Starting Soon:
Overview of the tire-derived chemicals 6PPD & 6PPD-quinone

- 6PPD Guidance Document: https://6ppd.itrcweb.org/
- CLU-IN training page (slides available): https://cluin.org/conf/itrc/6PPD-Q/

Housekeeping

- This event is being recorded; Event will be available On Demand after the event at the main training page: https://cluin.org/conf/itrc/6PPD-Q/
- If you have technical difficulties, please use the Q&A Pod to request technical support
- Need confirmation of your participation today?
  - Fill out the online feedback form and check box for confirmation email and certificate

Overview of the tire-derived chemicals 6PPD & 6PPD-quinone

Sponsored by: Interstate Technology and Regulatory Council
Hosted by: US EPA Clean Up Information Network

Host Organization

Network – 49 states, PR, DC

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Read trainer bios at https://cluin.org/conf/itrc/6PPD-Q/

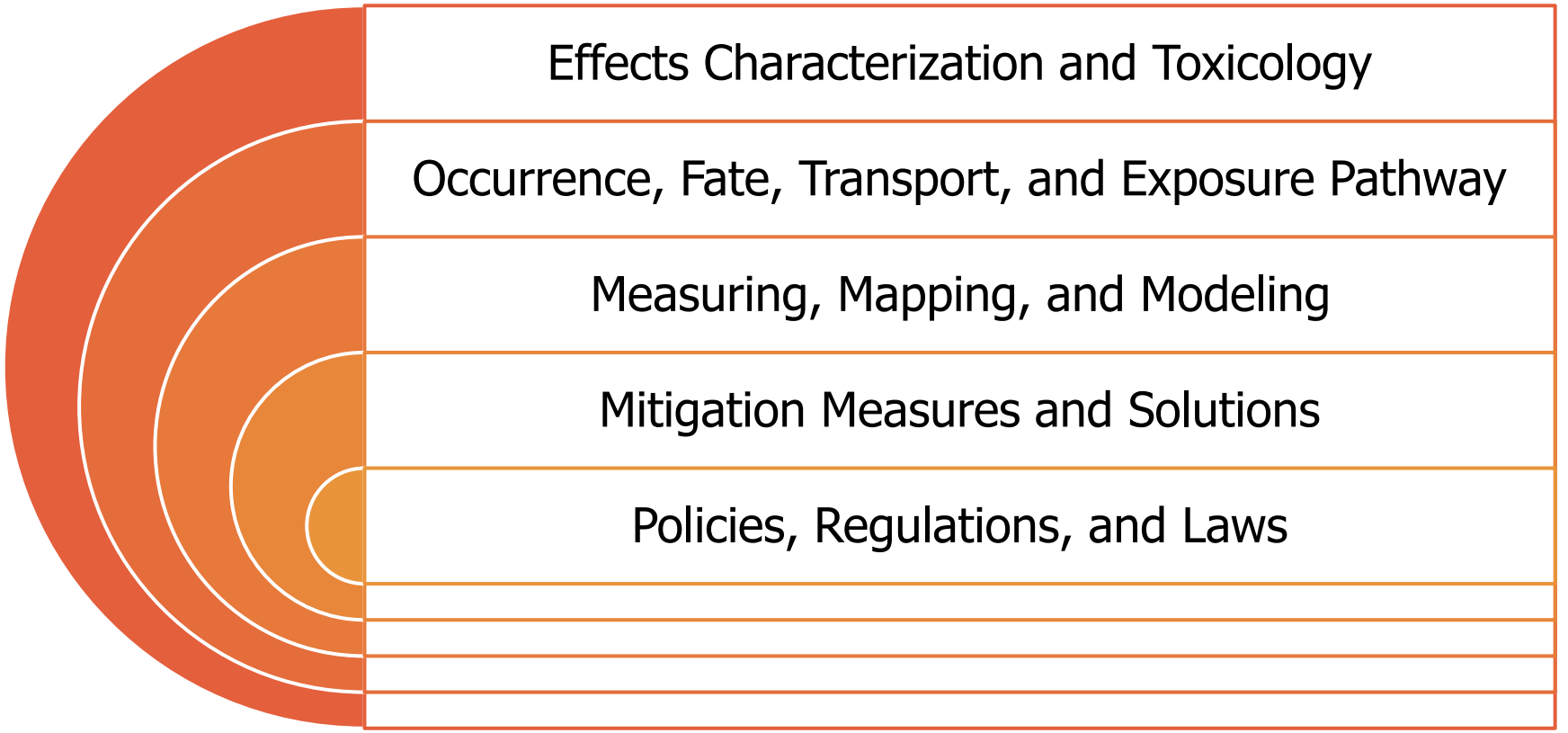
Overview of the tire-derived chemicals 6PPD & 6PPD-quinone

https://6ppd.itrcweb.org/

Video: Longfellow Creek Coho Salmon

Video: Puget Soundkeeper (2014)

Road Map


Effects Characterization and Toxicology
Occurrence, Fate, Transport, and Exposure Pathway
Measuring, Mapping, and Modeling
Mitigation Measures and Solutions
Policies, Regulations, and Laws

Acute Toxicity to Coho

- Up to 100% of coho salmon died before they could spawn
- Female carcasses showed >90% egg retention
- Symptoms: disorientation, swimming on side, gasping
- Hypothesized cause as road runoff and later defined as Urban Runoff Mortality Syndrome

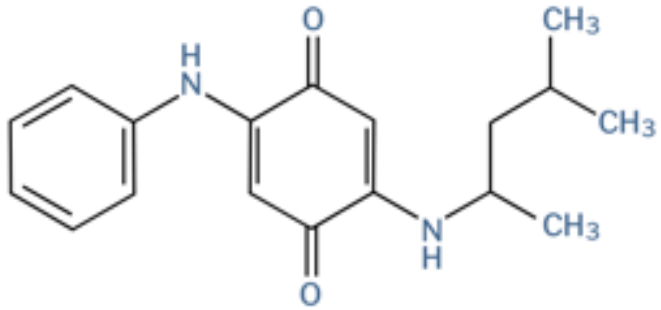
Scholz et al. 2011
Photo: Wild Fish Conservancy, 2021

Discovery of the Cause

- Research on chemicals in tires began in 2018
- Over 2,000 chemicals in tire wear particle leachate
- Discovered **6PPD-quinone** in 2020

6PPD-quinone

2-anilino-5-[(4-methylpentan-2-yl)amino]
cyclohexa-2,5-diene-1,4-dione



CASRN 2754428-18-5

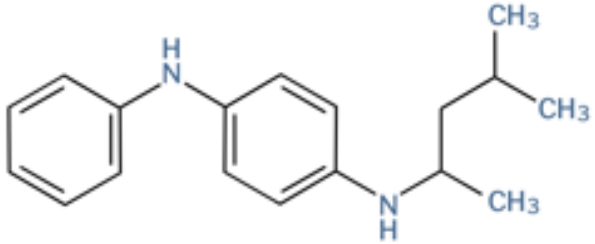
Source of 6PPD-quinone

6PPD

- Chemical anti-degradant that prevents tire rubber from cracking when exposed to ozone at tire surface
- The reaction of 6PPD and ozone protects the tire, but also produces 6PPD-quinone

6PPD

1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-



CASRN 793-24-8

With 6PPD | Without 6PPD

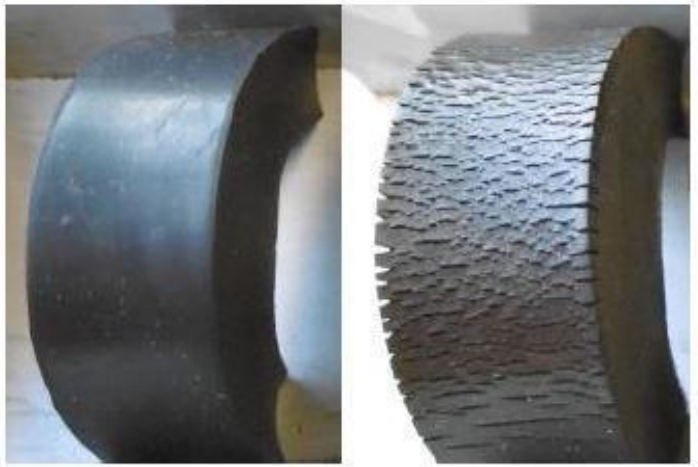
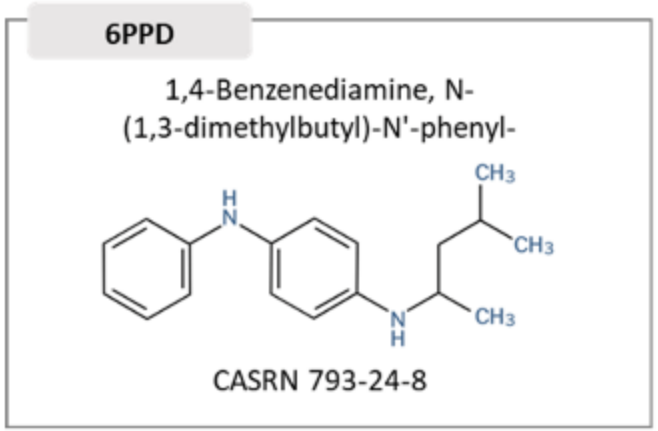


Photo credit: U.S. Tire Manufacturers Association

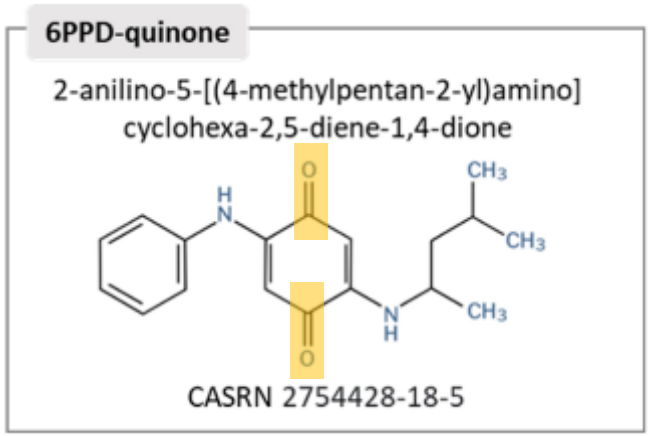
Chemical Structure/Transformation

6PPD



Reacts with ozone

6PPD-q



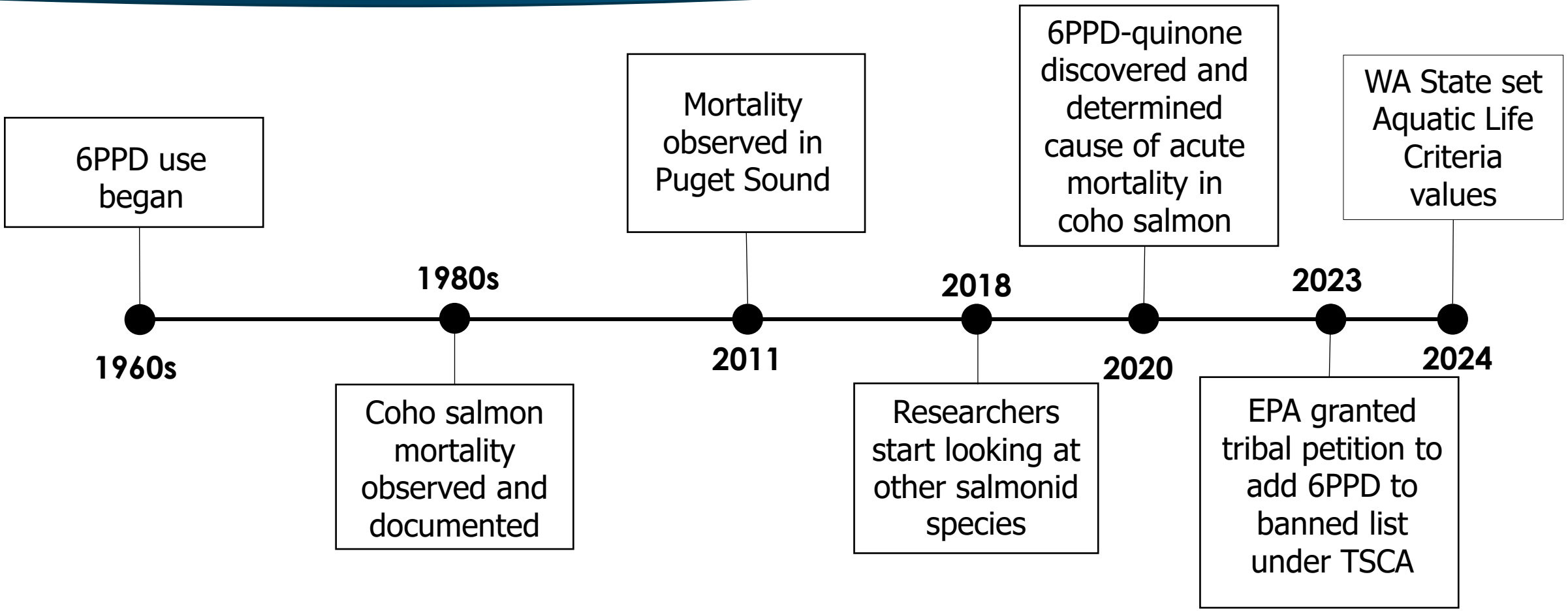
Tire Anti-degradant

Chemical class: *para*-phenylenediamines (PPDs)

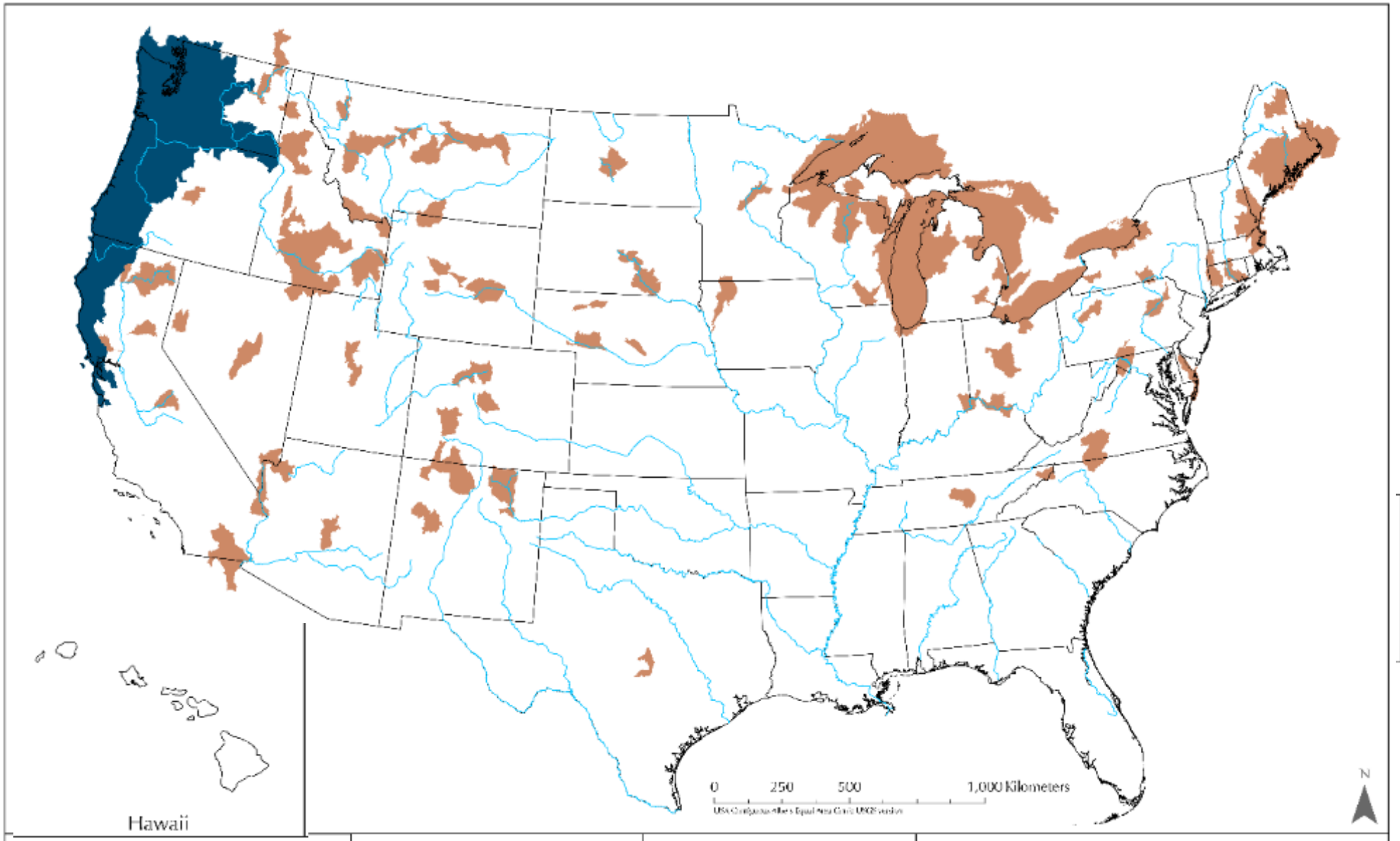
Aquatic Toxicant

One of several transformation products

6PPD-quinone Timeline



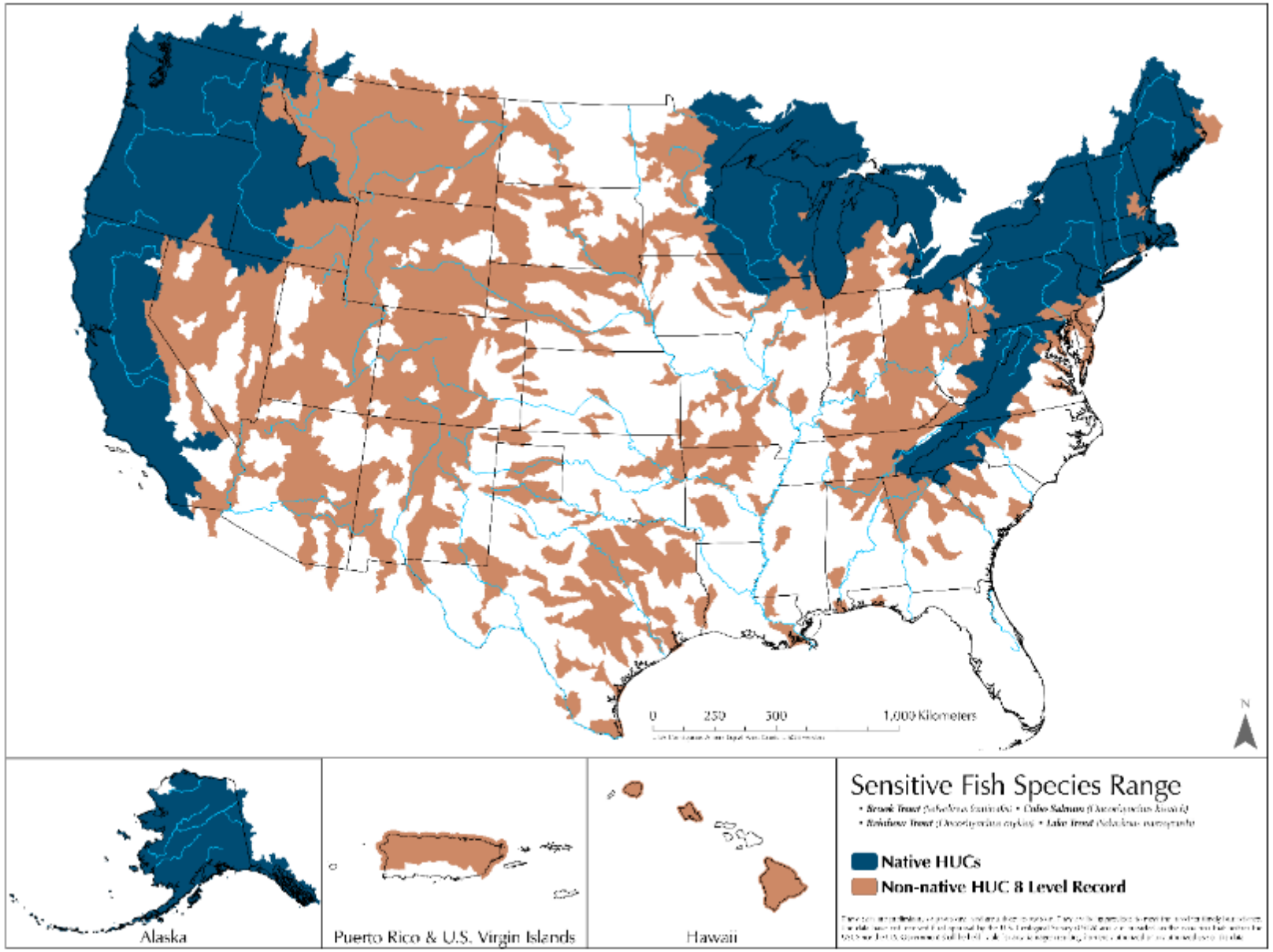
Coho Habitat



Oncorhynchus kisutch
Coho Salmon

Native HUCs
Non-native HUC 8 Level Record

6PPD-q – Toxic to Some Salmonids



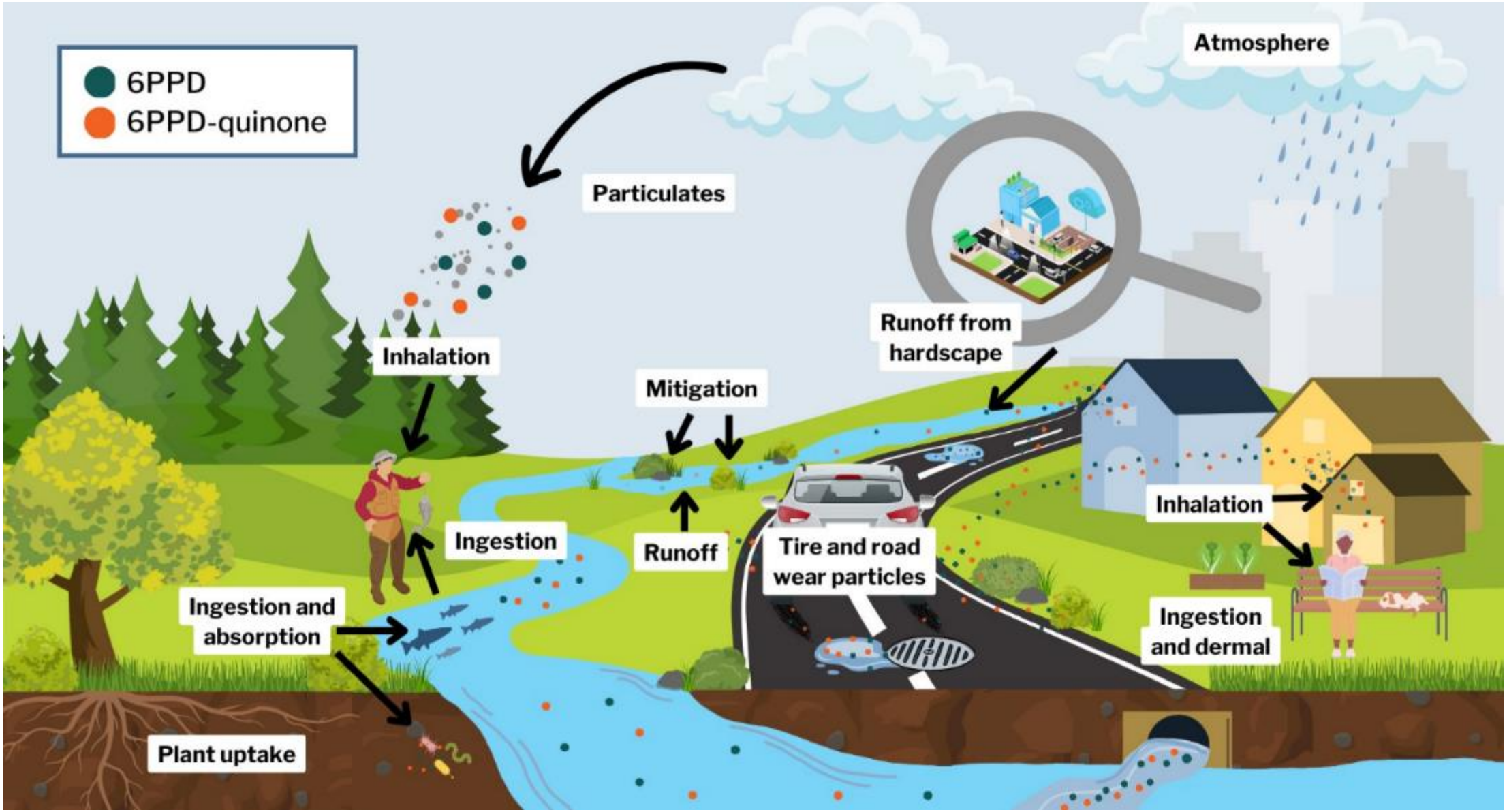
- Coho salmon
- Brook trout
- Lake trout
- Rainbow trout/steelhead
- Coastal cutthroat trout

Impacts to Tribal Nations

- Treaty rights to fish
- Salmon are culturally & economically significant
- Food web and human exposures
- Potentially impede Tribally-led salmon recovery efforts, including reintroduction, hatcheries, and habitat restoration

Member of the Yakama Nation dip netting in the Klickitat River (for Chinook salmon).
Courtesy of USFWS

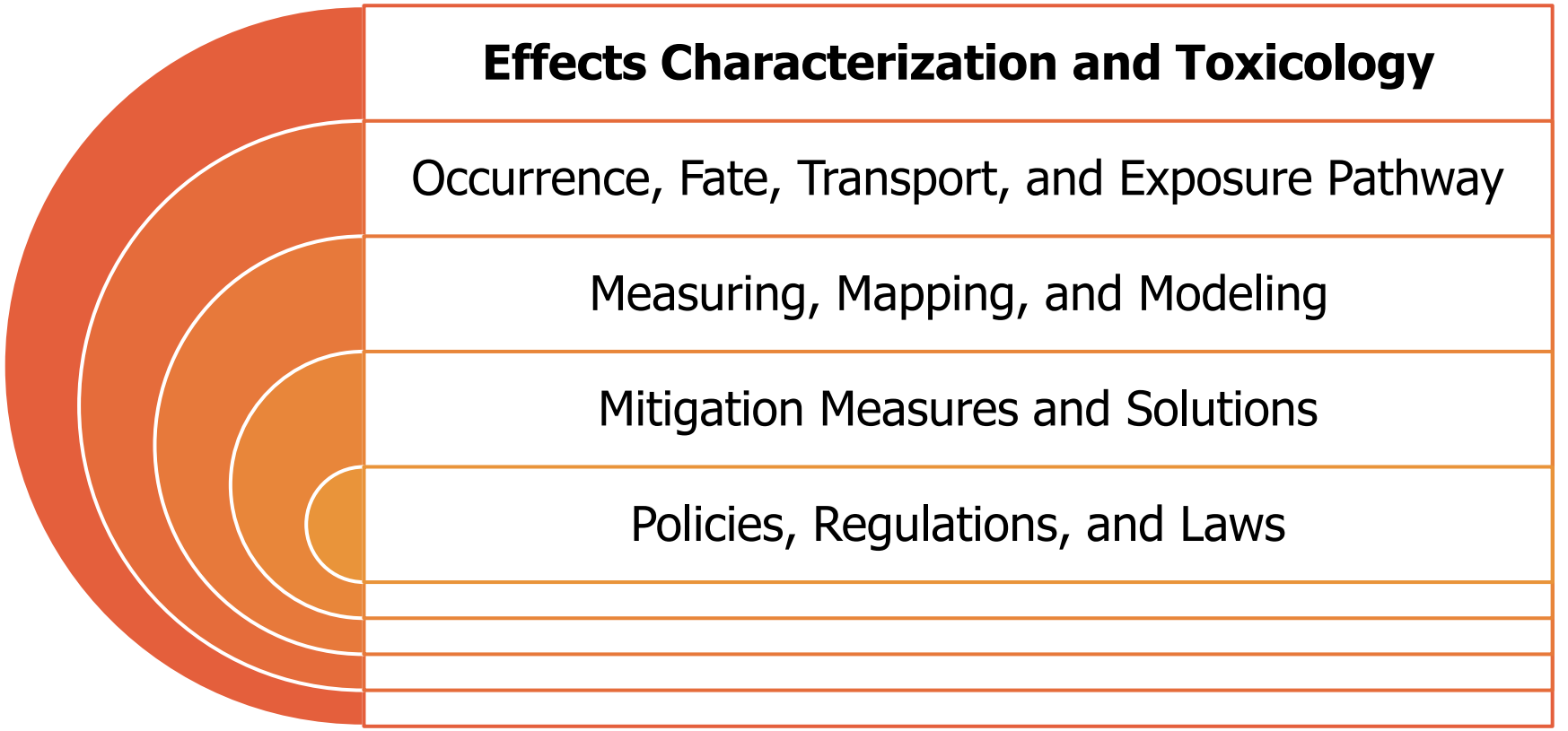
Conceptual Exposure Model



What We Don't Know: Knowledge & Research Gaps

- 6PPD and 6PPD-q are contaminants of emerging concern (CEC)
- Ecological toxicity & its mechanisms
- Human toxicity and exposure
- Widespread environmental monitoring
- Social and cultural impacts
- Solutions

Road Map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Toxicology & Effects Characterization: Learning Objectives

Identify sensitive and vulnerable aquatic species and understand the extent of current understanding of acute and chronic toxicity

Recognize that potential risk is determined by both:

- **Hazard**: effects on sensitive species
- **Exposure**: concentrations of 6PPD and 6PPD-q in the environment

Understand the extent of knowledge on human exposure and effects on human health

What We've Learned Since 2020

Existing data

- Acute toxicity data in fish
- Limited data on chronic toxicity to fish
- Limited data on toxicity to other aquatic species
- Almost no data on toxicity to terrestrial species

Toxicological responses vary

- Between species
- Age-dependent toxicity within a species

Mode of action still not fully understood

Species-Specific Acute Toxicity in Salmonids

Species	LC_{50} (µg/L)	Test duration (h)
Coho salmon *(Oncorhynchus kisutch)*	**0.08 (median)**	**24**

- LC_{50} = lethal concentration to half the population
- Coho LC_{50} frequently exceeded in stormwater runoff
- Observed concentrations in surface waters up to 2.85 µg/L

Guidance Document Table 1-1

Species-Specific Acute Toxicity in Salmonids

Species	LC_{50} (µg/L)	Test duration (h)
Coho salmon *(Oncorhynchus kisutch)*	**0.08 (median)**	**24**
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Lake trout *(Salvelinus namaycush)*	**0.51**	**24**
Brook trout *(Salvelinus fontinalis)*	**0.59**	**24**
Rainbow trout/steelhead *(Oncorhynchus mykiss)*	**1.0 (median)**	**96**

Guidance Document Table 1-1

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Brook trout *(Salvelinus fontinalis)*	**0.59**	**24**
Rainbow trout/steelhead *(Oncorhynchus mykiss)*	**1.0 (median)**	**96**
Chinook salmon *(Oncorhynchus tshawytscha)*	**82.1**	**24**
Sockeye salmon *(Oncorhynchus nerka)*	**Not acutely toxic up to 50**	**24**
Atlantic salmon *(Salmo salar)*	**Not acutely toxic up to 12.2**	**48**
Brown trout *(Salmo trutta)*	**Not acutely toxic up to 12.2**	**48**
Arctic char *(Salvelinus alpinus)*	**Not acutely toxic up to 12.7**	**24**
Pink Salmon *(Oncorhynchus gorbuscha)*	**Not acutely toxic**	**48**

Guidance Document Table 1-1

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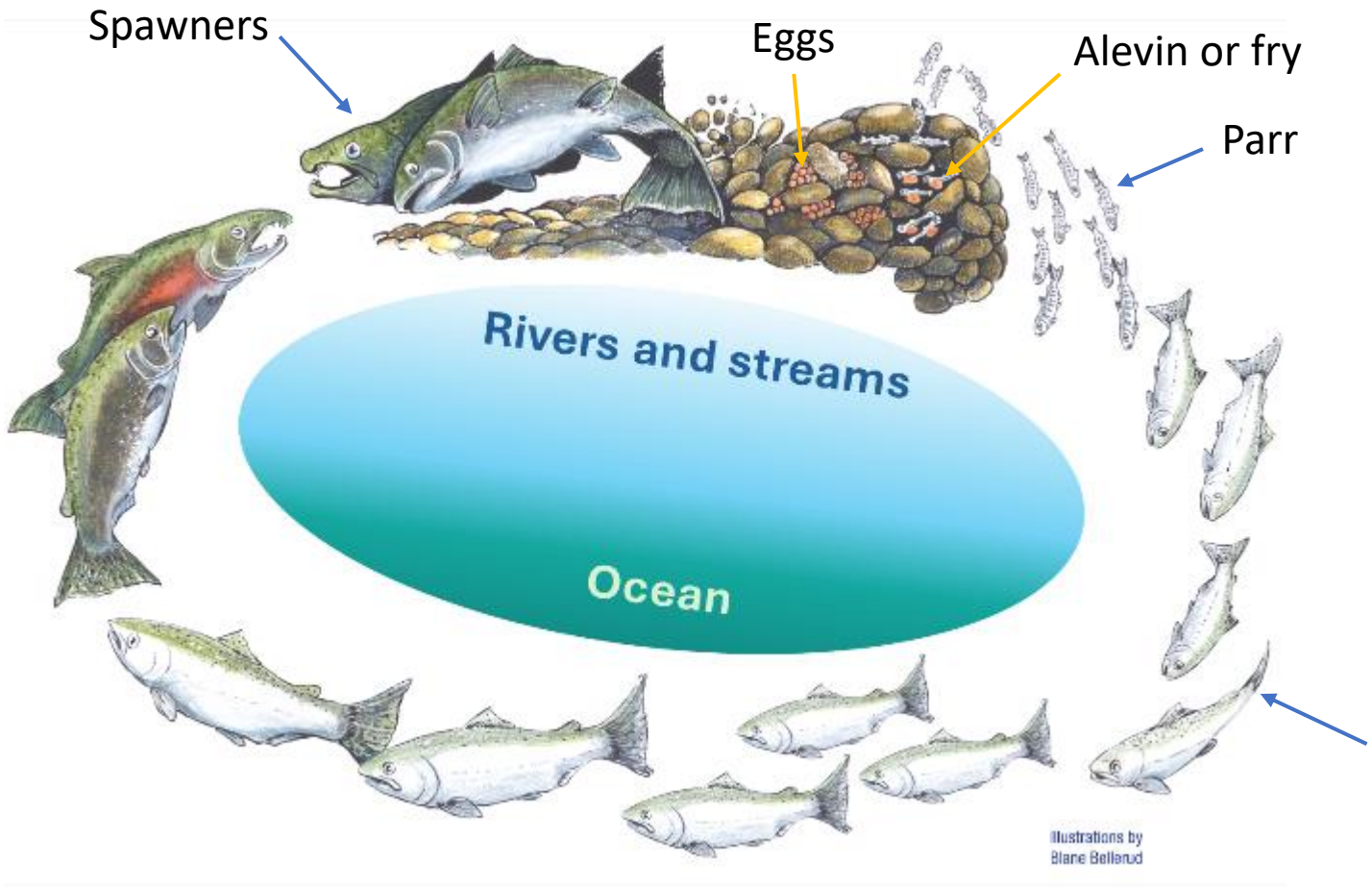
Not acutely toxic to: White sturgeon, zebrafish, medaka, fathead minnow, *Daphnia, Hyallela*

Guidance Document Table 1-1

Life Cycle of Salmonids



Age-dependent toxicity in coho salmon

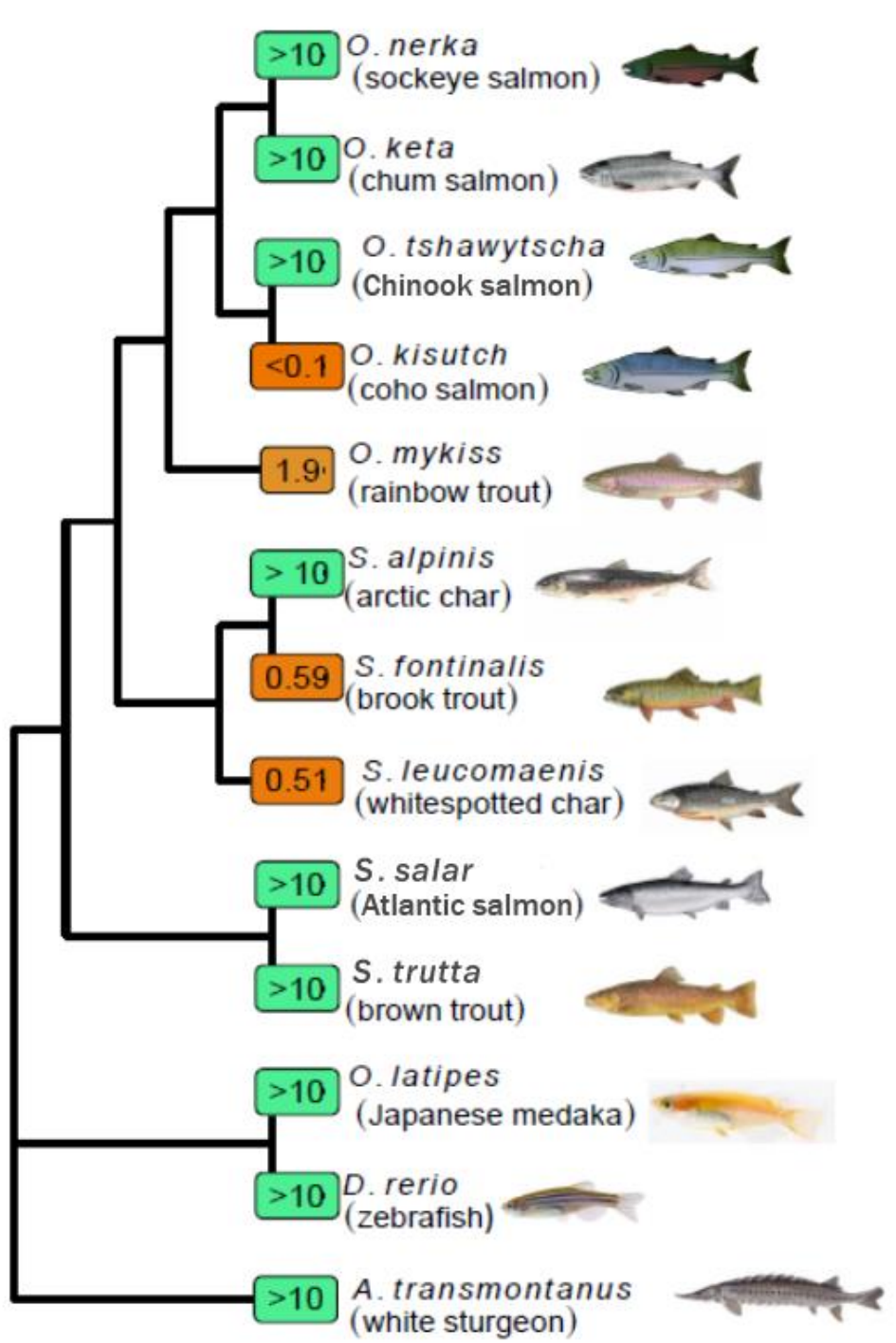
LC50 range:
0.041 µg/L (newly feeding hatchlings)
to 0.095 µg/L (fish over 1 year old)

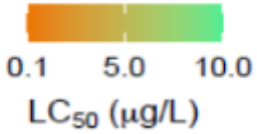
Image Courtesy: National Oceanic and Atmospheric Administration

Salmonid Family Tree

6PPD-q toxicity not necessarily linked to phylogenetic relationships

Difficult or impossible to predict toxicity to untested species.





Guidance Document Figure 2-2

Overview: Hypotheses for 6PPD-q's Mode of Action

Leakage from blood vessels

- Blood-brain barrier failure & neurotoxicity

Mitochondrial dysfunction

- Breakdown of the process cells use to make energy

Metabolic differences between sensitive and tolerant species

- Tolerant species may biotransform 6PPD-q more effectively

6PPD-q Can Cause Sublethal Effects

Developmental malformations

- Coho & lake trout

Altered gill morphology

- Brook trout

Zebrafish

- Development
- Behavior
- Respiration
- Heart rate
- Oxidative damage

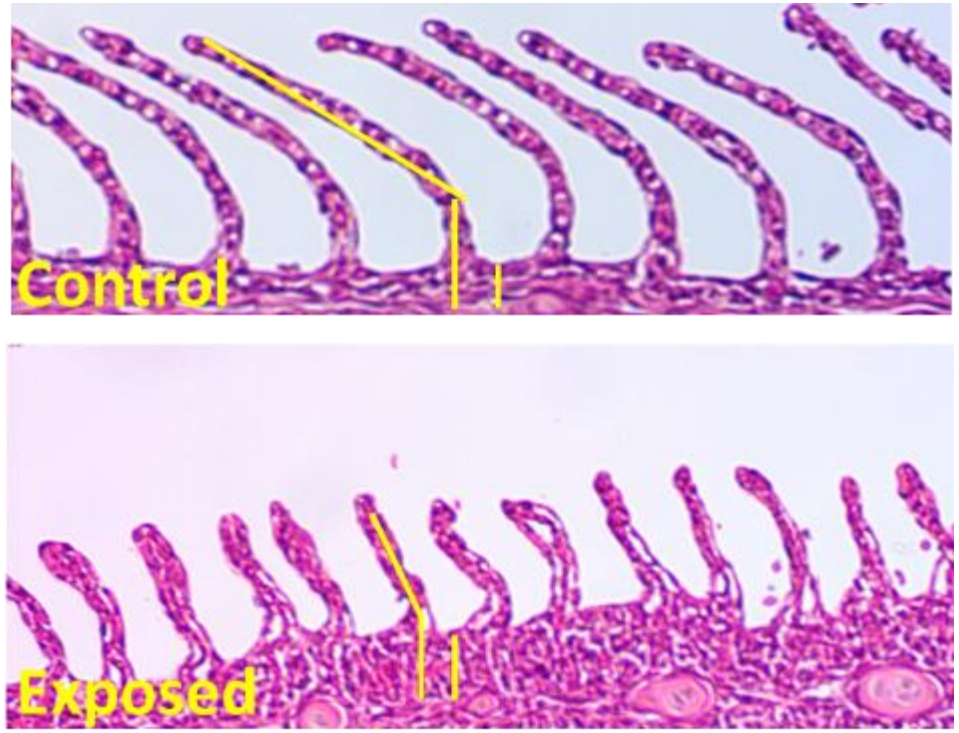
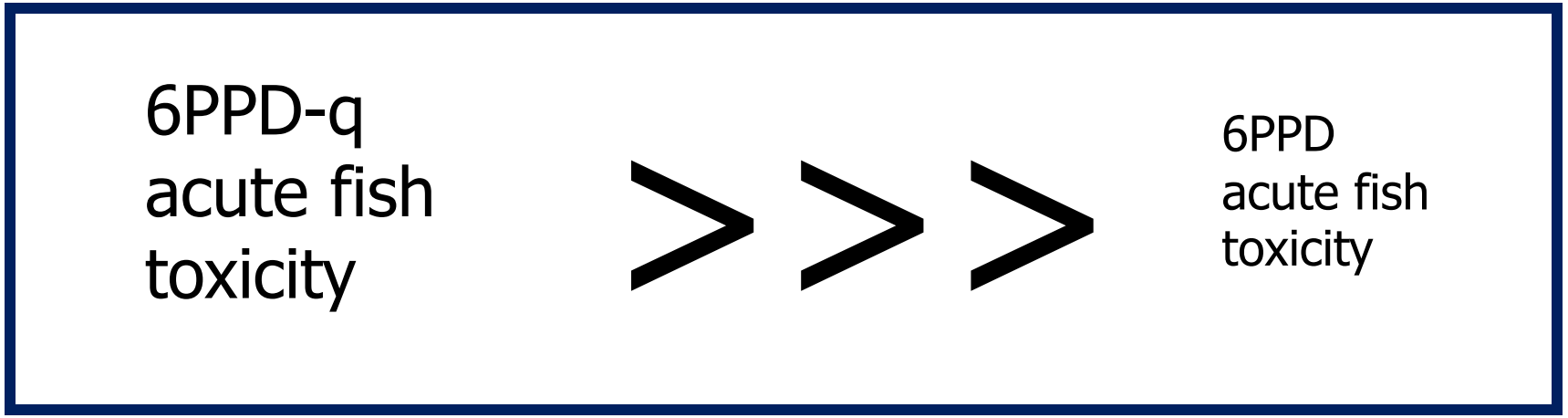


Image Courtesy: Danielle Philibert

6PPD Aquatic Toxicity

Chemical properties (high instability, and formation of transformation products) make toxicity hard to study



Water Quality Thresholds

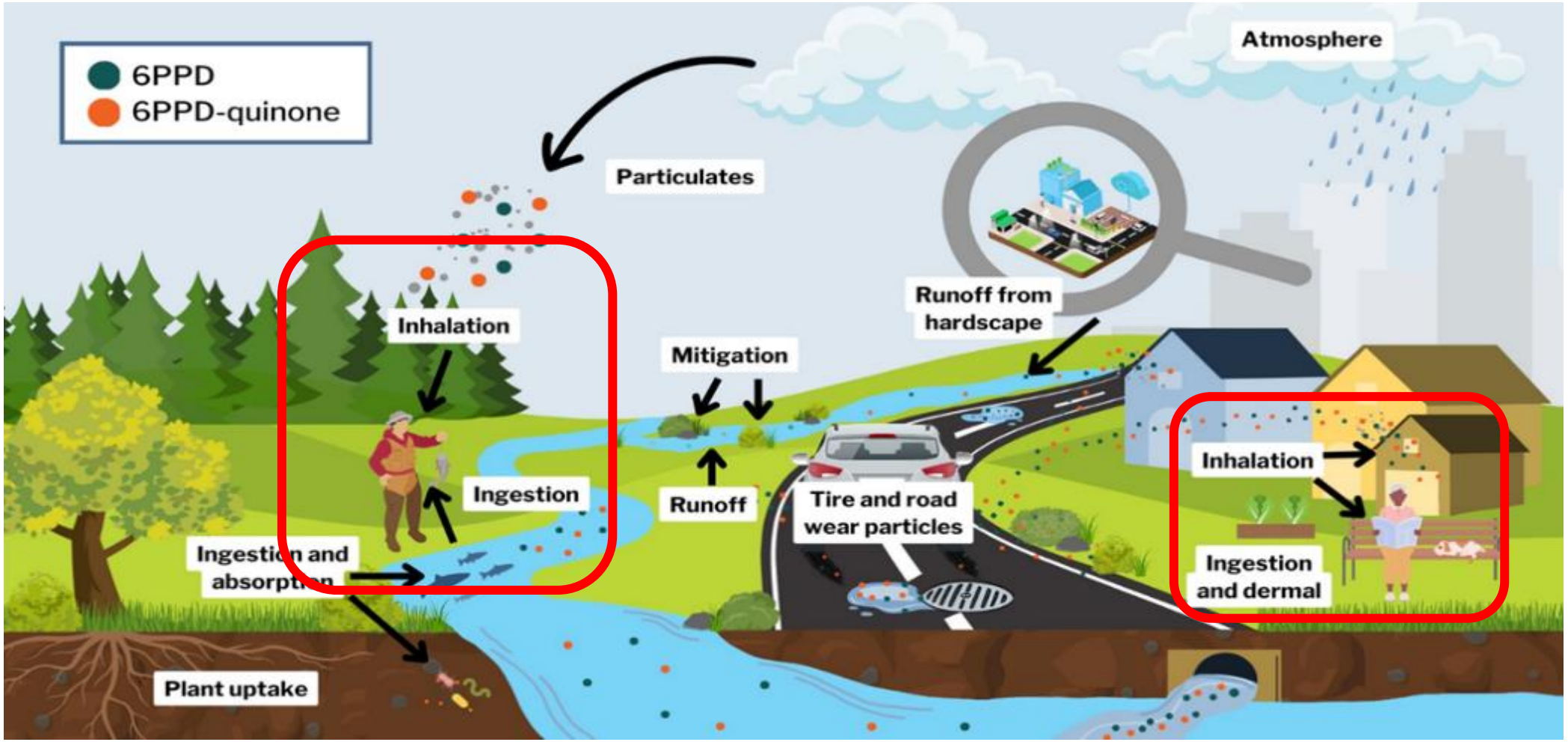
EPA freshwater acute screening values (non-regulatory)

- 6PPD-q: 0.011 µg/L
- 6PPD: 8.9 µg/L

WA State Acute Aquatic Life Criteria (regulatory)

- 6PPD-q: 0.012 µg/L

Human Exposure to 6PPD & 6PPD-q



Human Exposure & Toxicokinetics

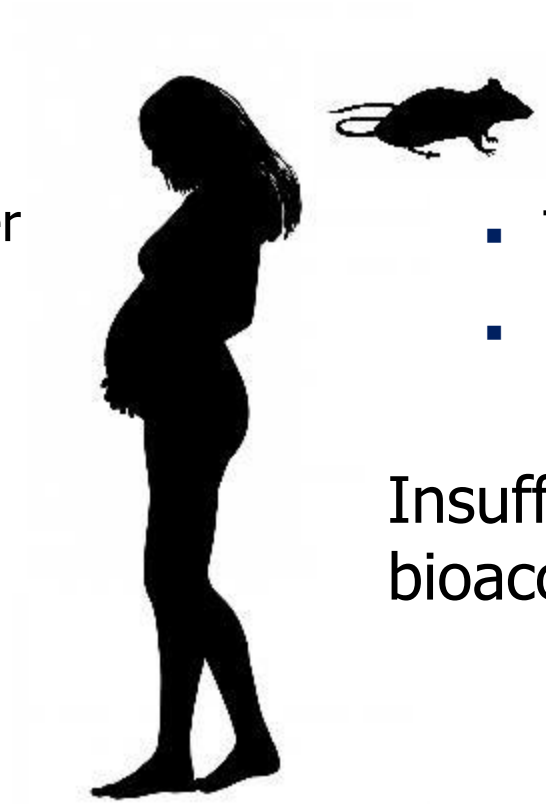
6PPD and 6PPD-q in human urine

- Pregnant people's urine had higher levels; unclear whether greater exposure or differences in metabolism

6PPD and 6PPD-q in blood serum

6PPD in breastmilk

6PPD-q in cerebrospinal fluid



Mouse models:

- Transmitted through the placenta
- Pass through the blood-brain barrier of adult and fetus

Insufficient information on bioaccumulation in mammals

Human Health Hazards

Very little information on toxicological hazard traits

6PPD

- Liver toxicity
- Reproductive toxicant, potential for developmental toxicity
- Skin sensitizer (causes skin allergies)

6PPD-q

- Liver toxicity
- Reproductive/ developmental toxicity? Carcinogenicity? Neurotoxicity?

Summary

Active field of research; numerous studies under way

6PPD-q is acutely toxic to some salmonids at very low concentrations

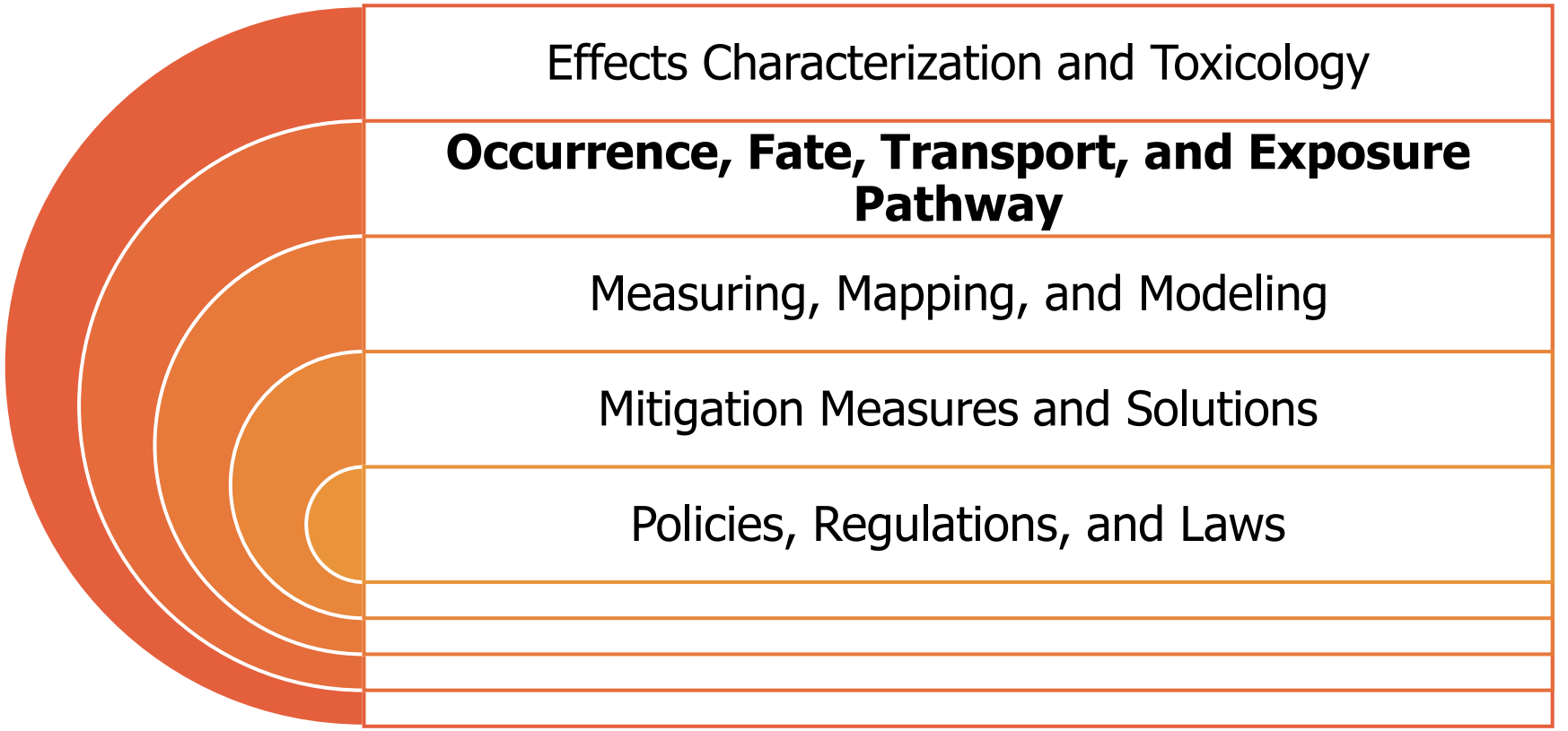
- Mode of action still unclear
- Chronic and sublethal toxic effects under investigation

Limited toxicity data for other aquatic and terrestrial organisms

6PPD appears generally less toxic, but is difficult to study

Humans are exposed, but human health implications remain unclear

Road Map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Occurrence, Fate, and Transport: Learning Objectives

Become familiar with the environmental matrices where 6PPD, 6PPD-quinone is found

Provide an overview of the release mechanism, fate and transport pathways impacting distribution of 6PPD, 6PPD-quinone in the environment.

Tire and Road Wear Particles (TRWP)

Friction between road & tire during driving, braking, and turning leads to generation and emission TRWP

The occurrence and persistence of 6PPD, 6PPD-q, TWP, and TRWP in the environment is poorly understood

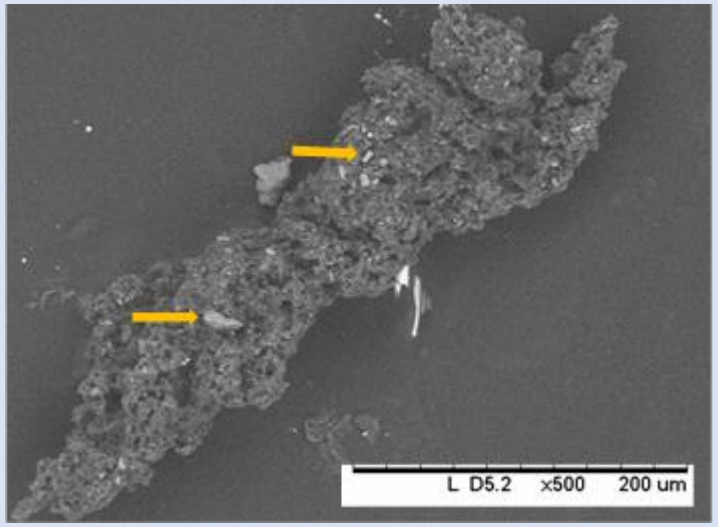
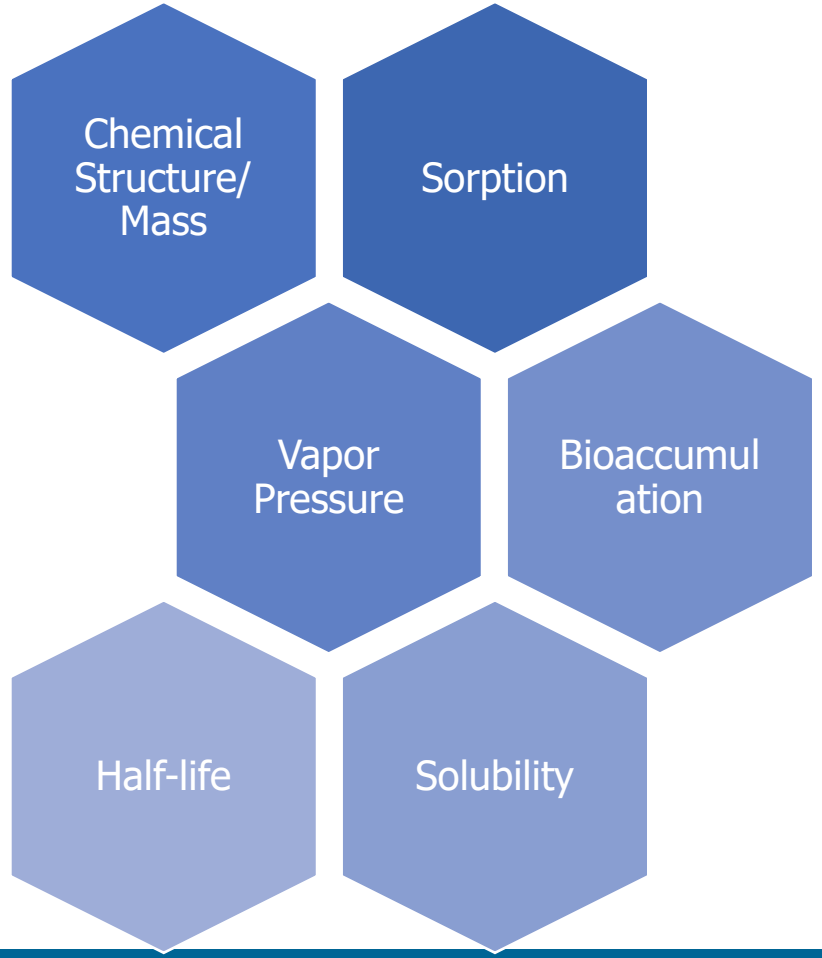


Figure 1-6. Scanning electron micrograph of TRWP collected from a storm drain. Yellow arrows indicate the inclusion of debris, from the road or brakes. The large surface area of the TRWP facilitates leaching of 6PPD and 6PPD-q.
Source: K. Paterson of the San Francisco Estuary Institute (Used with permission)

Physicochemical Properties

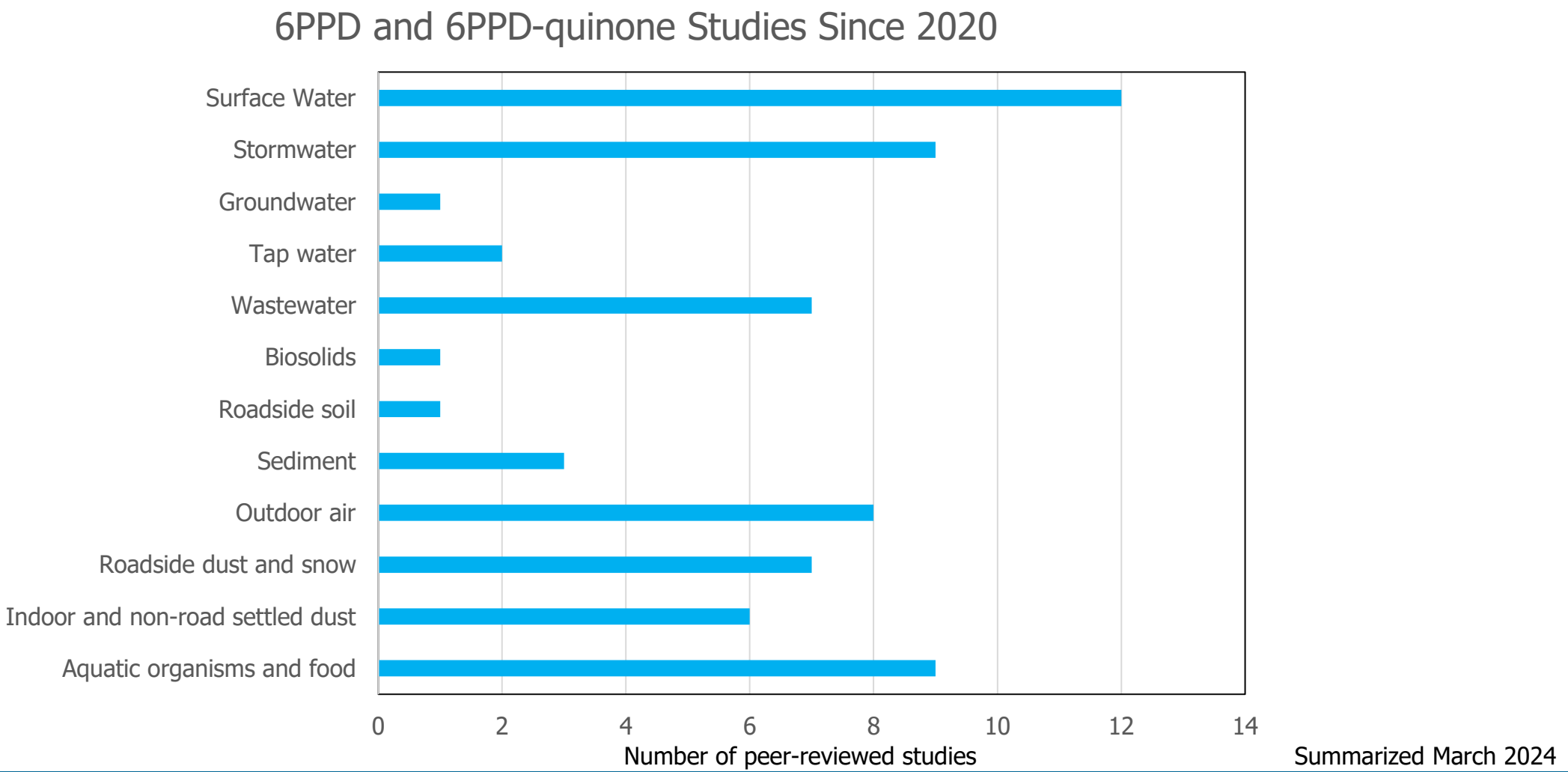
Detail about these properties included in Section 3:



Key Properties

	6PPD	6PPD-quinone
Solubility	mg/L solubility	µg/L solubility
Half-Life	Less than a day	Weeks
logK_{ow}	4.7	4.3
	Hydrophobic: Sufficiently soluble to be transported by water (until captured by organic matter)	

Peer-Reviewed Occurrence Studies



https://6ppd.itrcweb.org/section-4-tables-occurrence-fate-transport-and-exposure-pathways/

Surface Water & Stormwater

Surface runoff and stormwater are major mechanisms for transporting TRWP, 6PPD, and 6PPD-q to receiving surface water

- Stormwater – **6PPD** non-detect to 0.075 ug/L **6PPD-q** non-detect to 5.58 ug/L
- Surface water – **6PPD** non-detect to 0.099 ug/L **6PPD-q** non-detect to 2.85 ug/L

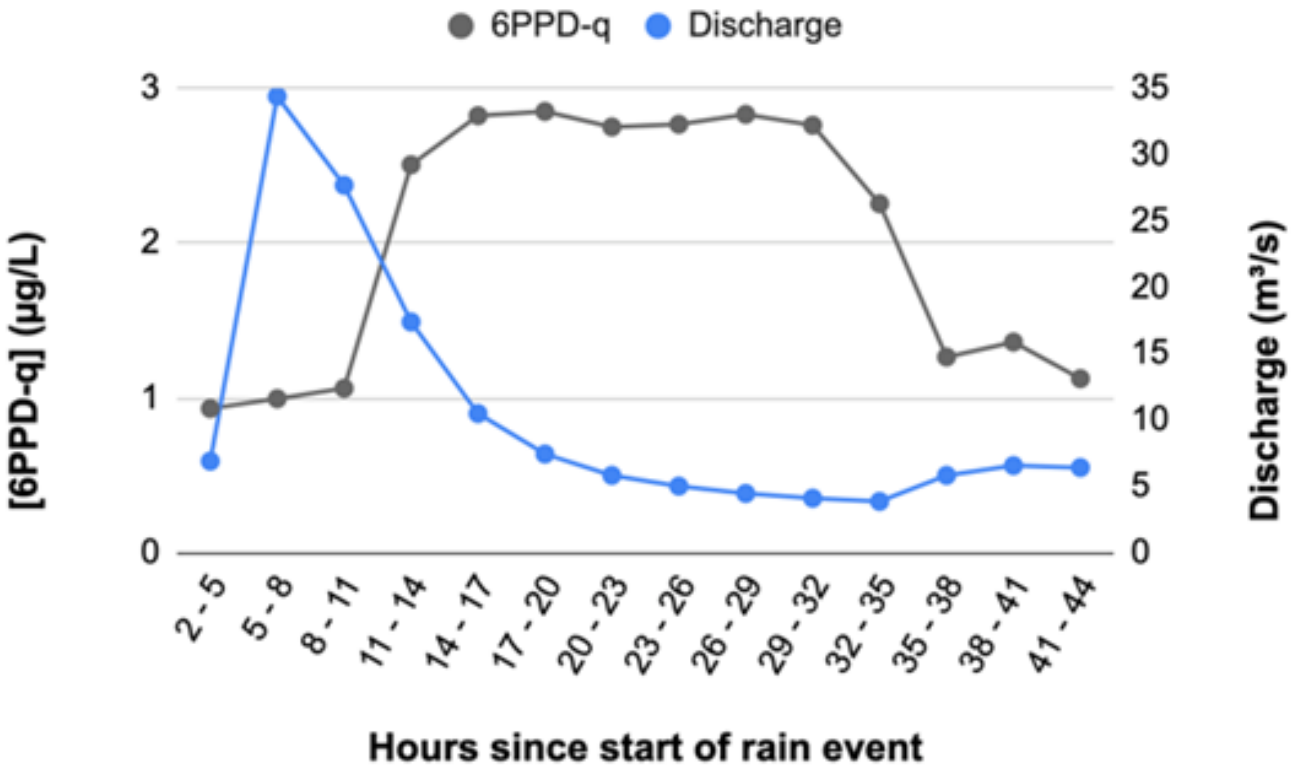
https://6ppd.itrcweb.org/4-occurrence-fate-transport-and-exposure-pathways/#4_1

Image: Oakland County, MI Stormwater Management Program

Image: Delaware DOT Erosion, Sediment, & Stormwater Section

6PPD-quinone Storm Hydrograph

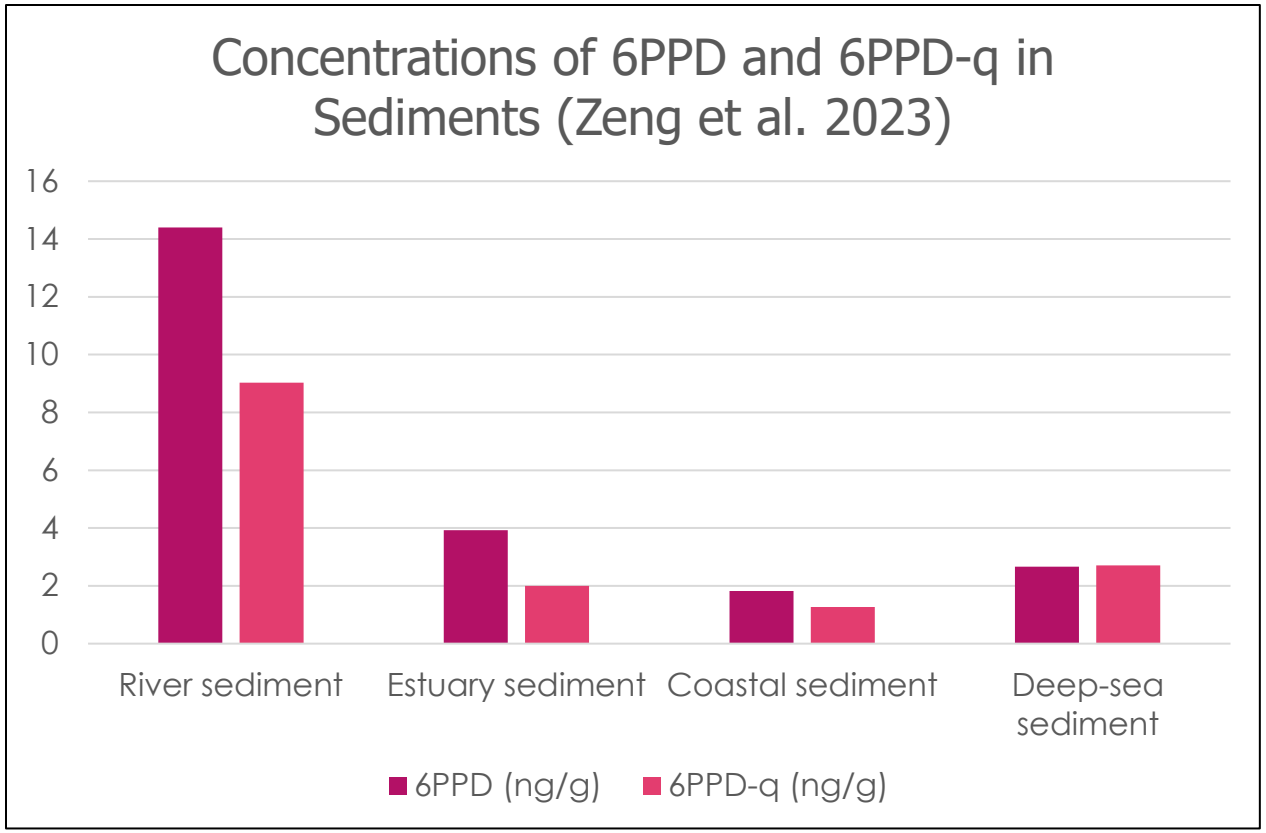
- Peak concentration of 6PPD-q may not be observed for many hours after peak discharge
- Single time-point grab samples may not represent an ecologically relevant concentration
- The greater the percent of impervious surface within a watershed, the more difficult it is to capture the pollutant peak



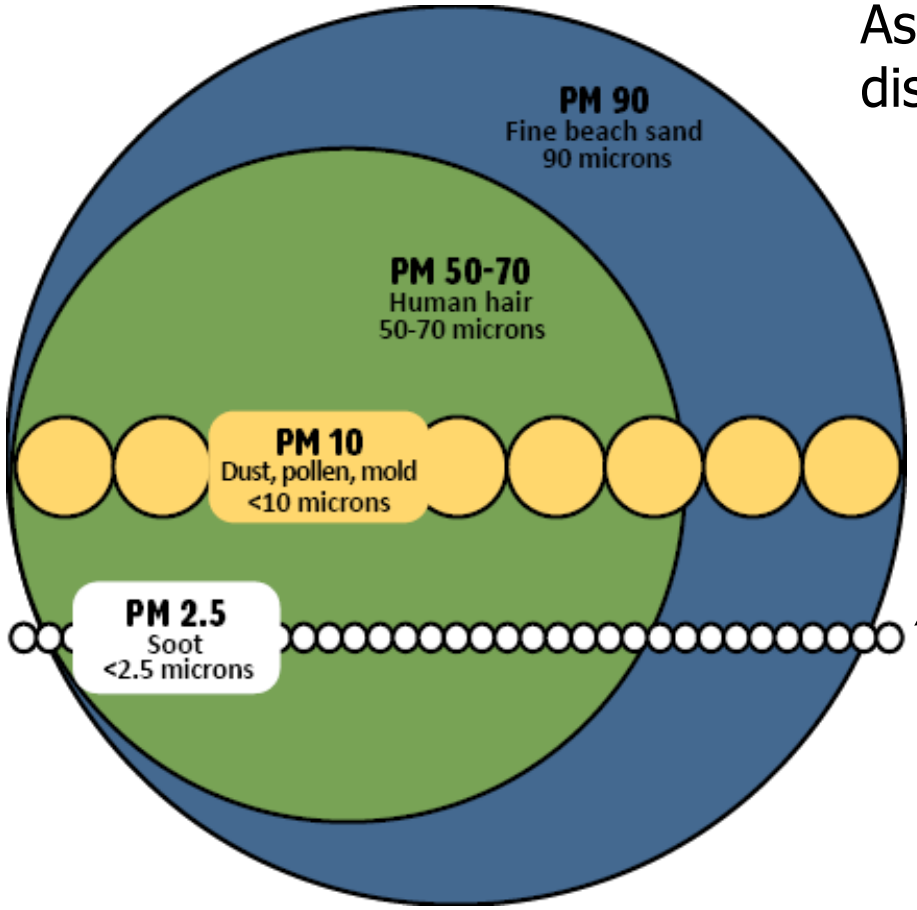
Reference C. Johannessen, 2021 10.1007/s00244-021-00878-4
Provided by Rhea Smith

Soil & Sediment

- Tire, road, and soil particles are transported by stormwater and surface water.
- The allocation between what stays suspended in water and what is deposited in the sediments and soils is unknown.
- Biodegradation of 6PPD and 6PPD-q in soil has been observed.



Air



As tires wear down, particles containing 6PPD and 6PPD-q are dispersed into the air primarily through TRWP.

Larger particles likely deposit near roads

Smaller particles can stay suspended in air for long periods and inhaled by organisms

Both 6PPD and 6PPD-q are unlikely to volatilize

Image Courtesy of Washington State Department of Ecology Air Quality Program

Potential Food Sources & Human Consumption

Lettuce

Fish Species

Property	6PPD	6PPD-q	Comments
Bioconcentration (BCF; unitless)	617 - 801	20.9	Below US EPA Sustainable Futures / P2 Framework Manual bioaccumulation risk value of 1,000 for fish.

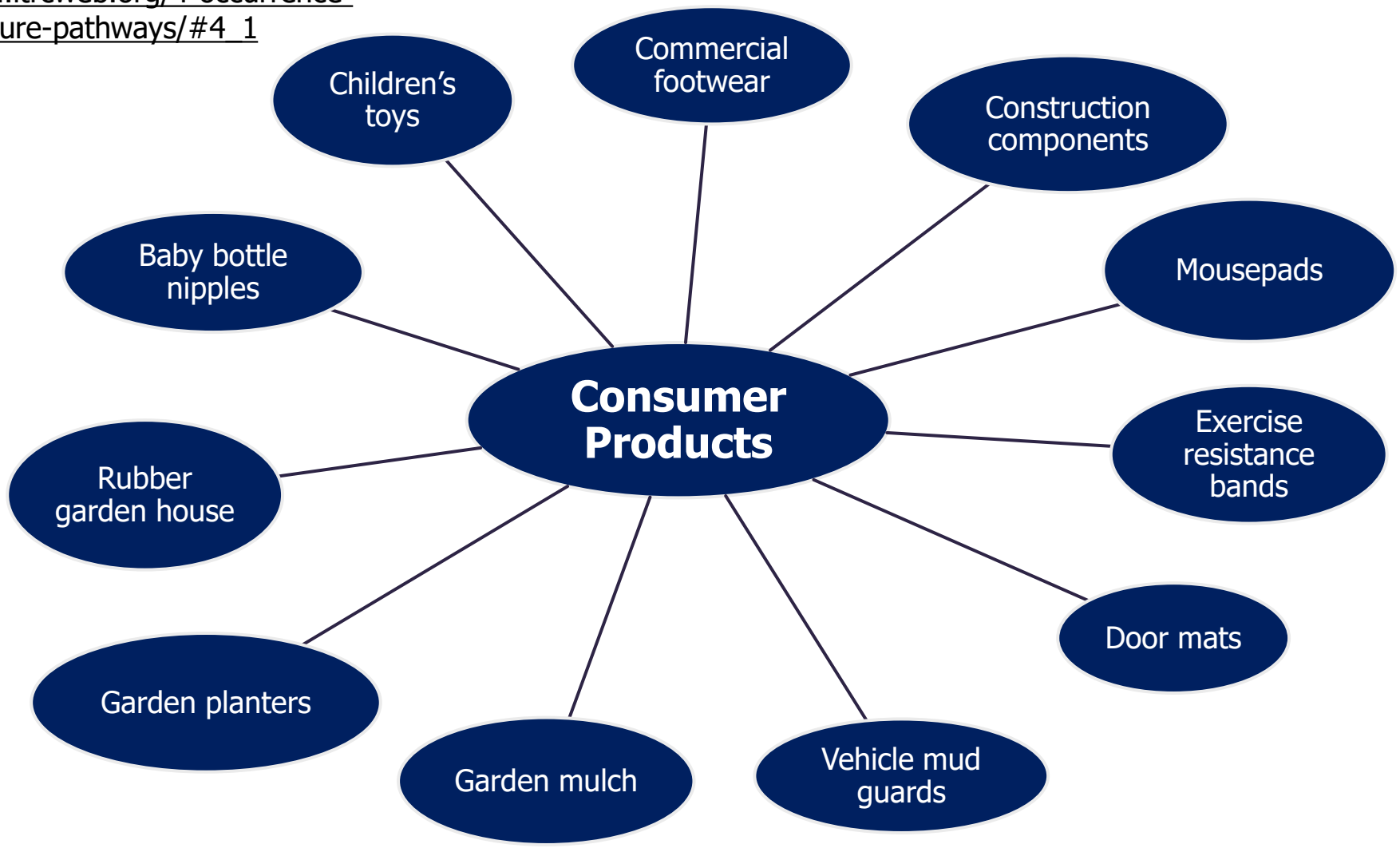
See Section 4.5 for additional information and references: https://6ppd.itrcweb.org/4-occurrence-fate-transport-and-exposure-pathways/#4_5

Image Courtesy of: US Department of Agriculture

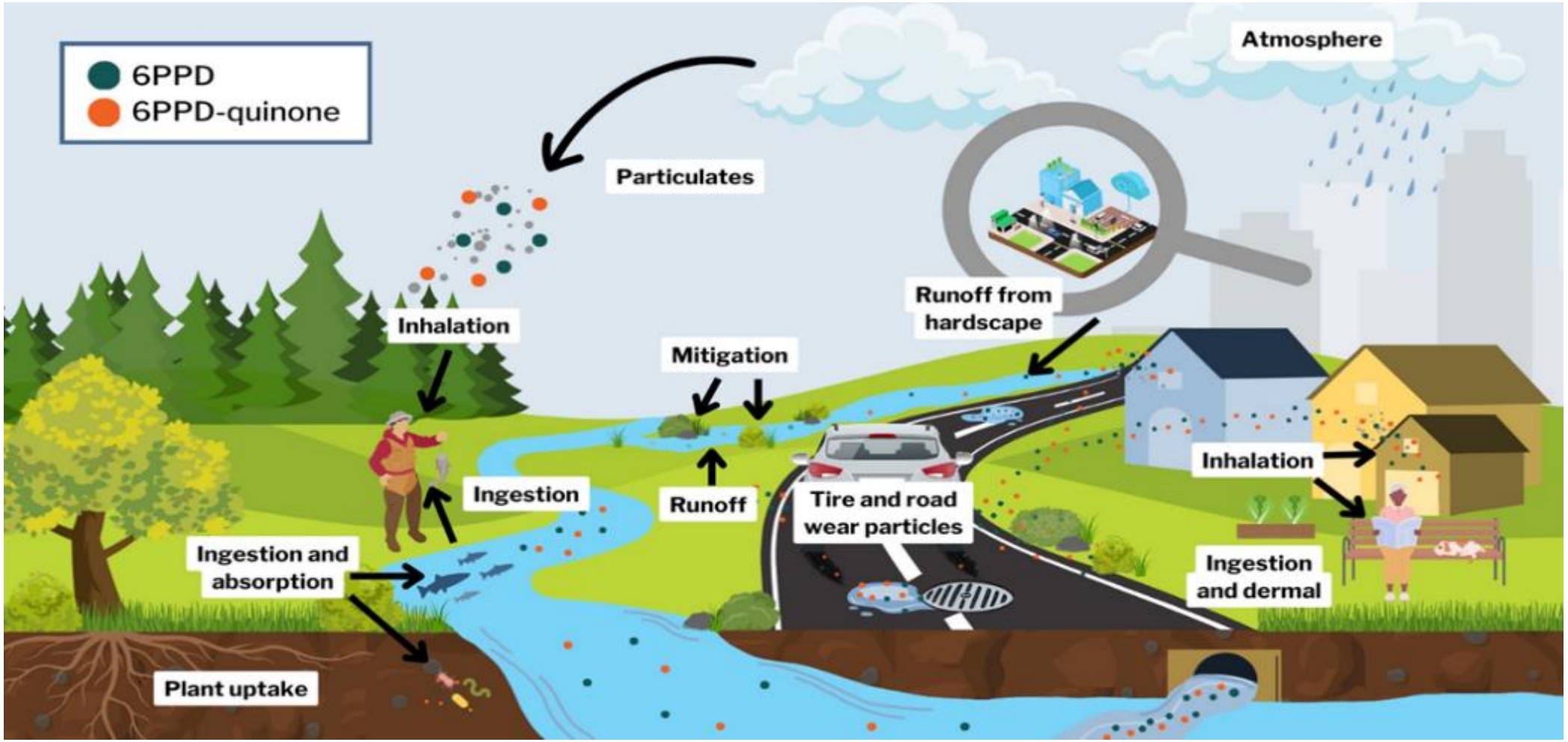
Image: Public domain

Consumer Products

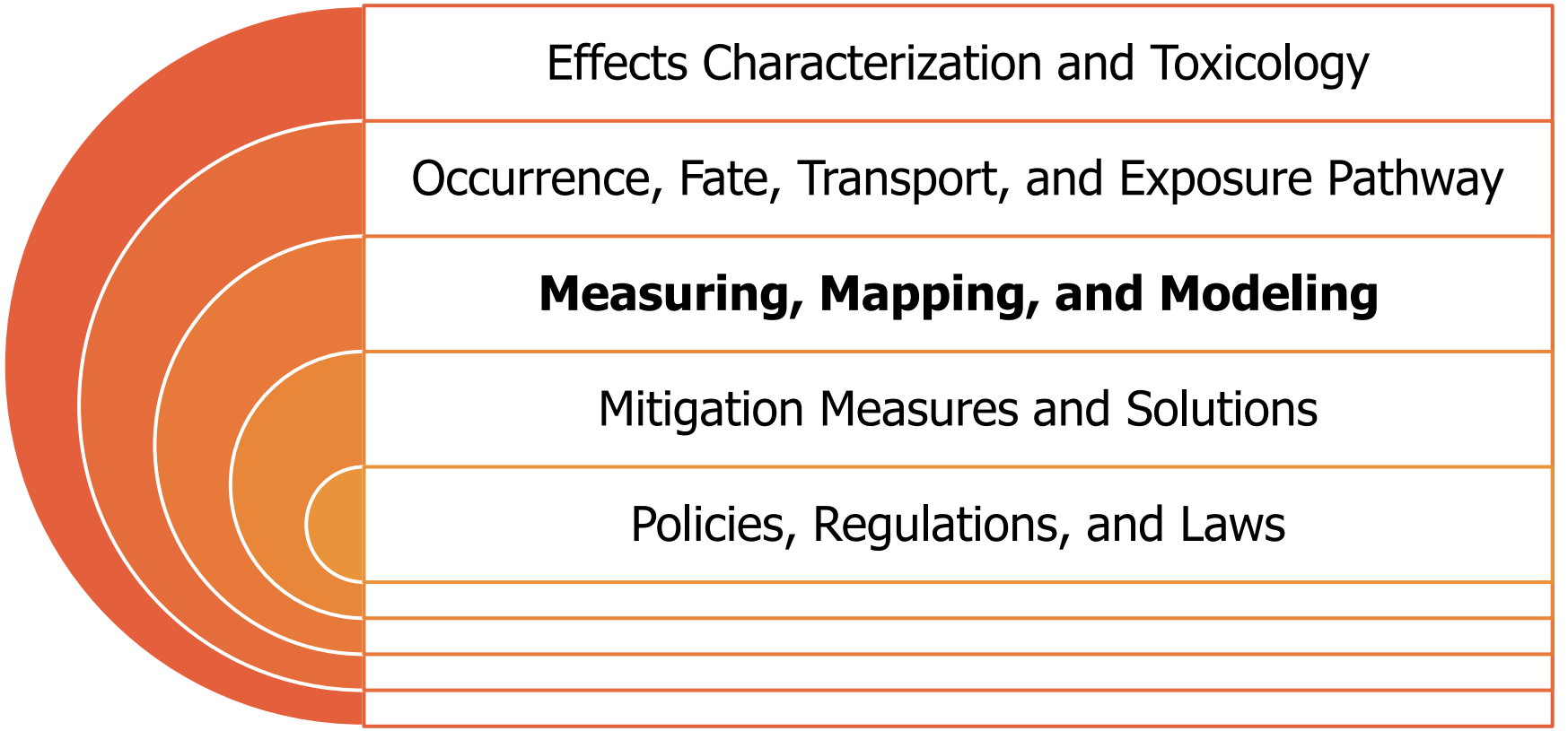
Section 4.6: https://6ppd.itrcweb.org/4-occurrence-fate-transport-and-exposure-pathways/#4_1



Occurrence, Fate, and Transport



Road Map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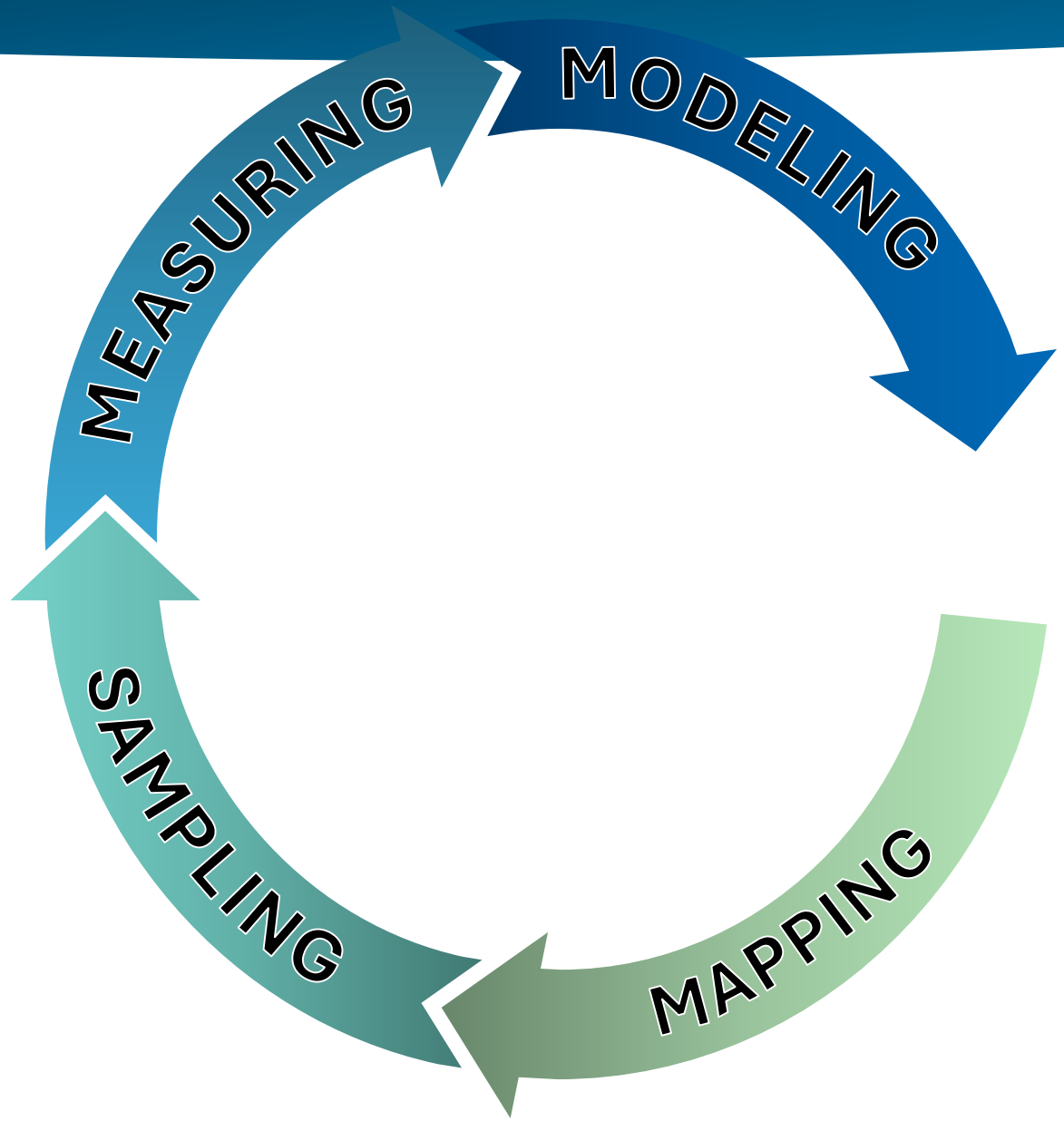
Learning Objectives

Understand available mapping tools that can assist in study design

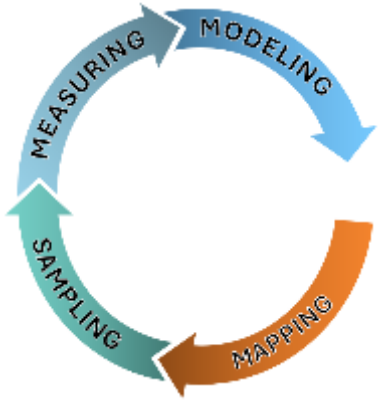
Understand different options of sampling & analysis for 6PPD and 6PPD-quinone in various media

Measuring, Mapping, and Modeling

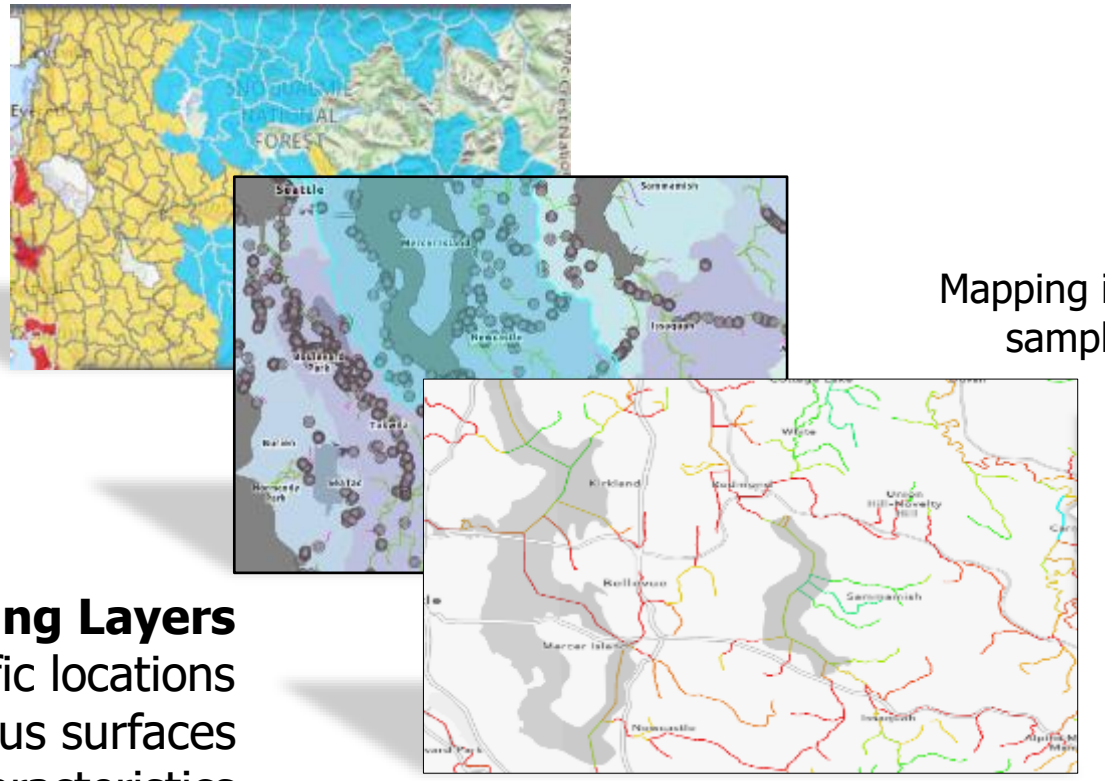


Critical tools to understand the occurrence, fate, and transport of contaminants

Adaption of tools for 6PPD and 6PPD-quinone



Mapping



Mapping is used to inform sampling locations

Hotspots can be identified based on key environmental locations

Key Mapping Layers

High-traffic locations
Impervious surfaces
Watershed characteristics
Precipitation
Dilution
Flow rate
Sensitive species locations

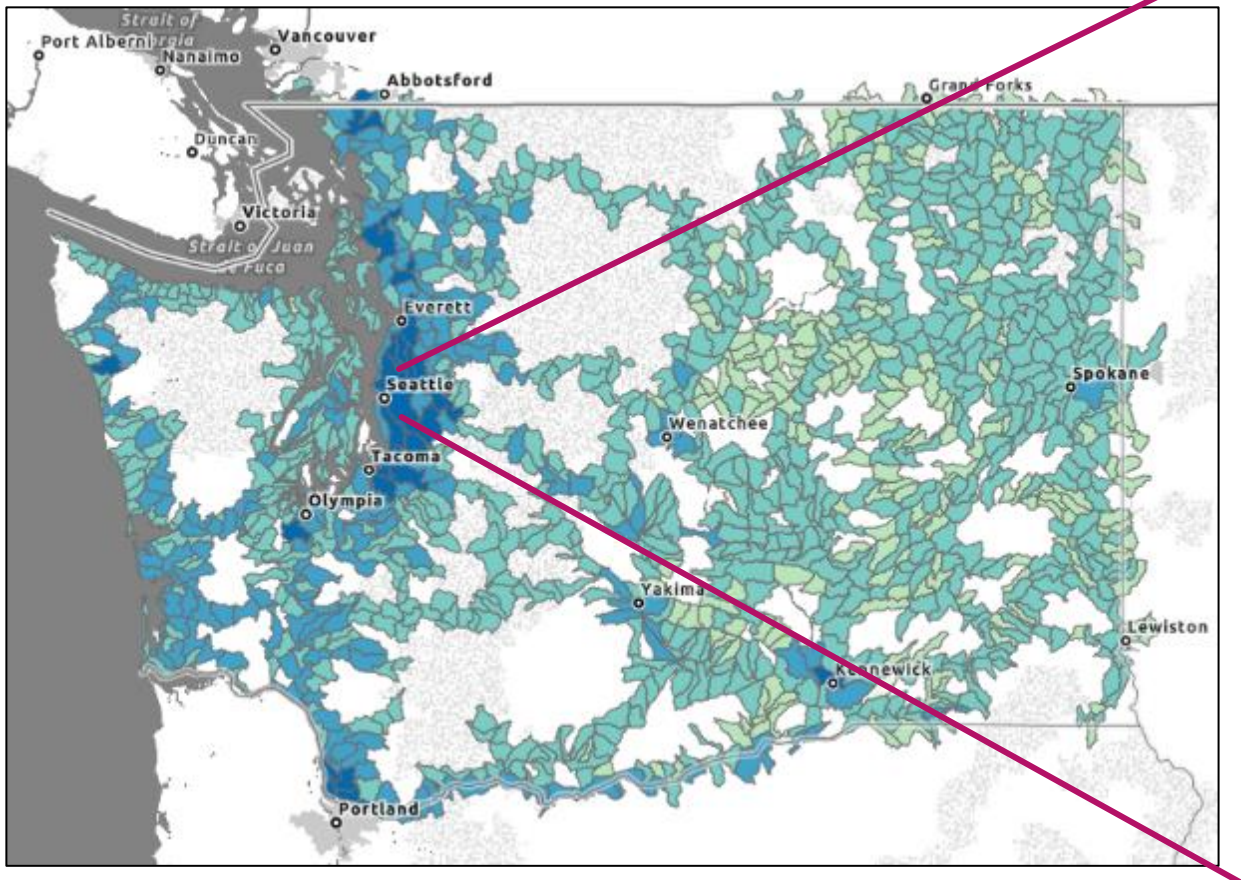
Example Mapping Tools

Storymap	Freshwater Explorer	Roads to Ruin
State	**Federal**	**Risk**

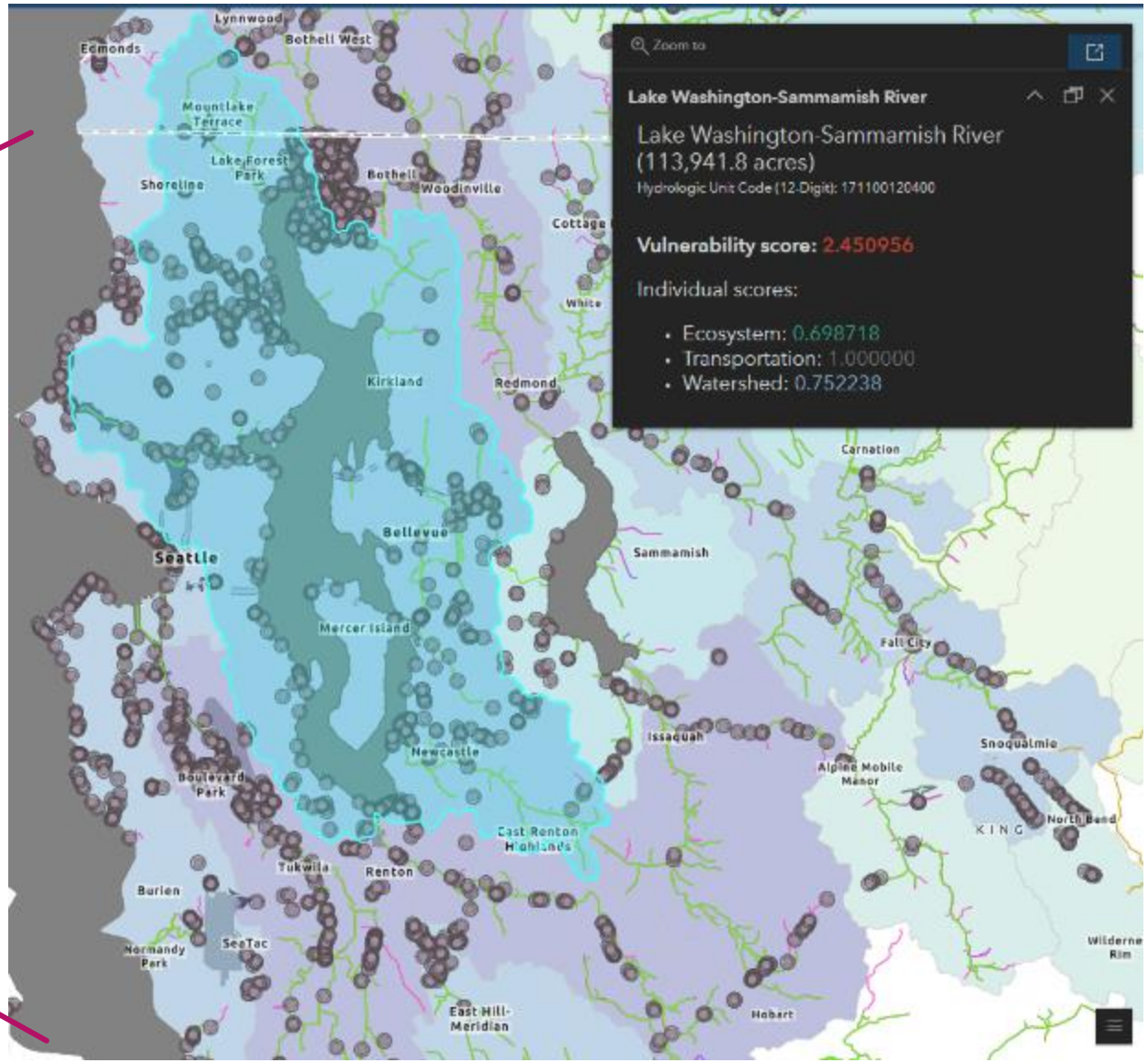
https://6ppd.itrcweb.org/5-measuring-mapping-and-modeling/#5

State Mapping Example Tool

Storymap Washington Department of Ecology
Visualizing the potential occurrence of 6PPD-quinone along roadways near salmon-bearing waterbodies



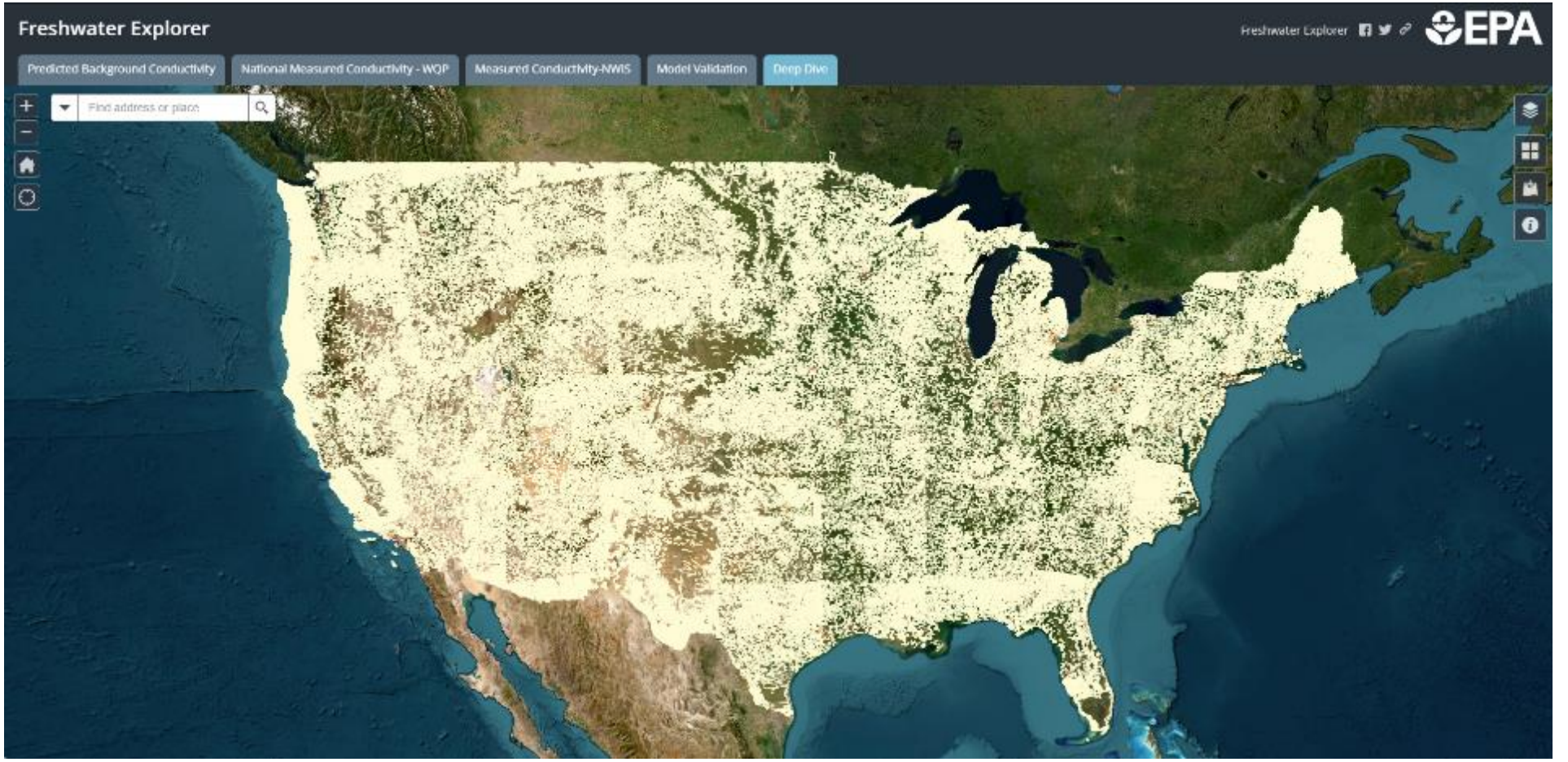
The Washington Department of Ecology Source: Washington Department of Ecology website, Tire Contaminants (wa.gov)



Federal Mapping Example Tool

USEPA Freshwater Explorer

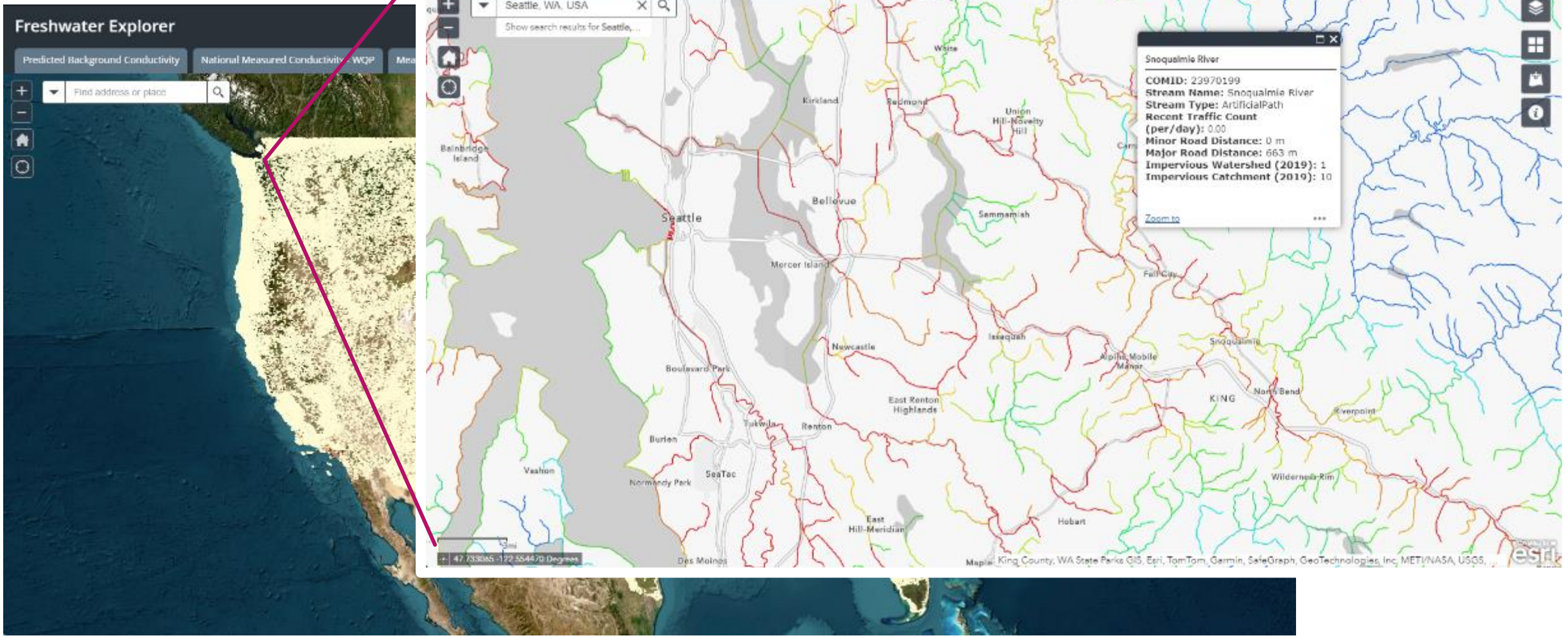
Visualizing impervious surfaces, traffic, and road proximity to streams



Source: Screenshot from USEPA Freshwater Explorer, https://www.epa.gov/water-research/freshwater-explorer

Federal Mapping Example Tool

USEPA Freshwater Explorer

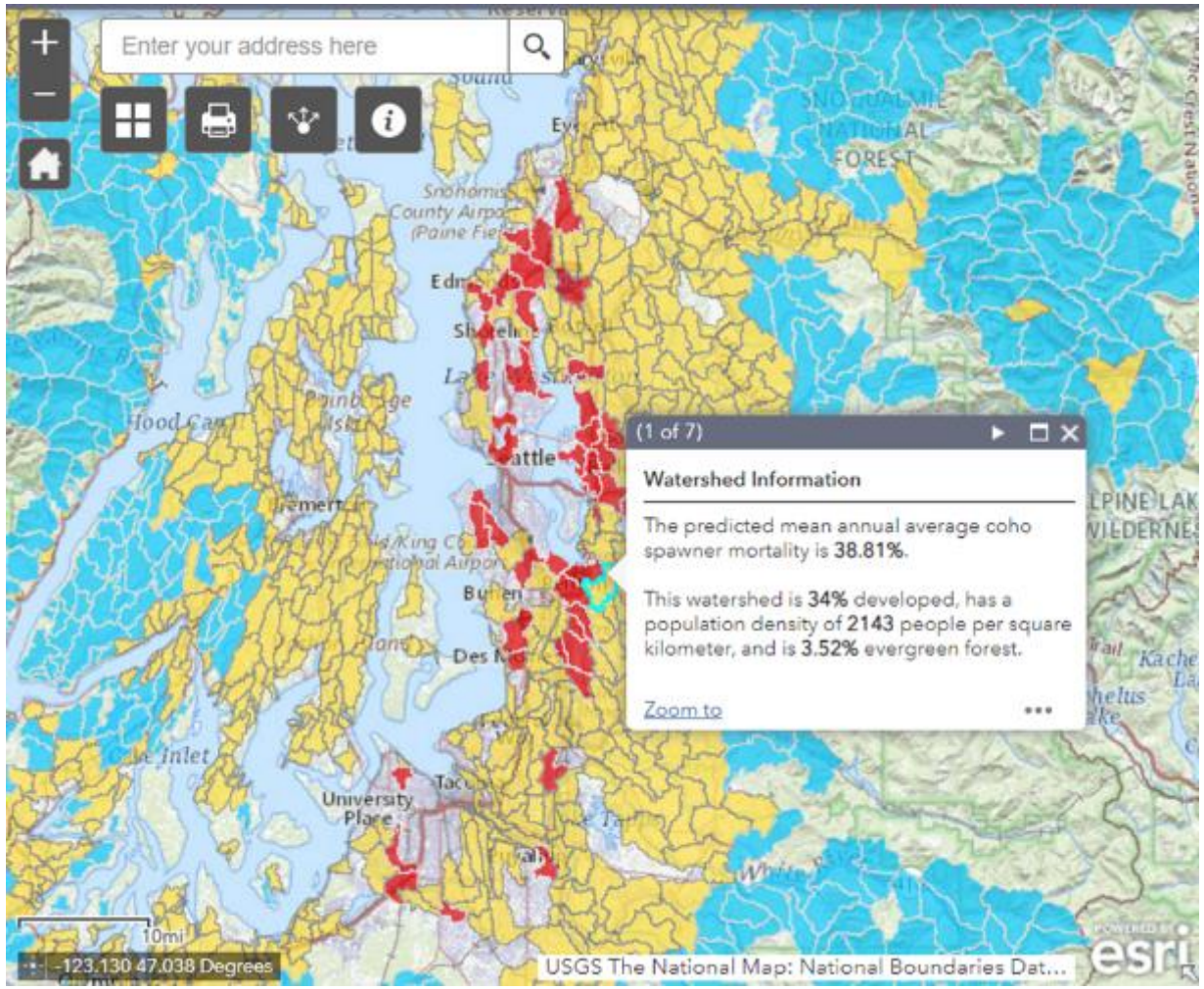


Source: Screenshot from USEPA Freshwater Explorer, 20240806, Seattle, Washington
https://www.epa.gov/water-research/freshwater-explorer

Risk Mapping Example Tool

Predicted Mean Annual Coho Spawner Mortality Map

- Visualize differences across the area and select drainage basins
- See predicted mean percentage annual average coho spawner mortality and a brief characterization of the area.
- Red areas predicted to have high mortality; yellow areas less mortality.



Source: USFWS, NOAA, and Washington State University (2019)
https://www.arcgis.com/apps/webappviewer/index.html?id=53ea11d4125146628026b80241716962

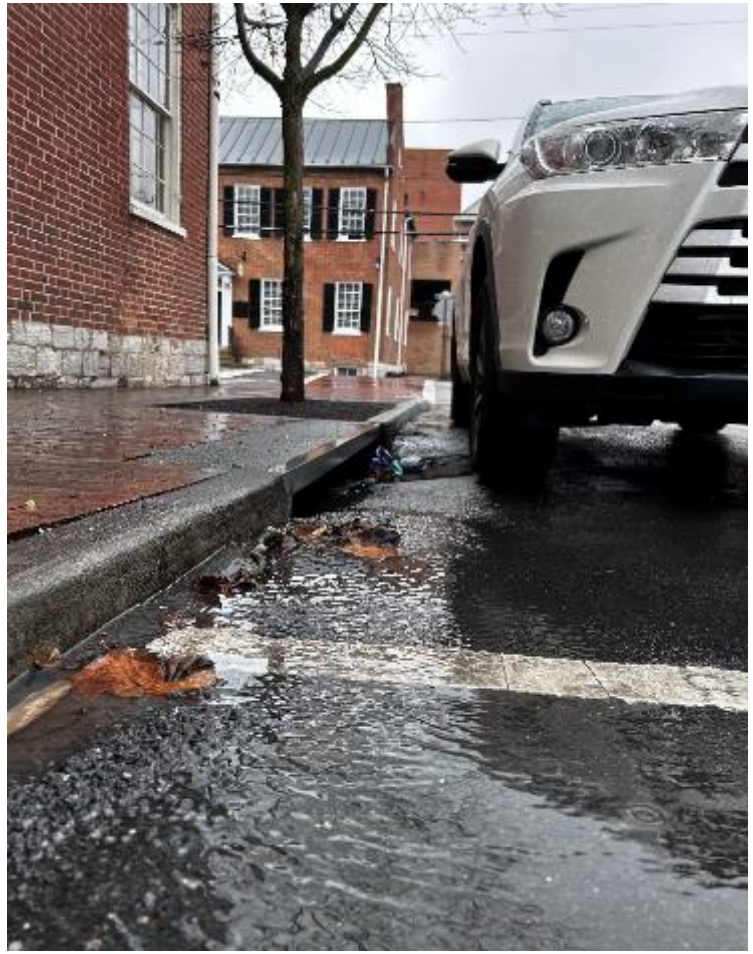
Sampling

Physicochemical Considerations

- 6PPD lower aqueous detection frequency
- 6PPD-quinone is hydrophobic and plastic materials should be avoided
- 6PPD and 6PPD-quinone interact with suspended solids

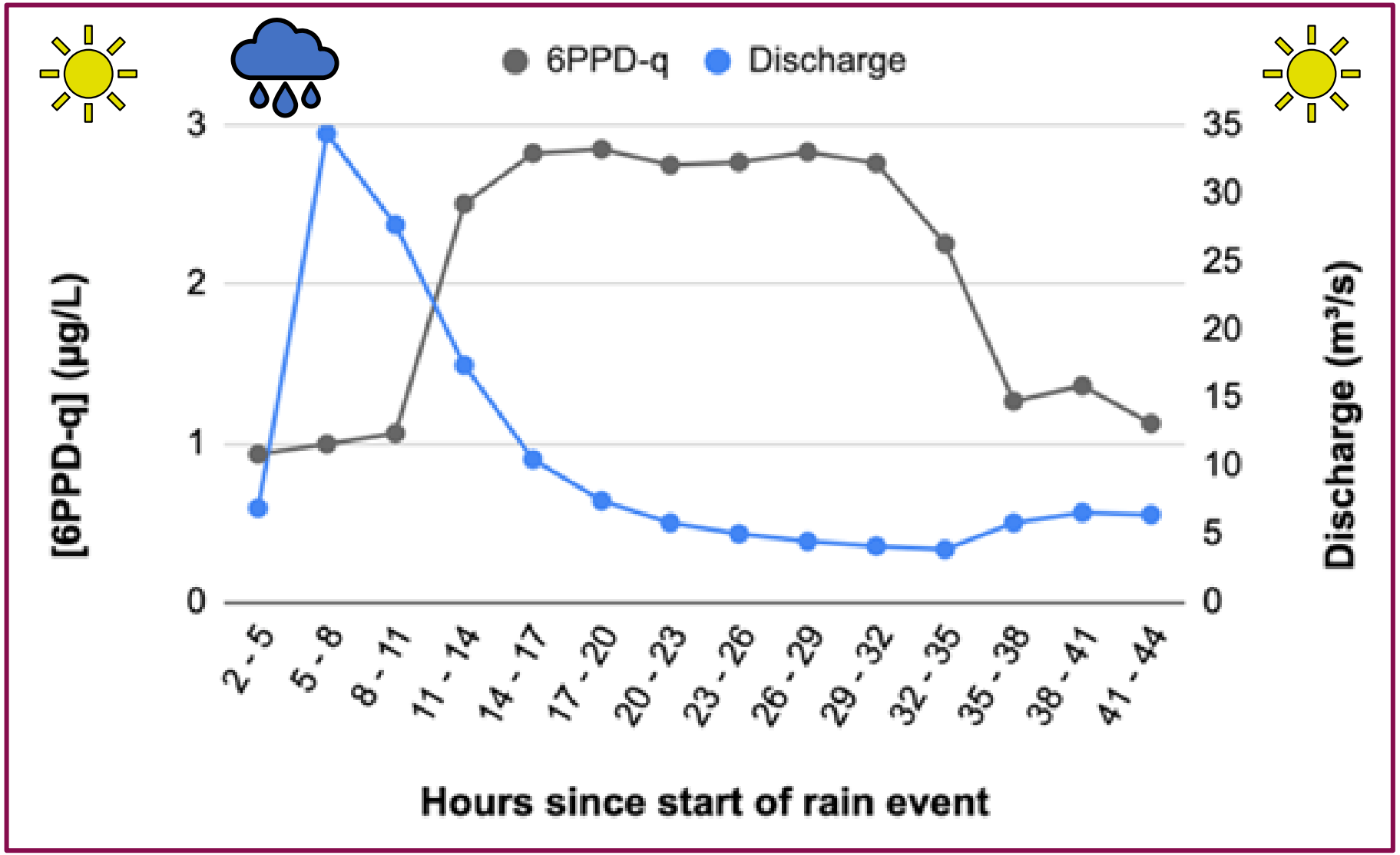
Grab, automated, and passive sampling

General guidance for field sampling is available in Chapter 5 of the Guidance Document



Photos Courtesy of US Geological Survey

Considerations for Watershed and Stormwater Sampling



Reference C. Johannessen, 2021
10.1007/s00244-021-00878-4
Provided by Rhea Smith

Grab Sampling

Pros	Cons
Requires minimal equipment	Requires storm chasing at odd times and days
Requires less technical training	Less likely to catch the pollutant peak
Flexible for short-term larger spatial studies	Requires more field technicians
Less likely to have equipment vandalized or stolen	It represents a snapshot in time

Photos Courtesy of WA Dept of Ecology

Autosampling

Programmed discrete and continuous sampling

Pros	Cons
Involves less storm chasing	Specialized equipment
Less field staff	Technical training
Standardized sample timing and duration	Cumbersome for short-term deployments
More likely to catch the pollutant peak associated with storm events	Risk theft and vandalism of equipment

Photo Courtesy of WA Dept of Ecology

Passive Sampling

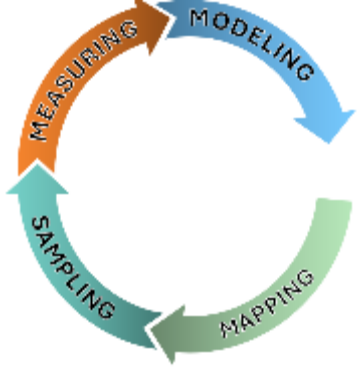
Pros	Cons
Involves less storm chasing	Specialized equipment
Less field staff	Technical training
Standardized sample timing and duration	Assumptions are made regarding the sampling rates
More likely to catch storm events, it's like filming a movie	Risk theft and vandalism of equipment

Photos Courtesy of WA Dept of Ecology

Air Sampling

Active	Passive
Captures particulate matter	Application of passive air samplers (PUF-PAS) for 6PPD and 6PPD-q
Quartz fiber filters and air samplers have been used to sample for 6PPD and 6PPD-q	Can be deployed for 24 hours to several months

Photos Courtesy of US EPA



Measuring

Commercial, public, & research laboratories

Considerations for laboratory analysis:

- method accreditation
- method detection limits
- sample holding times
- quality control parameters
- dissolved vs suspended fraction

Measuring for 6PPD

Relatively unstable

- Ozone scavengers can increase stability but cause instability for 6PPD-quinone

No standardized or approved methods for 6PPD

LC-MS/MS or GC-MS/MS common analysis methods

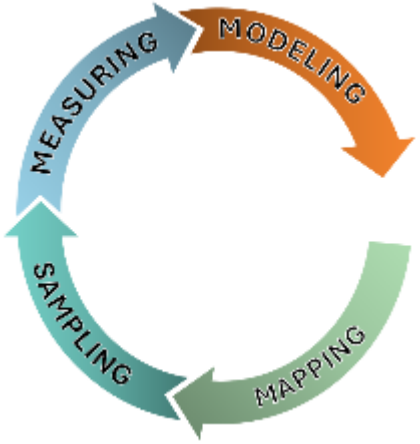
Methods without stabilizing agents provide an estimate of 6PPD

Measuring for 6PPD-quinone

- LC-MS/MS or GC-MS/MS
- After field collection keep on ice in the field and in the refrigerator
- ng/L reporting limits

Water
EPA 1634 Draft Method for 6PPD-q 14 day hold time pre-extraction 28 day hold time post-extraction 250 ml amber **glass bottles**
Research & commercial methods available
Whole water concentrations
USGS research method shows 6PPD-q stability during freezing

Various Media (air, sediment, soil, biotic)
Research & commercial methods available
A variety of extraction techniques are used to prepare non-aqueous matrices



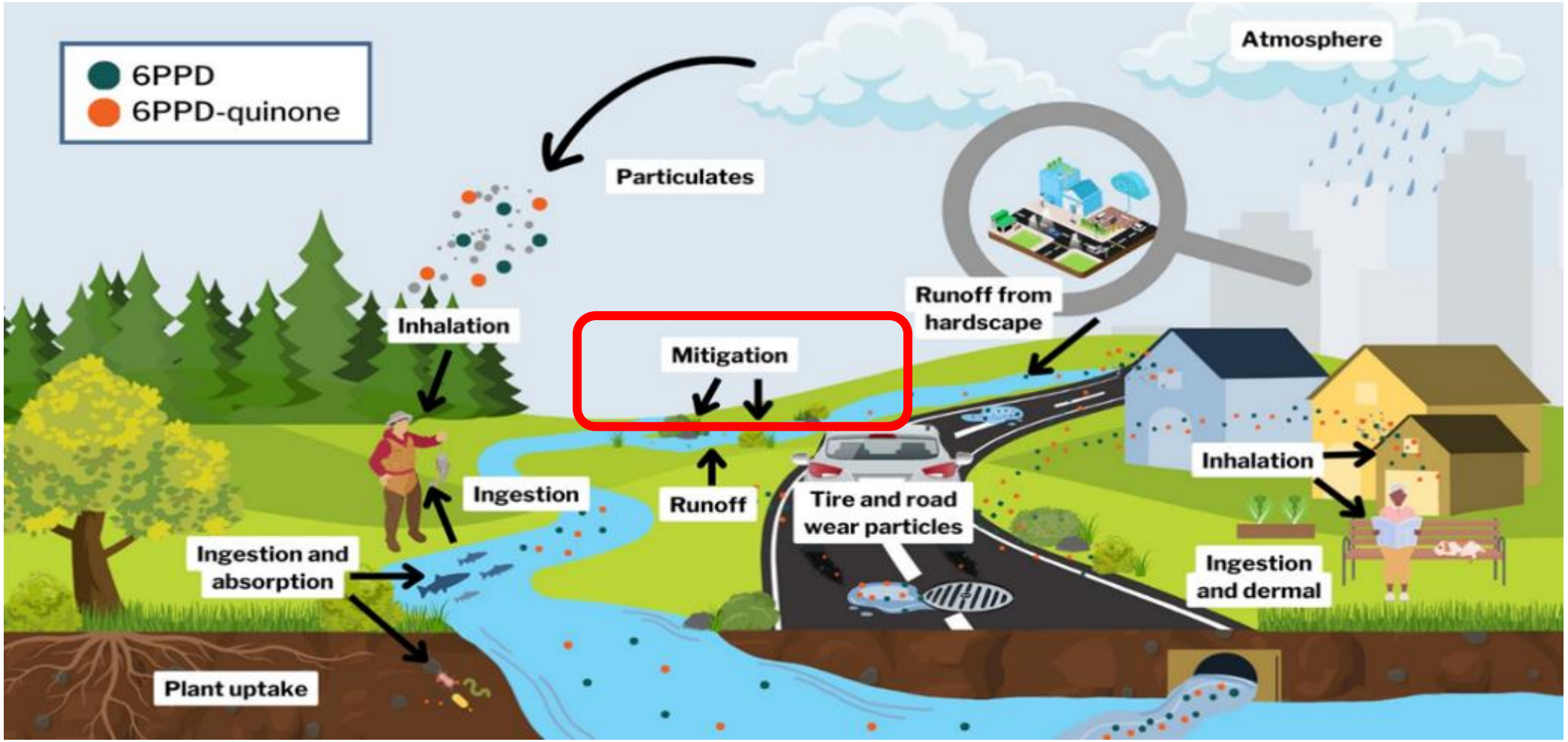
Modeling

- Modeling tools to predict the occurrence of 6PPD and 6PPD-quinone
- Focus sampling efforts
- Data needed to validate modeling

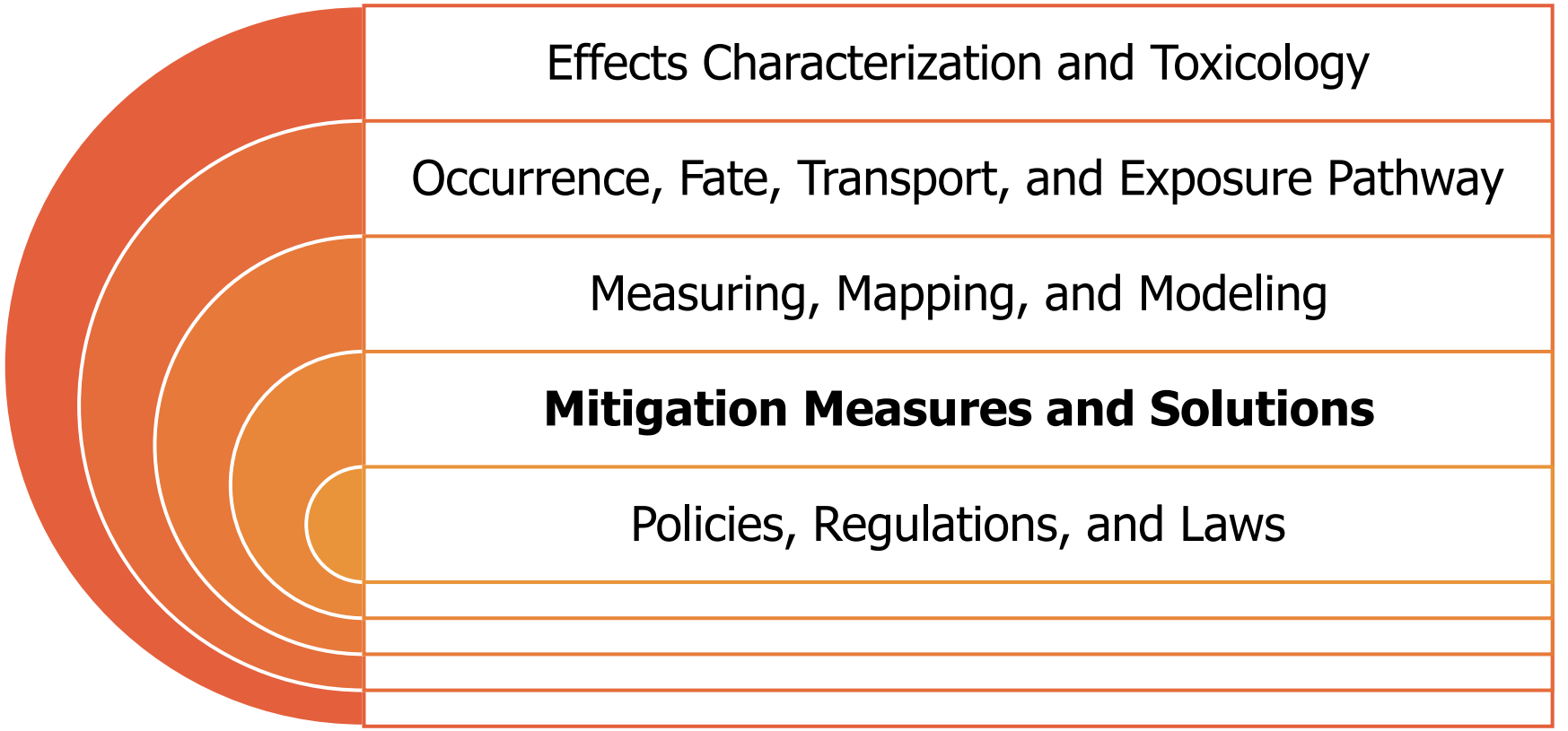
Atmospheric fate and transport modeling
Existing EPA tools for dispersion modeling methods: MOVES and AERMOD to estimate vehicle emissions and transport, including TRWP

Modeling 6PPD-quinone Stormwater Transport to Surface Water
USEPA's VELMA tool (Visualizing Ecosystem Land Management Assessments)

Measuring, Mapping, and Modeling



Road Map


Effects Characterization and Toxicology
Occurrence, Fate, Transport, and Exposure Pathway
Measuring, Mapping, and Modeling
Mitigation Measures and Solutions
Policies, Regulations, and Laws

Mitigation Measures: Learning Objectives

Identify alternative chemicals to replace the parent compound 6PPD.

Mitigation practices to reduce 6PPD-q inputs and implement stormwater control measures (SCMs).

Apply stormwater data and use existing tools to develop SCMs to reduce inputs.

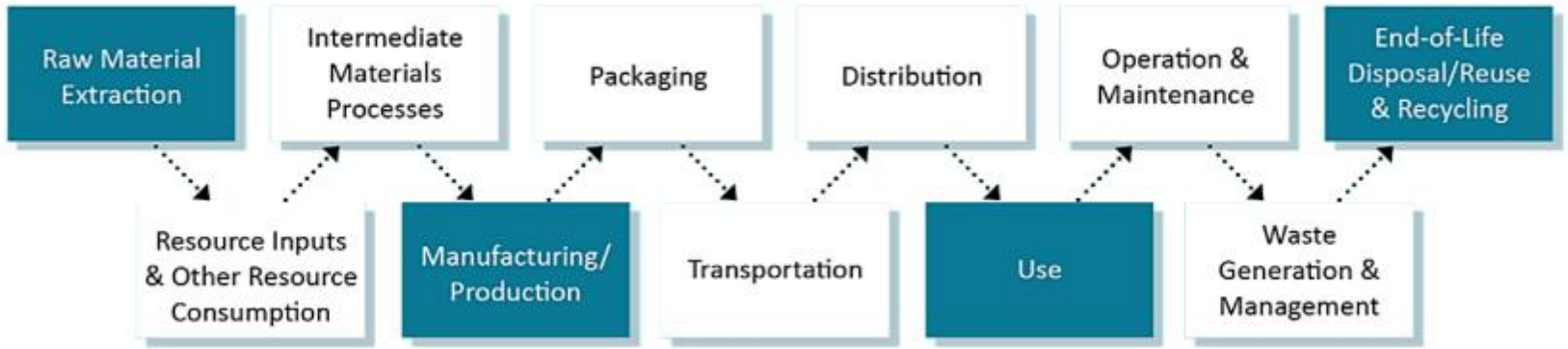
Optimize the balance between mitigation effectiveness and costs.

Alternative Assessments to 6PPD are Underway

Chemical alternatives must be:

- Compatible with tire materials and functionally equivalent
- Rigorously tested for toxicity
- Compliant with TSCA and Federal Motor Vehicle Safety Standards (durability, traction, and performance)
- Comparable in costs to consumers

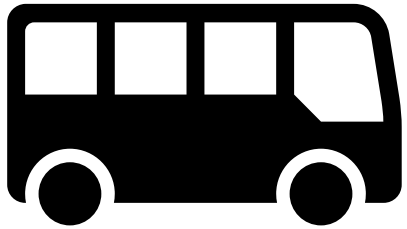
Likely years to decades until full implementation



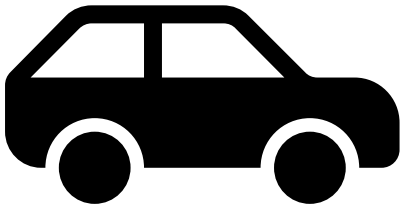
Source: California DTSC (2024)

https://6ppd.itrcweb.org/6-mitigation-measures-and-solutions/#6_2

Controlling the Source

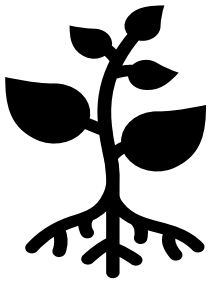


Public Transportation



Driver Behavior

Emerging Technologies



Stormwater Control Measures (SCMs)

Stormwater Planning

Green stormwater infrastructure capturing and treating runoff from heavily-trafficked highway bridge in Seattle.

Photo Courtesy of Madison Rose Bristol

Stormwater Control Measures

Source Control

Flow Control

Runoff Treatment

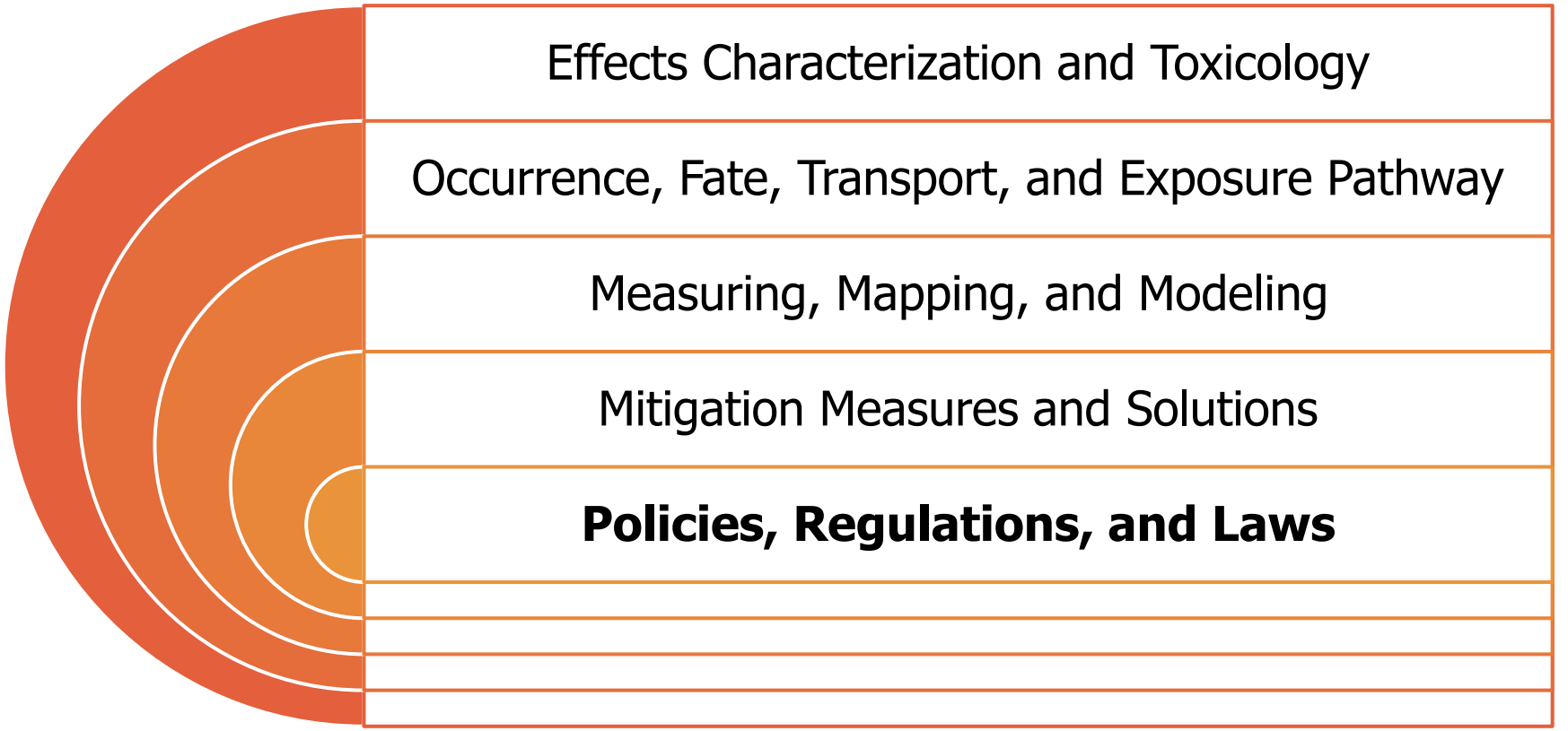
Photos Courtesy of BioCycle 2021, WA State Department of Ecology
Resource: https://stormwater-1.itrcweb.org/

Stormwater Control Measures Research

- Longevity of bioretention media
- Soils and sorbents effectiveness
- Street sweeping effectiveness
- Vegetated and non-vegetated bioretention mixes

Photo Courtesy of Washington State Department of Transportation
https://6ppd.itrcweb.org/6-mitigation-measures-and-solutions/#6_3

Road Map


Effects Characterization and Toxicology
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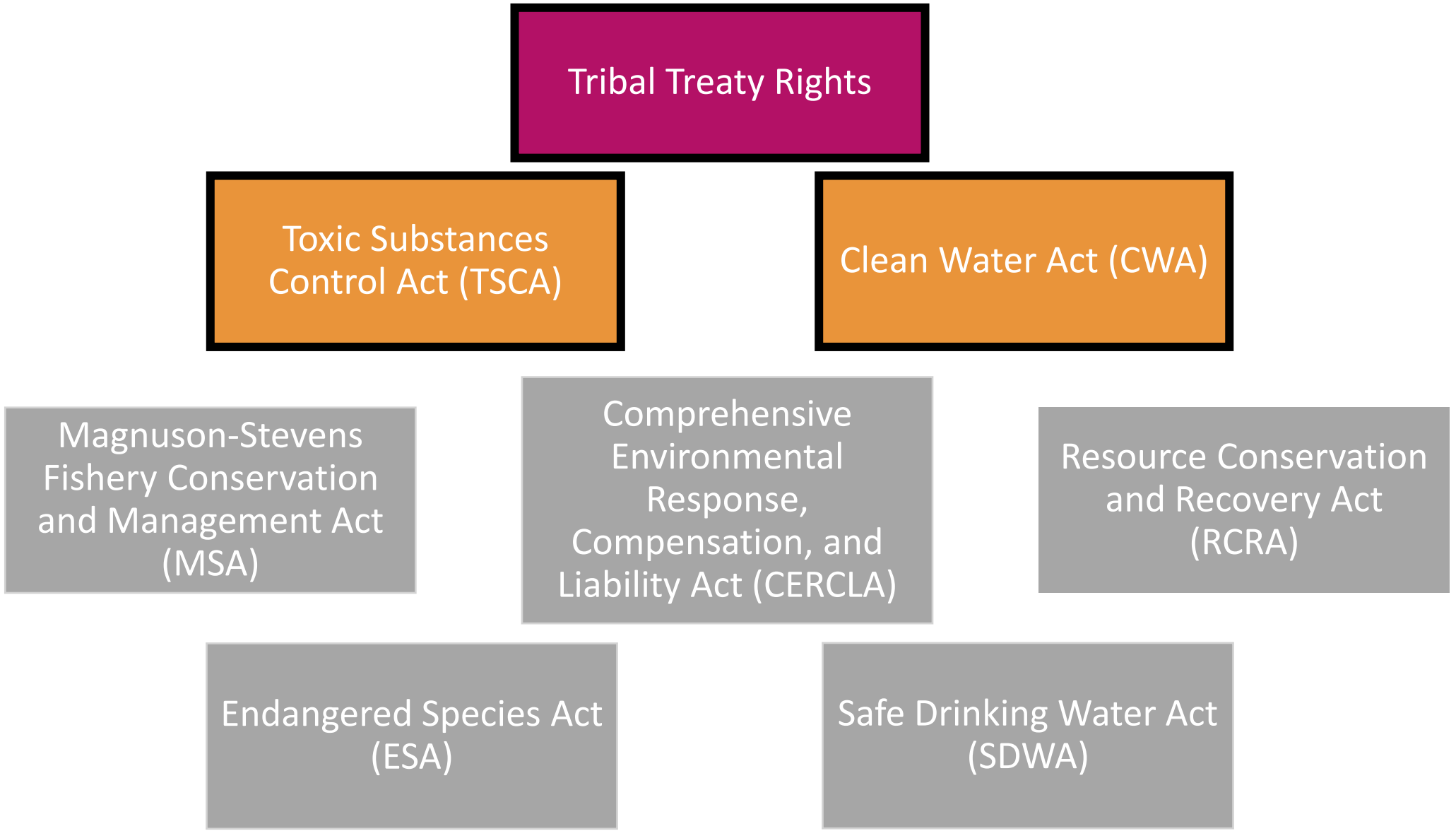
Policies, Regulations, and Laws

Policies, Laws, and Regulations Overview

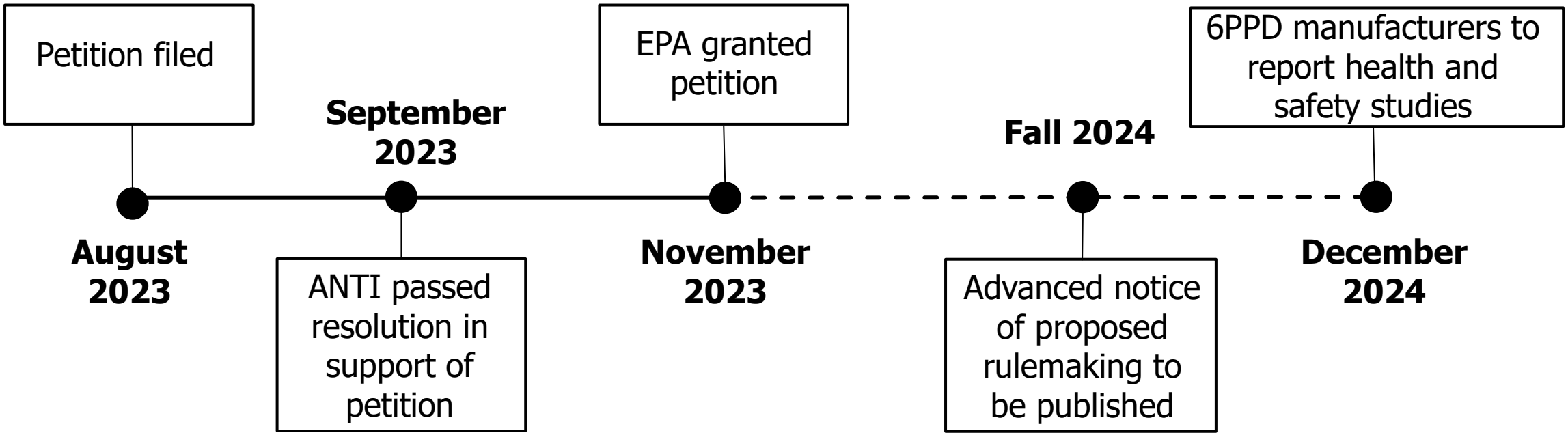
- Federal policies, laws and regulations
- Stakeholders for regulatory actions can be found at all levels of government: federal, state, and local
- States and tribes are currently the key drivers of regulatory actions
- As nationwide awareness grows, so will federal action

Legal Governance



TSCA Case Study – Section 21 Petition

Puyallup Tribe of Indians, Port Gamble S'Klallam Tribe, & the Yurok Tribe



U.S. EPA Response Under the Clean Water Act

Acute Aquatic Life Toxics Criteria: Screening values for freshwater

6PPD-q : 0.011 µg/L

6PPD: 8.9 µg/L

Developing a validated method for measuring 6PPD-q in surface water, Draft Method 1634

Section 7.8.2: Washington is the first state to adopt a numeric water quality criterion for 6PPD-q

Actions for 6PPD Alternatives

California Safer Consumer Products Regulation

75 tire manufacturers have completed Stage 1 Alternatives Analyses with 17 possible alternatives to 6PPD.

Safer Products for Washington Program

WA DOE completing an Alternatives Assessment using hazard criteria developed specifically for 6PPD, including data requirements for sensitive species and other trophic levels.

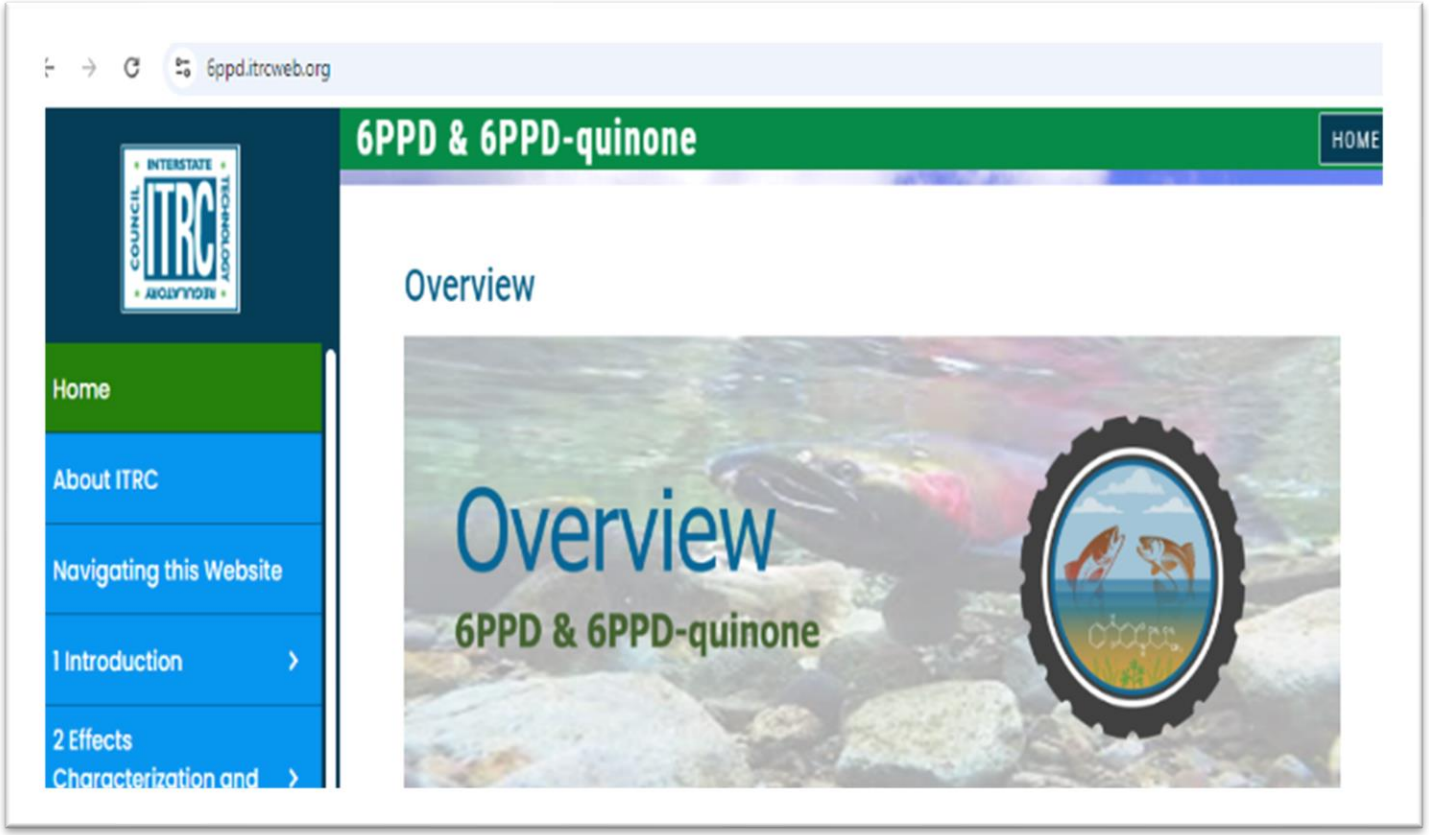
What's Next? Policies & Regulations

Regulation relies on the ongoing scientific research described in previous sections

Mitigation strategies are guided by policy

High priority is finding alternative chemicals to 6PPD and the process for a long-term replacement

Guidance Document



https://6ppd.itrcweb.org

SCAN ME

- Overview
- Introduction
- Effects Characterization and Toxicology
- Chemical Properties
- Occurrence, Fate, Transport, and Exposure Pathways
- Measuring, Mapping, and Modeling
- Mitigation Measures and Solutions
- Policies, Regulations, and Laws
- Information Gaps and Research Needs
- References
- Acronyms, Glossary, Team Contacts

Questions

https://6ppd.itrcweb.org/

Certificate of Completion https://cluin.org/conf/itrc/6PPD-Q/
(emailed after you complete the Feedback Form)