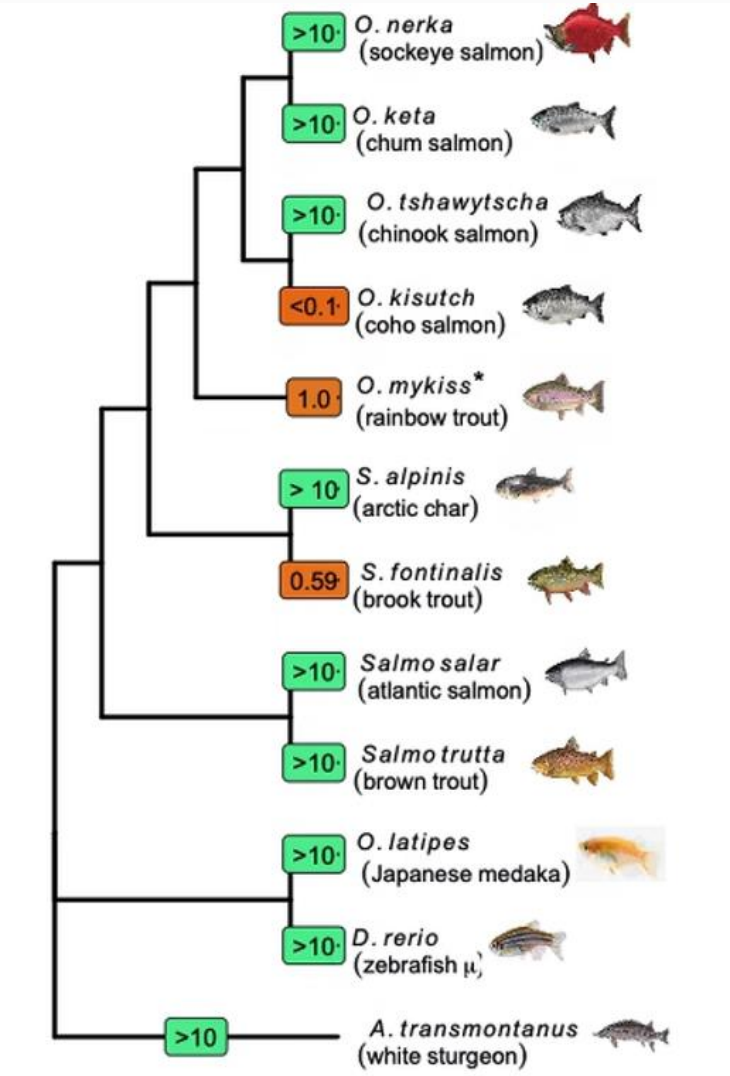
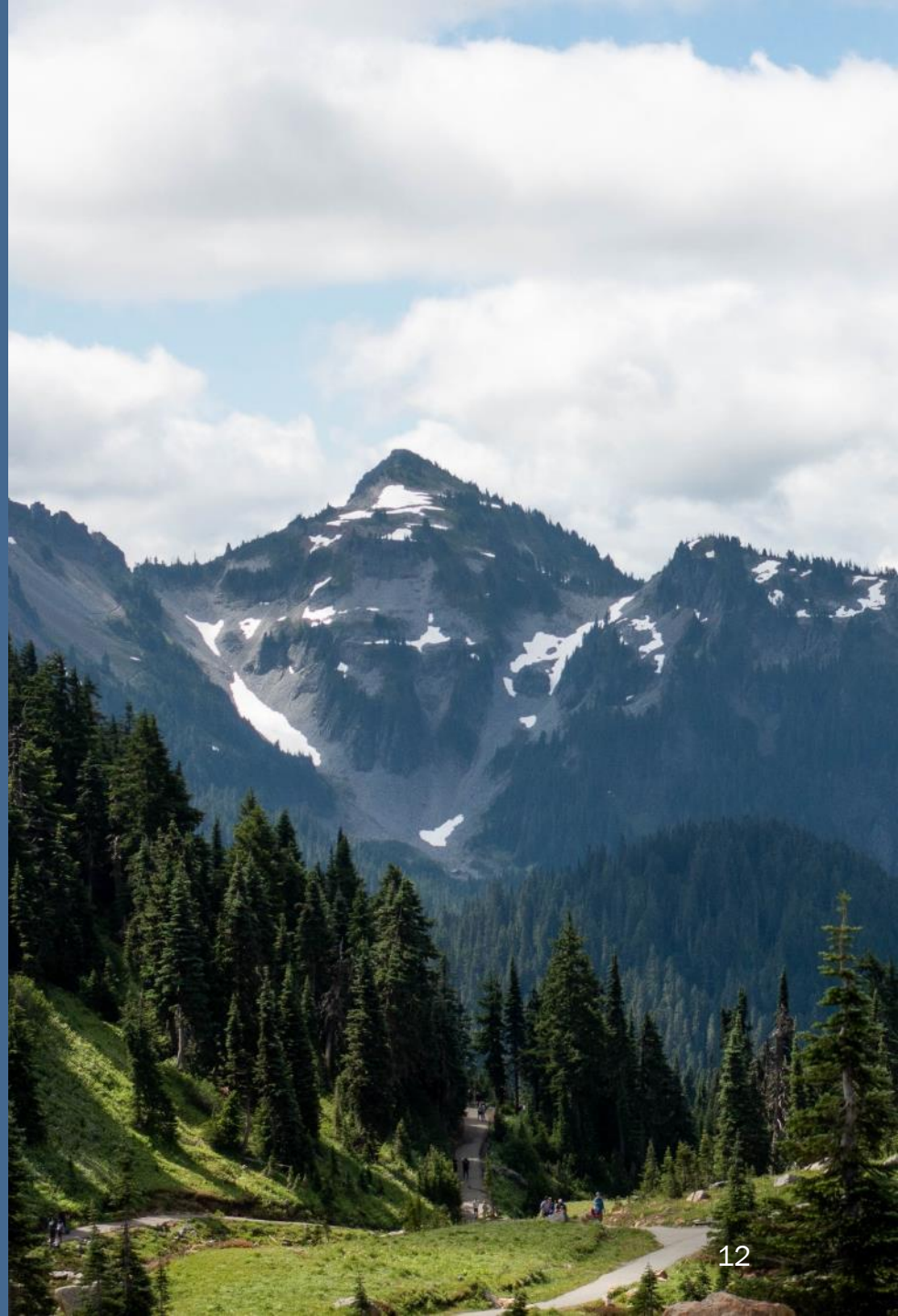


Photo: *John Hansen, US Geological Survey*
Data: *McIntyre et al., 2022 Memo for 6PPD Proviso, Brinkmann et al., 2022*

Common Name	LC-50 (µg/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 µg/L

Finding a Solution



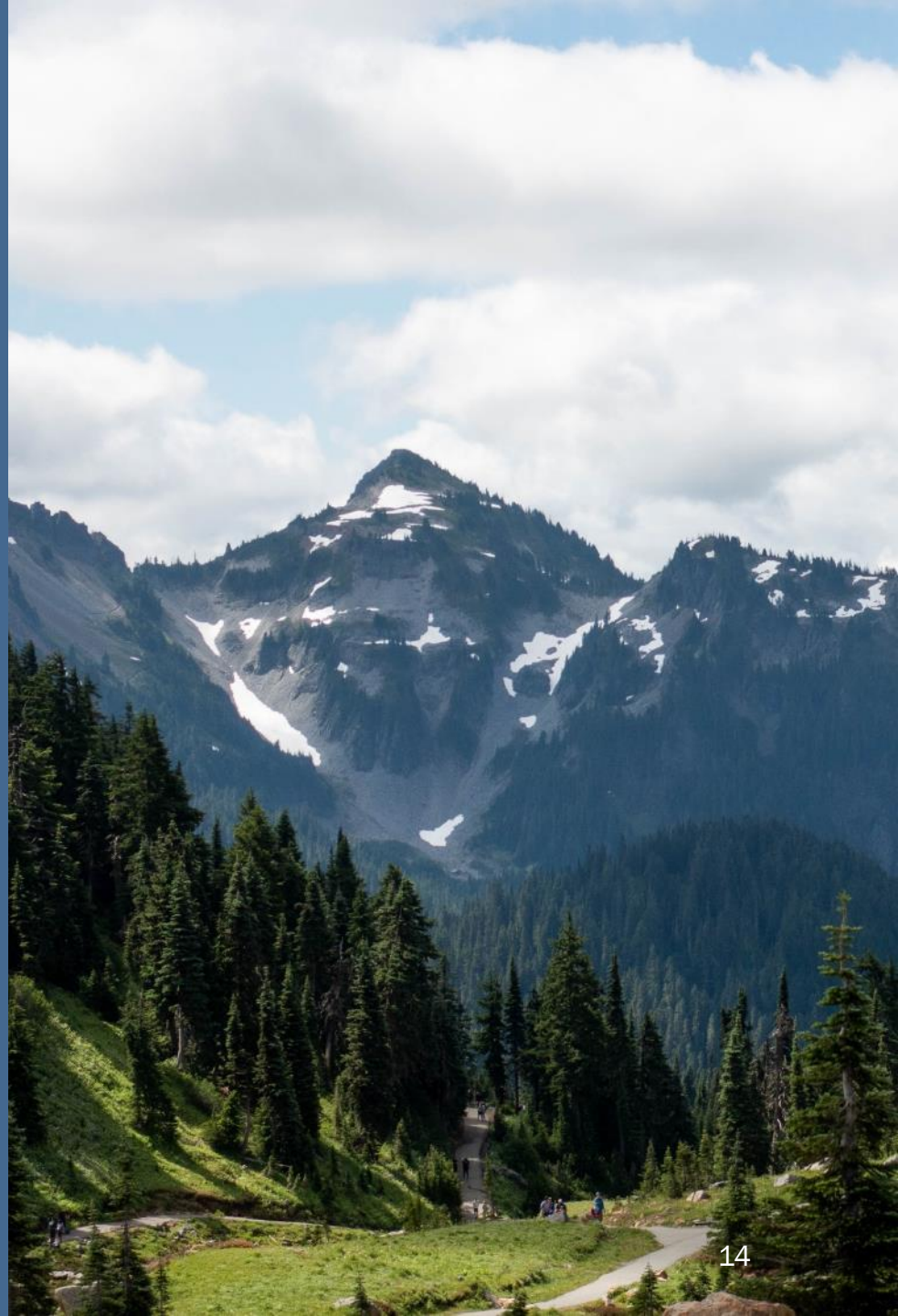
Ecology's 3-Part Approach

Reducing sources of 6PPD & evaluating alternatives

Mapping the problem & developing lab and field methods

Stormwater Best Management Practices (BMPs)

Source Reduction



Reducing Sources of 6PPD

- Are there chemicals that meet the same tire performance requirements as 6PPD?
- Are the potential replacement chemicals safe for salmonids, other aquatic species, and humans?
- What criteria will we use when determining whether a chemical is safer than 6PPD?
- Can manufacturers make changes to tire design that remove the need for 6PPD or eliminate the pollution of 6PPD and its transformation products from tires?
- Are there environmental and/or human health impacts from products (other than tires) containing 6PPD?

Source Reduction Road Map

- Hazards Assessment
- Hazard Criteria
- Research to fill data gaps
- Alternatives Assessment
- Action Plan

Hazards Assessment

- Completed in November 2021
- 6PPD and nine other antioxidants/antiozonants

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)	$BM\text{-}3_{DG}$ – Use but Still Opportunity for Improvement

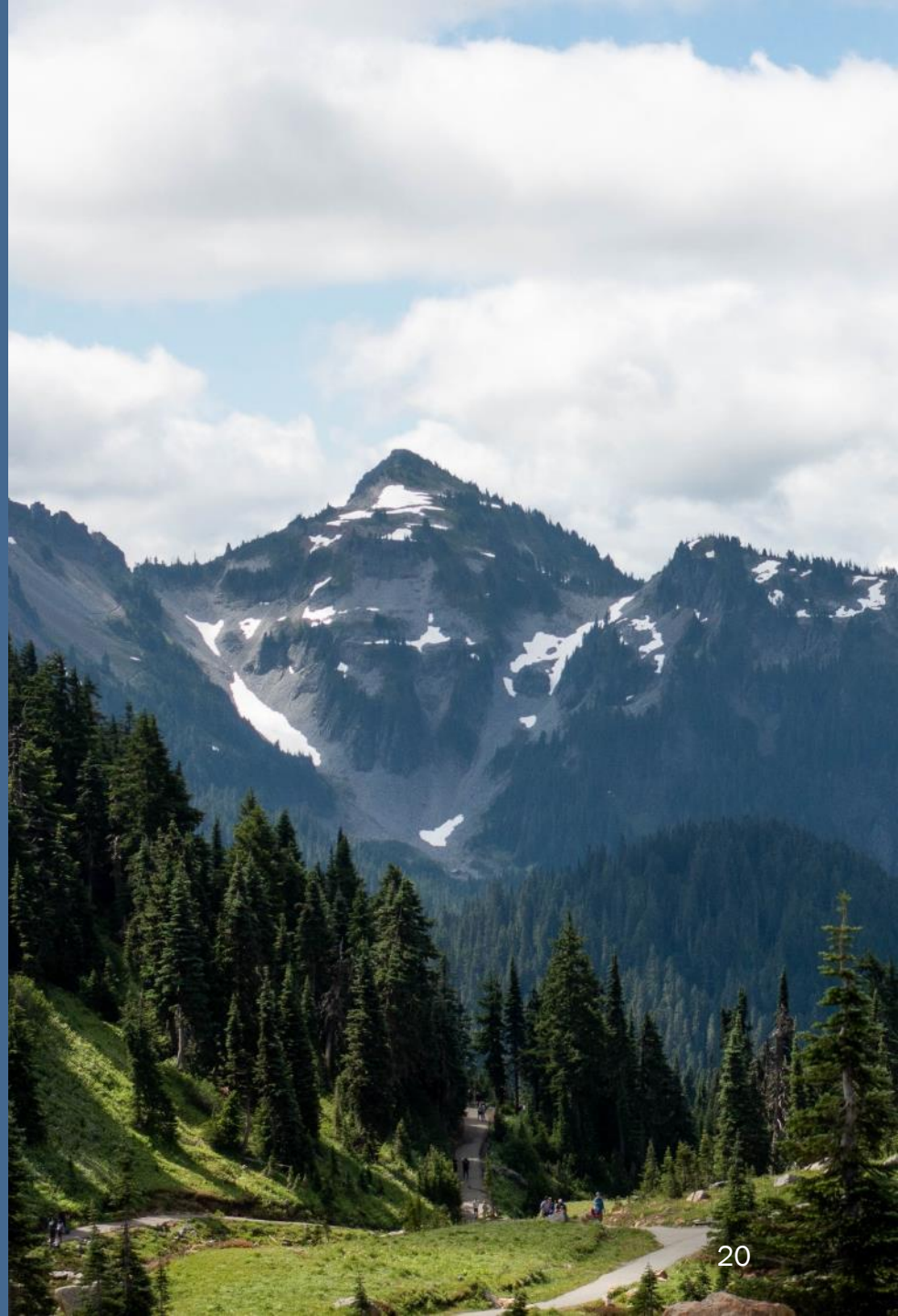
Alternatives - Industry Concerns

Alternative	Benchmark	Industry Comments
77PD	BM-2	"…provides a shorter period of protection than 6PPD…. It is unclear how long the protection would last in a modern tire." "Equally important is the fact that as a member of the PPD family, it would be expected to form a quinone like 6PPD."
TMQ	BM-2	"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."
Ethoxyquin	BM-2	"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."
Dilauryl thiodipropionate	$BM\text{-}3_{DG}$	"It is expected to have little, if any antiozonant activity."

Alternatives Assessment

- 2022 – Legislature allocated funding for 6PPD Alternatives Assessment
  - Identify, compare, and select safer alternatives to 6PPD
    - Toxicity, performance, availability, and cost
    - “If the department finds safer alternatives exist, include recommended regulatory, policy, or legislative actions to advance safer alternatives.”
- Research to fill data gaps
  - Toxicity of 6PPD, 6PPD-q, and alternatives to aquatic organisms
- Establish hazard criteria
  - Specific data requirements and standards to assess chemical safety
  - Based on Safer Products for Washington standards

Analytical Methods, Mapping, & Monitoring



Analytical Method

- Develop a laboratory method for measuring the concentration of 6PPD-q in water
- Have a reporting limit much lower than the LC50
- 6PPD is not stable so focus on 6PPD-q
- Liquid Chromatography Tandem Mass Spectrometry (LCMSMS)

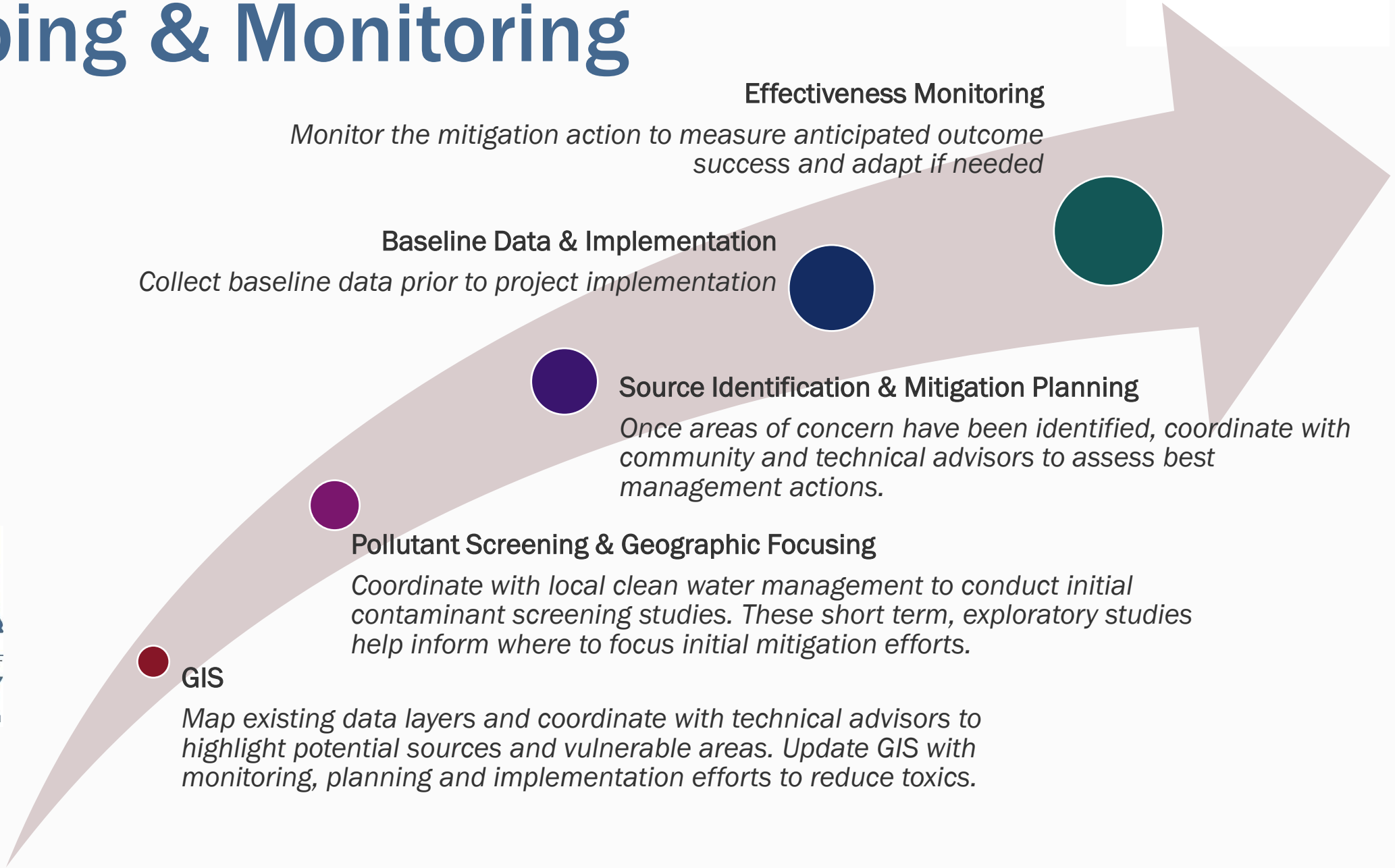
6PPD-q Laboratory Accreditation

- 6PPD-q Chemical Quantitation Accreditation
  - Led by Ecology's Laboratory Accreditation Unit
  - 4 labs submitted Standard Operating Procedures
  - 2 labs submitted chemistry data packages
  - As of March 1, 2023, no lab accredited

Sampling Method Development

- Method for sediment
- Method for tissue
- Test alternative field sampling methods
- Add related chemicals
- Add additional tire chemicals

Mapping & Monitoring



Effectiveness Monitoring

Monitor the mitigation action to measure anticipated outcome success and adapt if needed

Baseline Data & Implementation

Collect baseline data prior to project implementation

Source Identification & Mitigation Planning

Once areas of concern have been identified, coordinate with community and technical advisors to assess best management actions.

Pollutant Screening & Geographic Focusing

Coordinate with local clean water management to conduct initial contaminant screening studies. These short term, exploratory studies help inform where to focus initial mitigation efforts.

GIS

Map existing data layers and coordinate with technical advisors to highlight potential sources and vulnerable areas. Update GIS with monitoring, planning and implementation efforts to reduce toxics.

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Identifying Vulnerable Areas

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

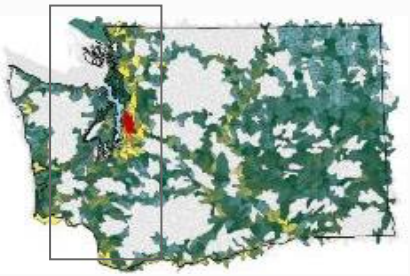
- Level of traffic and impervious surfaces
- Transformation rate and stability of 6PPD-q
- How 6PPD-q is transported from road to streams and the volume, flow rate, and duration of these processes
- How 6PPD-q binds to other particles
- Dilution factor (big river vs. small river)
- Residence time of water (pools, ripples, watershed size, and slope)
- BMPs or retrofits to capture and treat 6PPD-q

Vulnerable Ecological Areas

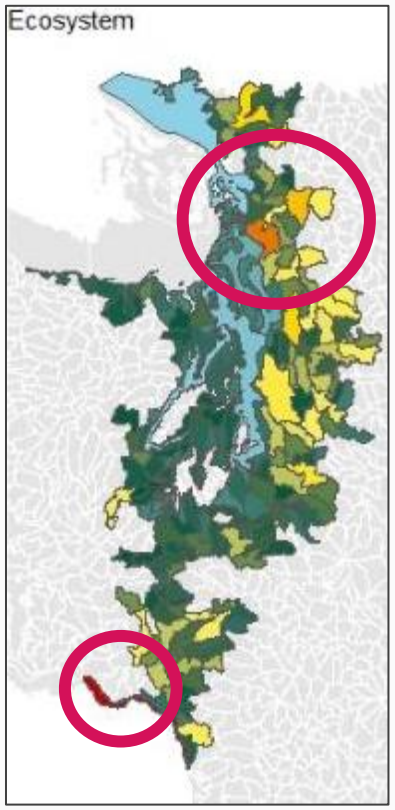
Indicator Mapping

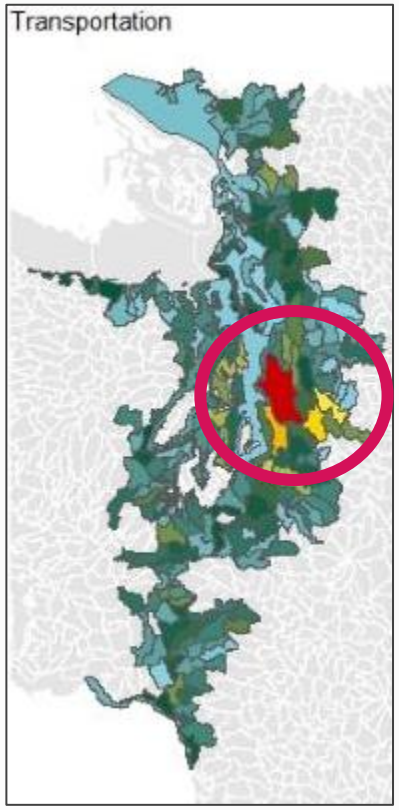
Watershed ID	Ecosystem	Transportation	Watershed	Vulnerability Score
A	Salmon distribution	Traffic counts (AADT)	Land cover	
A	Salmon habitat type	Vehicle type	Land use	
A	Salmon habitat length	Road length	Precipitation	
A	Presence of ESA listed	Road type		
A		Road and stream crossings		
A	Ecosystem +	Transportation +	Watershed +	Total

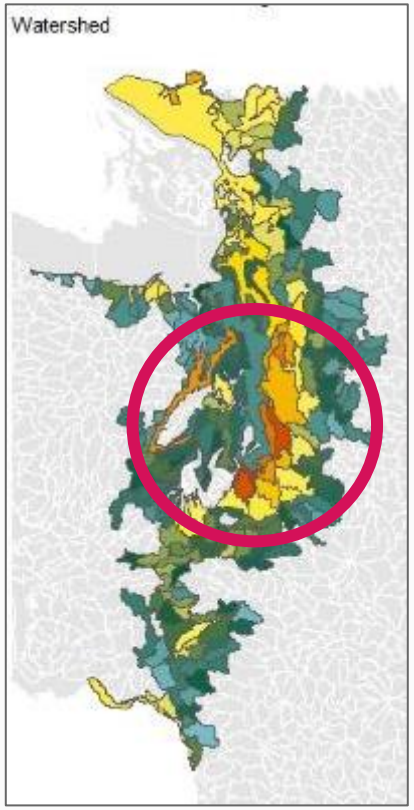
Indicators of Vulnerability & Exposure

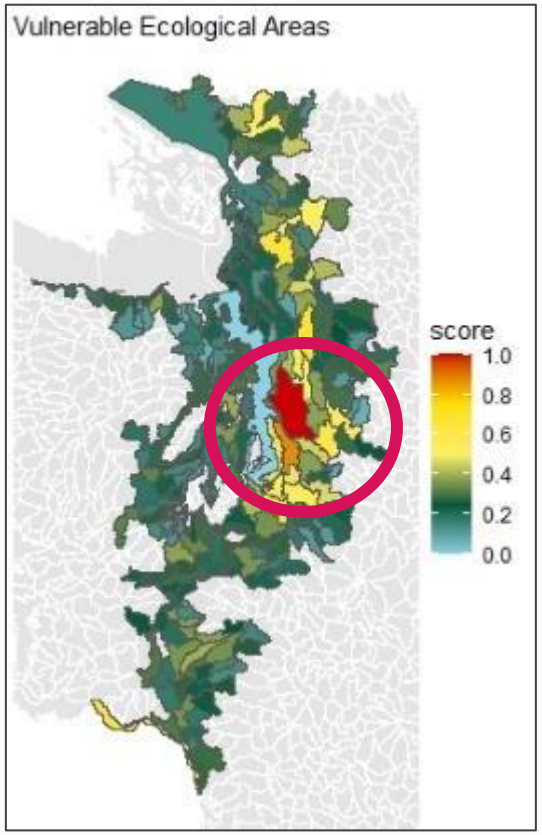


Vulnerable Areas









Ecosystem
e.g. Salmon

Transportation
e.g. Cars

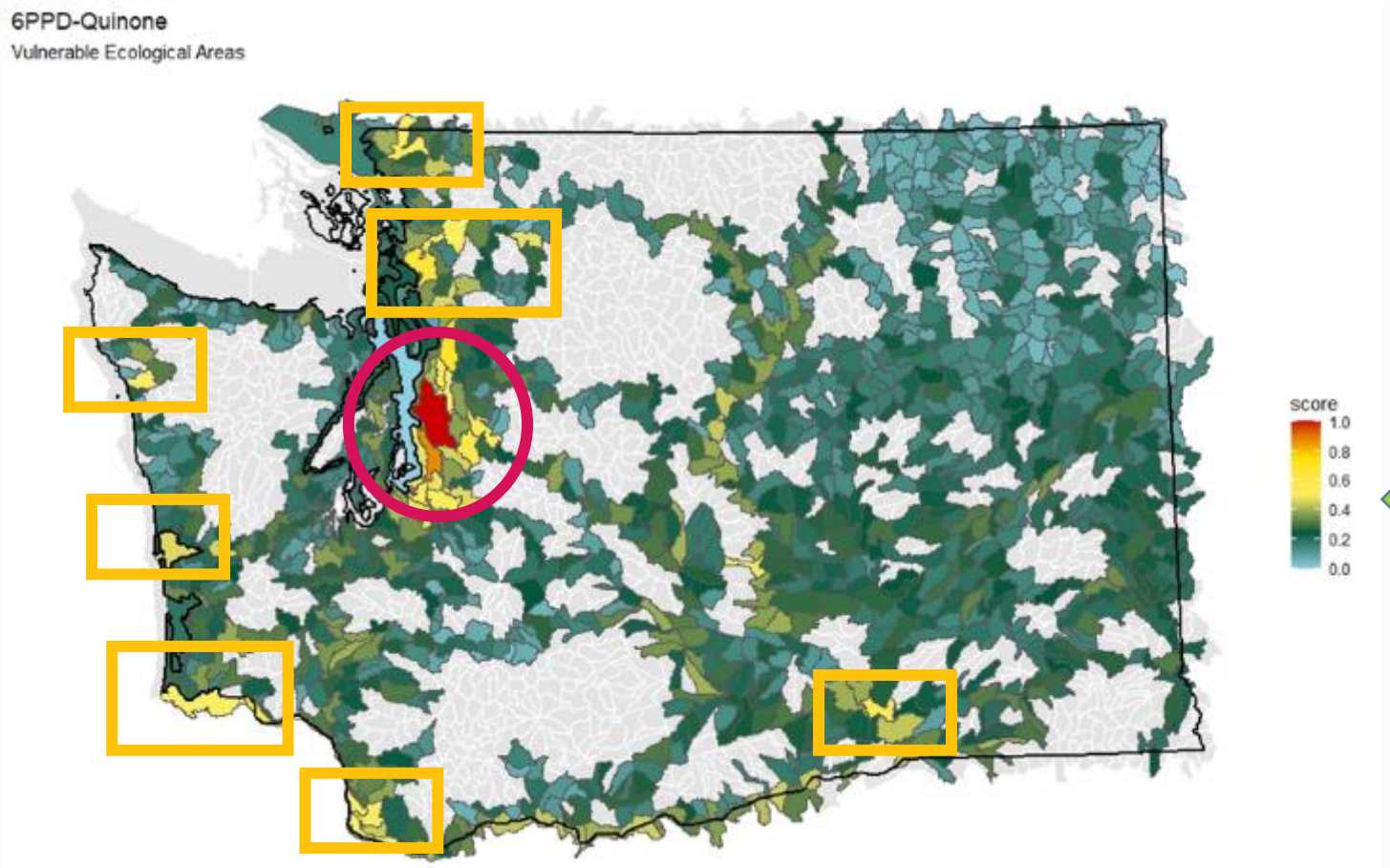
Watershed
e.g. Land Use

TOTAL VULNERABILITY

Scope and Scale of the Tire Contaminant Problem

Most Vulnerable Areas

Somewhat Vulnerable Areas



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*Scoring strengthens understanding of problem and helps direct further studies

Stormwater Best Management Practices (BMPs)

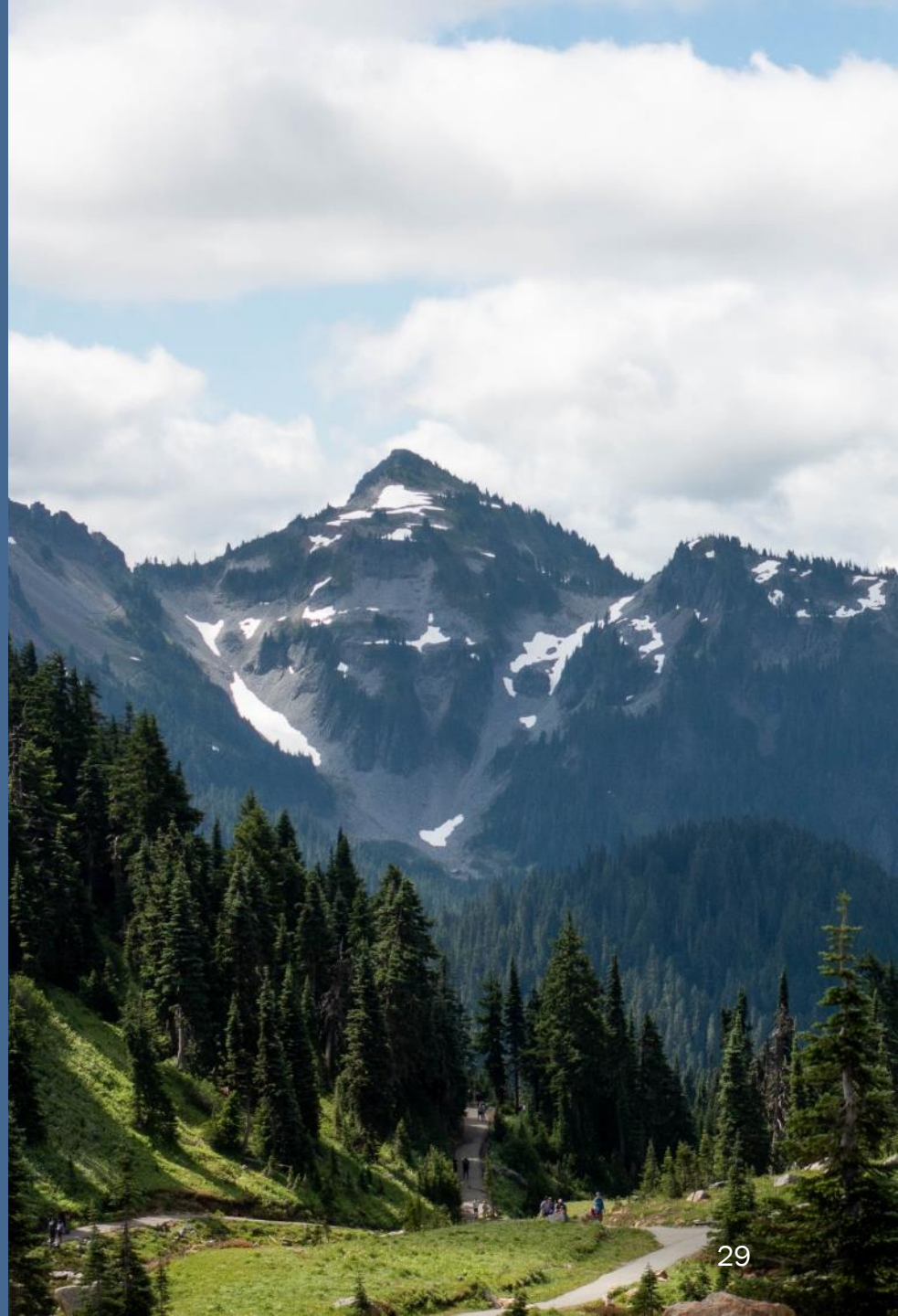


Photo: Mugdha Flores and Rhea Smith, WA Department of Ecology

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 starting July 2023*

Best Management Practices (BMPs)

- "Schedules of activities, prohibitions of practices, maintenance procedures, and structural and/or managerial practices, that when used singly or in combination, prevent or reduce the release of pollutants and other adverse impacts to waters of WA State" - *2019 Stormwater Management Manual for W WA*
- Have 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: Evergreen StormH20 et al. 2022

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

Photo: Bortek 2023

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

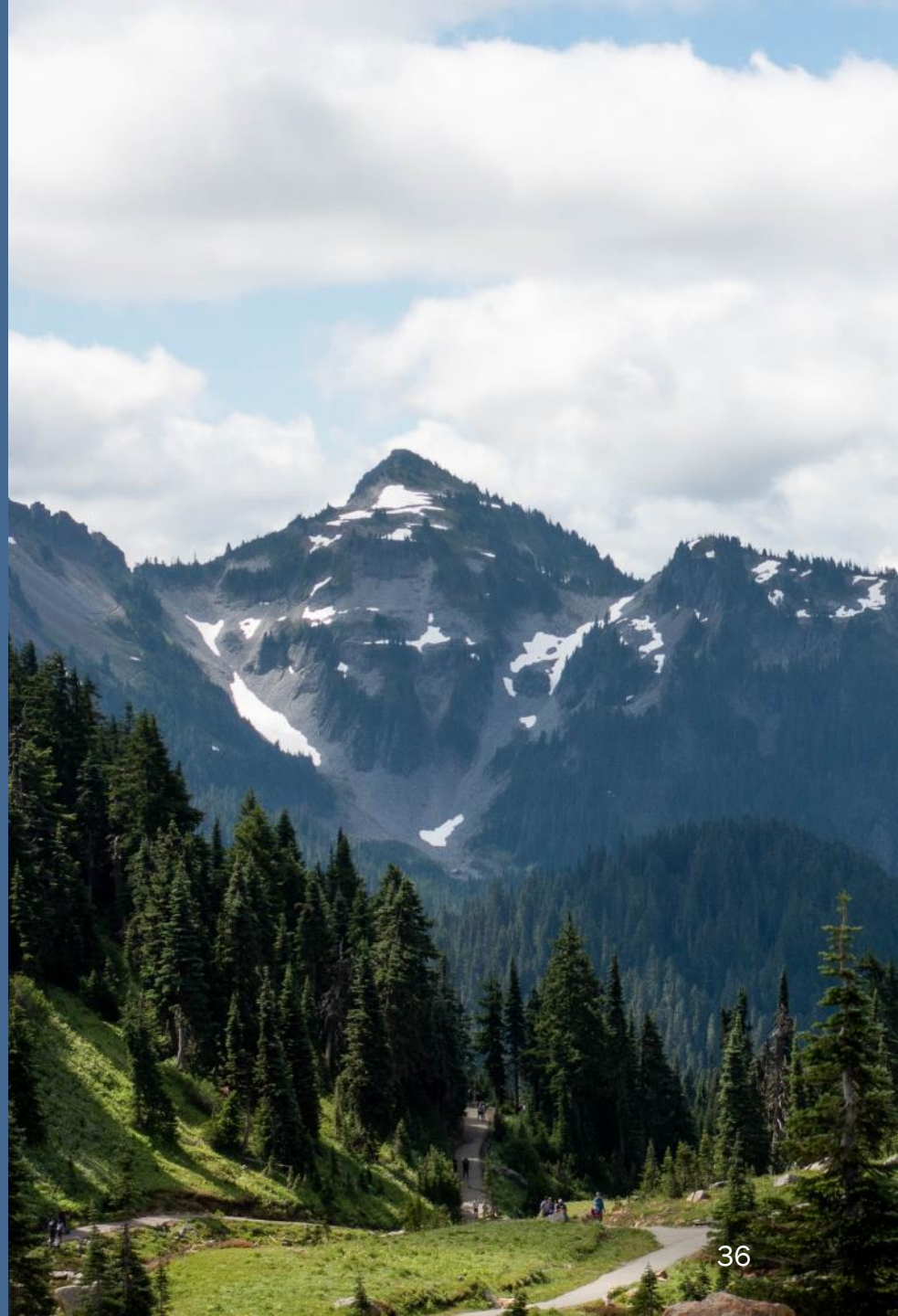
Examples: Trash racks, sorbent media, bioretention soil mix

Photo: BioCycle 2021

Current 6PPD/q BMPs Projects

- **WSU-Puyallup** – longevity of bioretention media
- **Redmond** – street sweeping effectiveness
- **Osborn & Evergreen StormH2O Consulting** – BMPs report, 6PPD subgroup, and 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

Collaboration & Conclusion



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
- Review research and technologies to create training and educational materials that will guide decision-making and policy across the nation
- Identify data gaps

6PPD/q Action Plan

- Goals & Objectives
  - Follow the public process and economic analysis of WAC 173-333
  - Problem review
    - Other forms of 6PPD (recycled tire stockpiles, tire reefs, playfields/tracks, bicycle tires, etc.)
  - Identify impacts to human health and the environment
  - Provide actionable recommendations
  - Environmental Justice review and prioritization
  - Scoping - determine other components with input from advisory committee and informed by current level of knowledge
- Advisory committee: DOH, Tribal Partners, other state agencies, industry, local government, NGOs, and other stakeholders


Photo: Eiko Jones

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Key Takeaways

- Addressing 6PPD/q will have important implications for:
  - Tribal Treaty Rights
  - Environmental Justice
  - Commercial, recreational, & subsistence fisheries
  - Ecosystem health & resilience
  - Human health
- Challenges
  - Many knowledge gaps still to fill
  - Actively implementing BMPs and policy solutions amidst uncertainty

Questions & Discussion

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