SMART Remediation

6ppd and 6ppd-Q, Environmental Fate and Transport and Current Regulatory Environment;
6-Ppd Quinone: Occurrence and Best Practices in Measurement

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Ottawa | February 8, 2024

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www.vertexenvironmental.ca

Introduction to 6PPD and 6PPD-Q:

Toxicity, Occurrence, Measurement, and Regulatory Status

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SMART Remediation 2024

Brampton, ON

January 25, 2024

MYSTERY CHEMICAL

1980s

Coho Salmon* fish kill events and decreasing populations observed in Pacific Northwest

2011

Road runoff suspected as the cause of fish kills

2018

Research into chemicals identified in tire wear leach

Oncorhynchus kisutch

TERRAPEX SGS

MYSTERY CHEMICAL

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Coho Salmon* fish kill events and decreasing populations observed in Pacific Northwest

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

Nathaniel L. Scholz, Mark S. Myers, Sarah G. McCarthy, Jana S. Labenia, Jenifer K. McIntyre, Gina M. Ylitalo, Linda D. Rhodes, Cathy A. Laetz, Carla M. Stehr, Barbara L. French, Bill McMillan, Dean Wilson, Laura Reed, [...], Tracy K. Collier

[view all]

Published: December 14, 2011 • https://doi.org/10.1371/journal.pone.0028013

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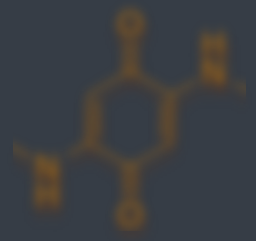

2020

A previously unknown chemical determined to be the cause of acute pre-spawn mortality

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

ZHENYU TIAN, HAOQI ZHAO, KATHERINE T. PETER, MELISSA GONZALEZ, [...], AND EDWARD P. KOLODZIEJ +22 authors Authors Info & Affiliations

SCIENCE · 3 Dec 2020 · Vol 371, Issue 6525 · pp 185-189 · DOI: 10.1126/science.abd6951

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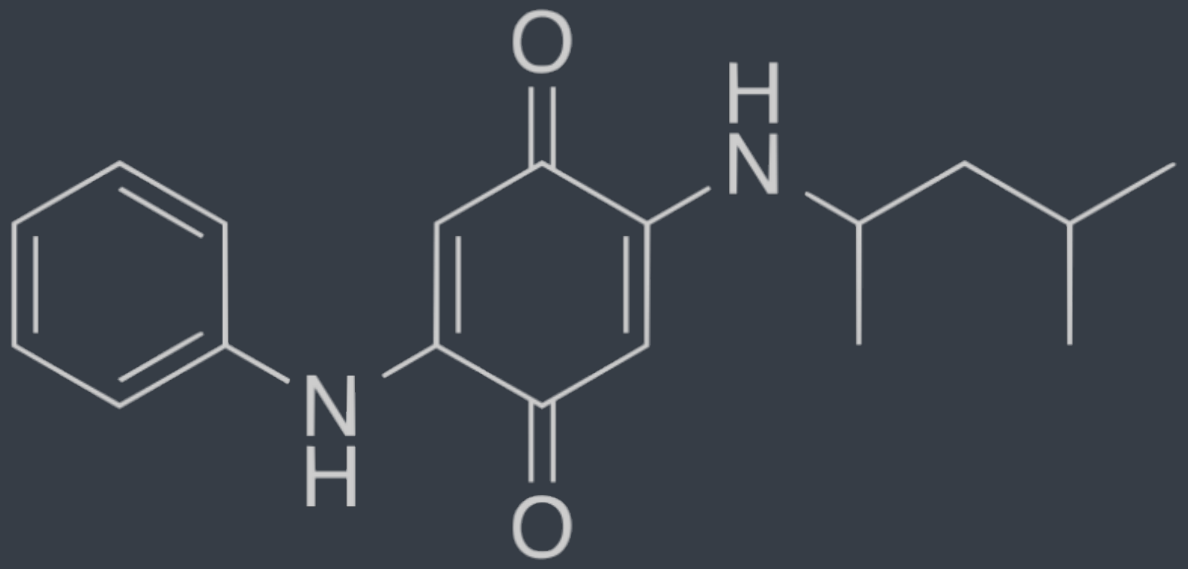
MYSTERY CHEMICAL



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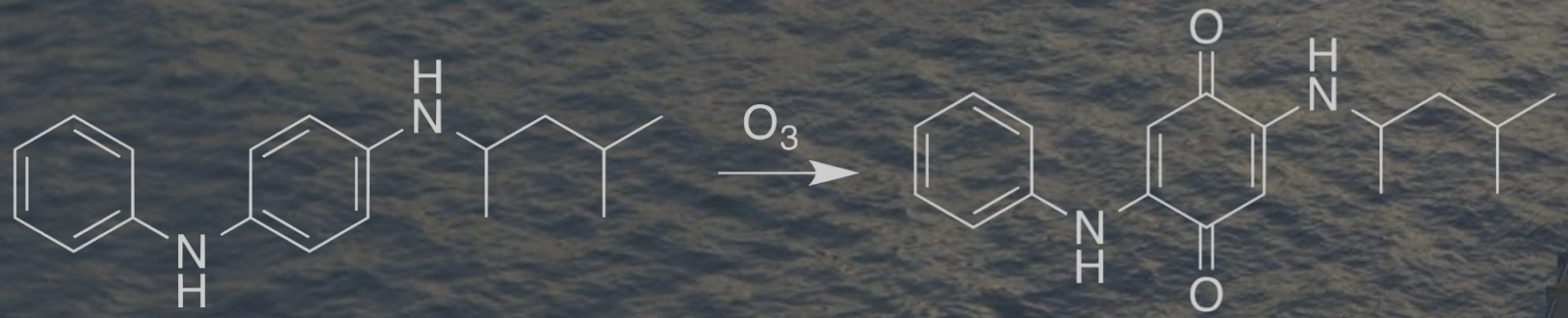
MYSTERY CHEMICAL

N-(1,3-DIMETHYLBUTYL)-N′-PHENYL-
P-PHENYLENEDIAMINE



6PPD **6PPD-Q**

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TERRAPEX

WHO WE ARE

Founded in 1995

Employee-Owned

120+ employees

Health and Safety Focused

Commitment to Diversity and Inclusion

Inogen Alliance Partner for Canada

INOGEN ALLIANCE

TERRAPEX

Multi-disciplinary engineering and science consultancy

- Environmental
- Geotechnical
- Hydrogeology
- Ecology
- Building Science
- EHS

Diverse client base

- Real Estate Development
- Property Management
- Petroleum
- Insurance
- Government Agencies
- Municipalities

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SGS CANADA

I&E

01 Conventional

Most extensive testing capabilities for soil, sediment, water, air, waste and radiochemistry analytical services

02 Field Services

Multidisciplined fleet to provide a variety of techniques and services

03 Specialty

Most extensive CEC & POP test list in the region with lowest DLs available

04 Government

25+ years supporting government contracts municipal-federal

05 Industrial Hygiene

Largest depth of Industrial Hygiene analytical services and equipment rentals

06 Built Environment

Full scope of designated substance analytical capabilities with rush turnaround capabilities

07 Innovative Solutions

Industry leading technical solutions in client portals and real time monitoring

08 Mobile Lab

Availability of mobile laboratory based in US Northeast for customized on-site solutions

SUPPORTING PROJECTS

Remediation, Due Diligence, Risk Assessments, Drinking Water, Wastewater, Landfill, Waste Rock & Acid Rock Drainage, Ambient Air, Incineration & Stack Testing, Ecological & Human Monitoring, Product Testing, Designated Substances, Abatement, Research Support

PRESENTATION GOALS

- 6PPD Basics
- Problems with 6PPD-Q
- 6PPD in the Environment
- Pilot Studies
- Regulatory Status
- What Next?

Are 6PPD and 6PPD-Q
the next major emerging contaminants?

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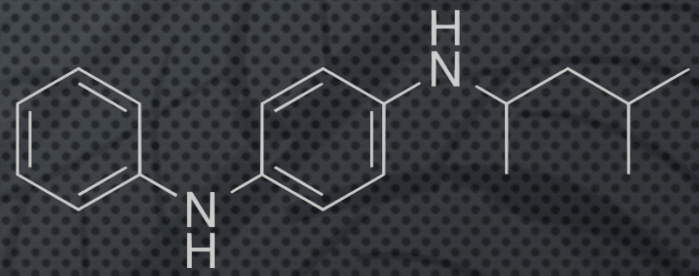
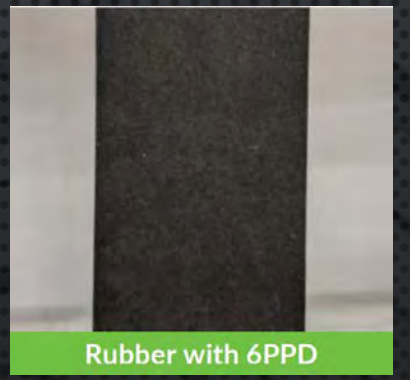
6PPD BASICS

- Part of the *p*-phenylenediamine (PPD) group of anti-oxidants
- Highly reactive anti-oxidant and anti-ozonant



- Allow tires to resist cracking and degradation
- Up to 2% of tire rubber by weight
- Most widely consumed rubber anti-oxidant



U.S. Tire Manufacturers Association

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6PPD BASICS

6PPD used as a Tire Anti-Degradant since 1960s

6PPD transformed to 6PPD-Q via ozone exposure

Rubber products degrade, releasing 6PPD and 6PPD-Q containing tire wear particles

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THE PROBLEM WITH 6PPD-Q

- Unknown until 2020; rapidly evolving state of science
- Second most toxic substance to aquatic species compared to US EPA *Aquatic Life Criteria*
- Widespread in surface water affected by road runoff and stormwater but difficult to quantify

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THE EXTREMELY RAPID TIMELINE OF 6PPD-Q

Jan 2021

- Discovery announced and initial toxicity

Mid-2021

- Synthesis of commercially available standards

Late 2021

- Commercially available analysis
- Regulatory concern and alternatives evaluation (WA State)

Feb 2022

- Revised toxicity estimate to 95 ng/L in juvenile Coho

Through 2022

- Toxicity assessment in multiple species

2023

- Updated estimate of 41 ng/L LC-50 in newly feeding juvenile Coho
- Establishment of an ITRC working group for 6PPD-Q

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6PPD-Q TOXICITY

Table 1. Reported 6PPD-quinone LC_{50} concentrations (50% observed mortality) of salmonids.

Species	LC_{50} (µg/L)	Test duration (h)	Toxicity Key
Coho salmon (*Oncorhynchus kisutch*)	0.04, [24] 0.08, [25] 0.095 [2]	24	Higher
White-spotted char (*Salvelinus leucomaenis pluvius*)	0.51 [26]	24	
Brook trout (*Salvelinus fontinalis*)	0.59 [3]	24	
Rainbow trout/steelhead (*Oncorhynchus mykiss*)	0.64,[29] 1.0,[3] 2.26 [5]	96	
Chinook salmon (*Oncorhynchus tshawytscha*)	67.3 [24], 82.1 [25]	24	
Sockeye salmon (*Oncorhynchus nerka*)	Not acutely toxic at 50 [25]	24	Lower
Atlantic salmon (*Salmo salar*)	Not acutely toxic at 12.2 [28]	48	
Brown trout (*Salmo trutta*)	Not acutely toxic at 12.2 [28]	48	
Arctic char (*Salvelinus alpinus*)	Not acutely toxic at 12.7 [3]	24	
Southern Dolly Varden (*Salvelinus curilus*)	Not acutely toxic at 3.8 [26]	48	
Cherry salmon (*Oncorhynchus masou masou*)	Not acutely toxic at 3.5 [26]	48	

ITRC 6-PPD Factsheet, 2023

- Toxicity goes well beyond Coho Salmon
- **Highly toxic ≤ 1000 µg**/L; Globally Harmonized System of Classification and labeling (UN, 2019)

(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

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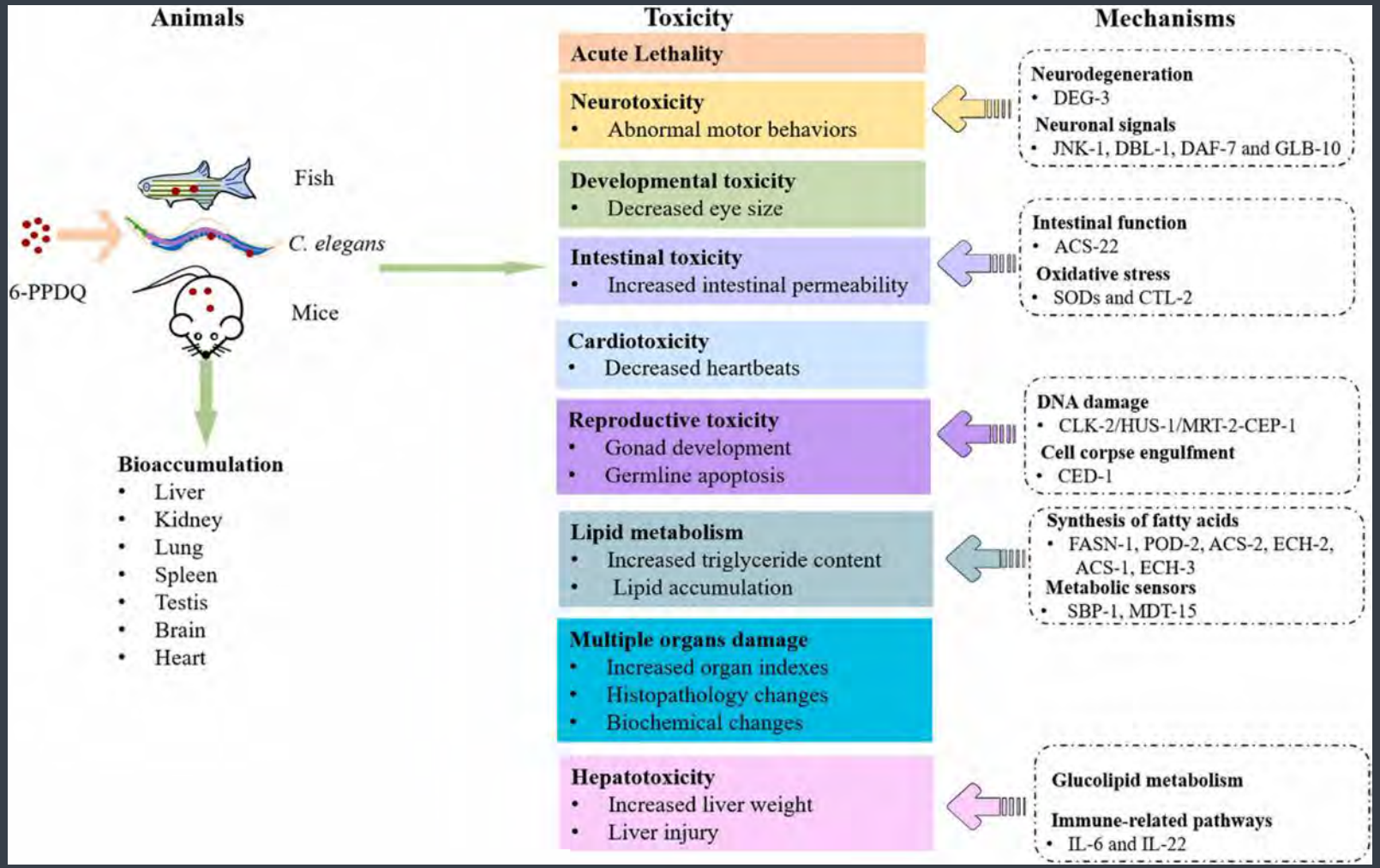
6PPD-Q TOXICITY



Hua and Wang, 2023

More toxicity mechanisms emerging

- Salmonid lethality related to neurotoxicity
- *C. elegans* nematode worms showed multiple sub-lethal effects in chronic exposure studies
- Very recent studies in mice show bioaccumulation potential

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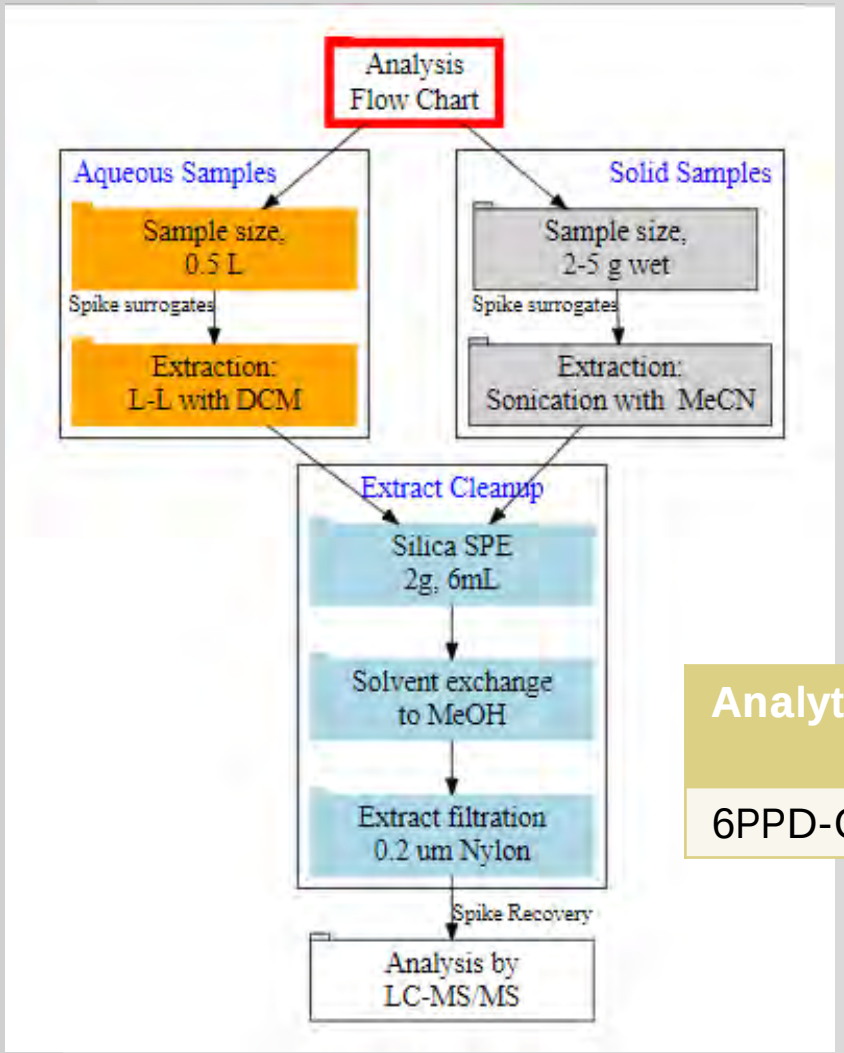
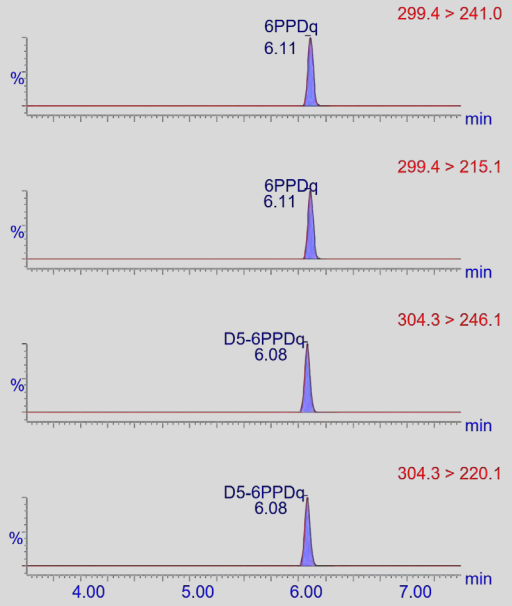
ADVANCES IN MEASUREMENT

- Best practice – Extraction, cleanup and measurement by LC-MS/MS
- Ultra-trace level measurement possible with Liquid Chromatography-Tandem Mass Spectrometry (same as PFAS)
- Reporting limits 0.1 ppt for aqueous samples and 50 ppt in soils/sediments
- Lab has now run hundreds of samples across multiple Canadian and US studies





Analyte	Aqueous (n=5) %rec ± RSD	Solids (n=5) %rec ± RSD
6PPD-Q	94.6 (±1.6%)	103 ±1.6%

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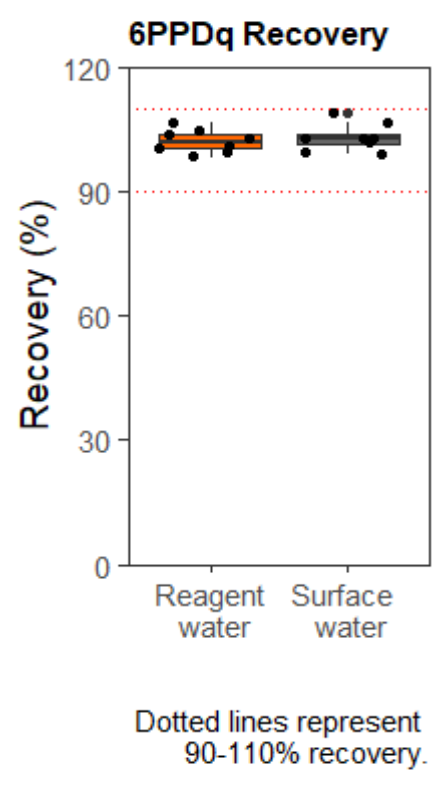
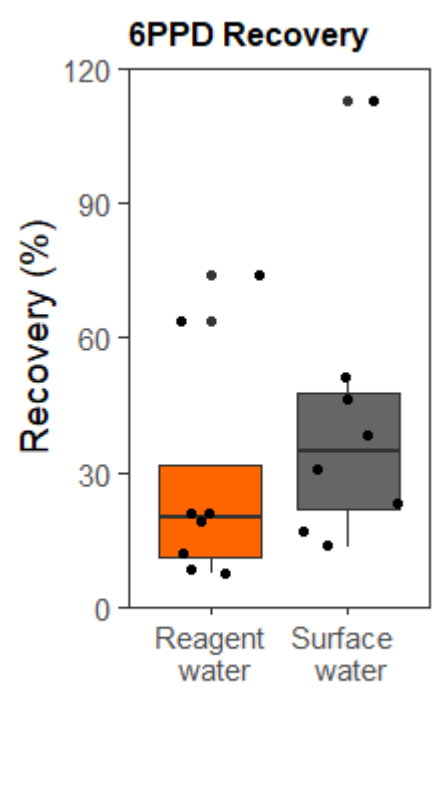
ADVANCES IN MEASUREMENT





Measuring 6PPD is challenging!

- 6PPD is reactive and unstable can be affected by light, heat, and oxygen or ozone
- 6PPD hydrolysis half-life 4.83 to 64.1 hrs
- We could stabilize 6-PPD enough for semi-quantitative measurement, but it affected 6-PPDQ stability, so we have focused on 6-PPDQ

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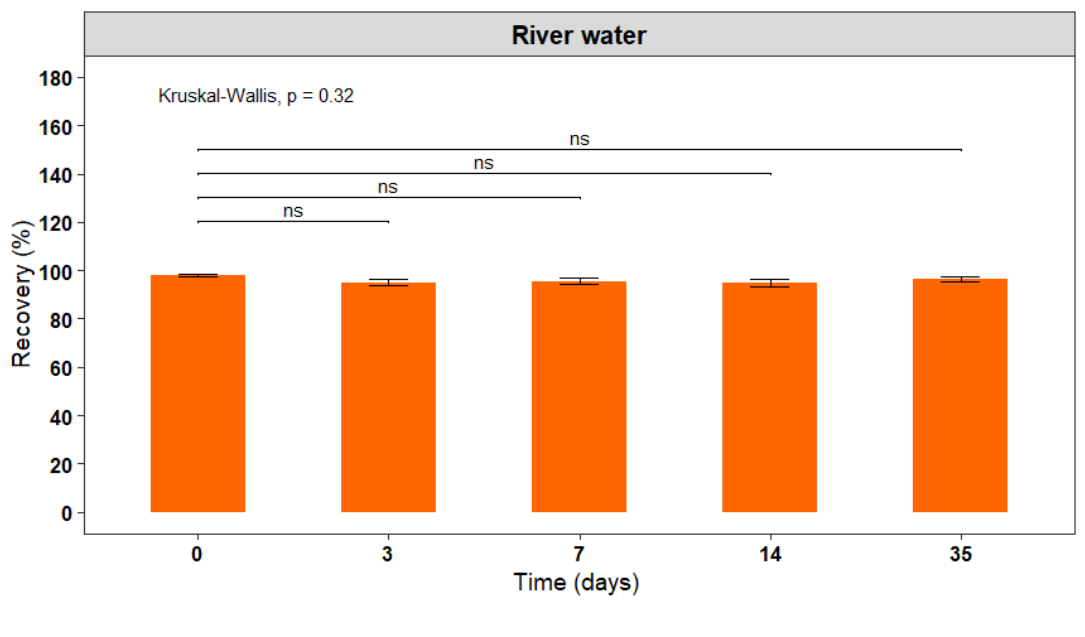
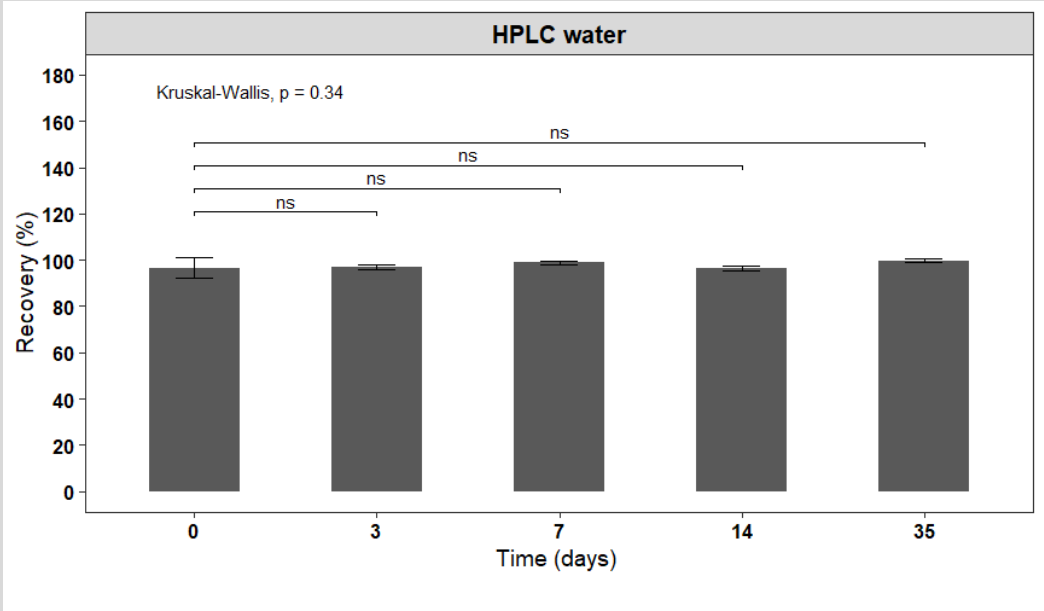
ADVANCES IN MEASUREMENT



Best Practice – Aqueous Sample Storage

- Hold time – No 6PPD-Q loss observed in aqueous samples when stored at 4°C in amber glass bottles for 35 days



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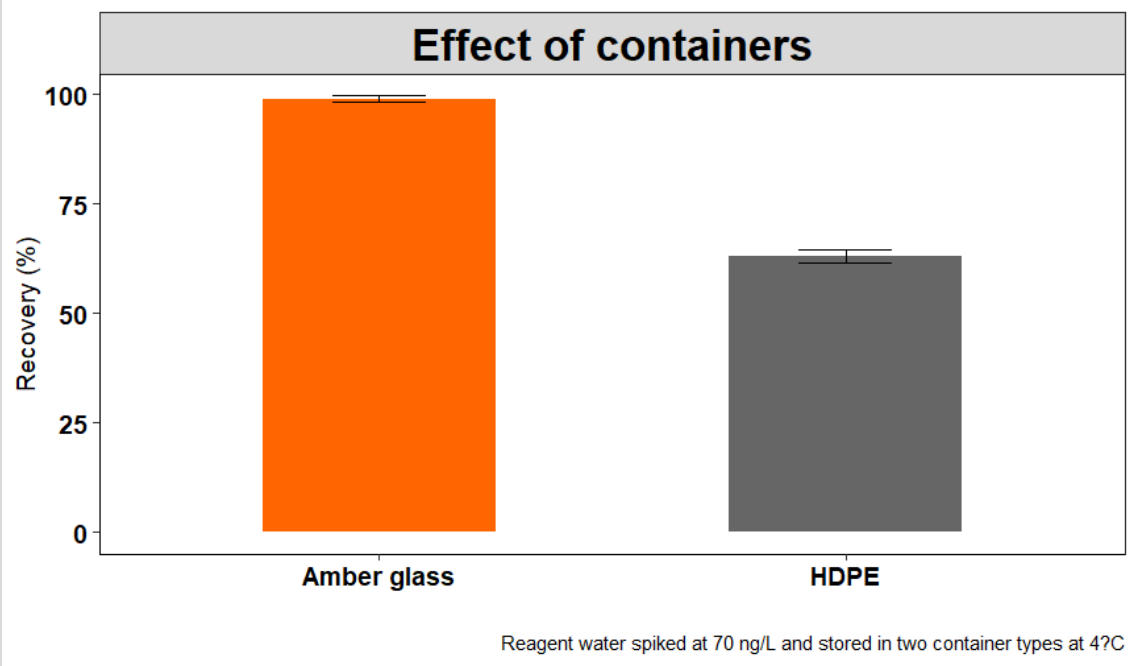
ADVANCES IN MEASUREMENT

Best Practice – Sample Containers

- There is significant difference between container types
- HDPE bottles are not suitable for 6PPDq sampling



6PPD IN THE ENVIRONMENT

- 6PPD and 6PPD-Q are being detected in surface water
- Increased concentrations in surface water after rain events

- 6PPD and 6PPD-Q are expected to:
  - have relatively short half-lives
  - preferentially adsorb to soils

- Unknown how 6PPD and 6PPD-Q reside in soil and groundwater

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ENVIRONMENTAL OCCURRENCE AND DATA GAPS

Sample type	6PPDq (ppt)	6PPD (ppt)	References
Surface water, Toronto, Canada	930-2,850	N/M	Johannessen et al. 2022
Stormwater, Saskatoon, Canada.	600	N/M	Challis et al. 2021
Snow melt, Saskatoon, Canada.	80-370	N/M	Challis et al. 2021
Stormwater, Australia	88	N/M	Rauert et al. 2022
Road water (puddle), Michigan, USA	12-37	N/M	Nedrich, Sara, 2022
Surface water, BC, Canada	<0.1-740	<0.1-5,100	SGS AXYS 2022
Urban runoff, Hong Kong	210 – 2710	210 – 2430	Cao et al. 2022
Roadside soil, Hong Kong	31,400–831,000	9,500-9,360	Cao et al. 2022
WWTP influent, Germany	Nd - 105	300-11,200	Seiwert et al 2022
WWTP effluent, Germany	n.d	900-14,300	Seiwert et al 2022

- ITRC identified 6PPD and 6PPDq in WWTP matrices as a data gap, 2023.
  - https://6ppd.itrcweb.org/

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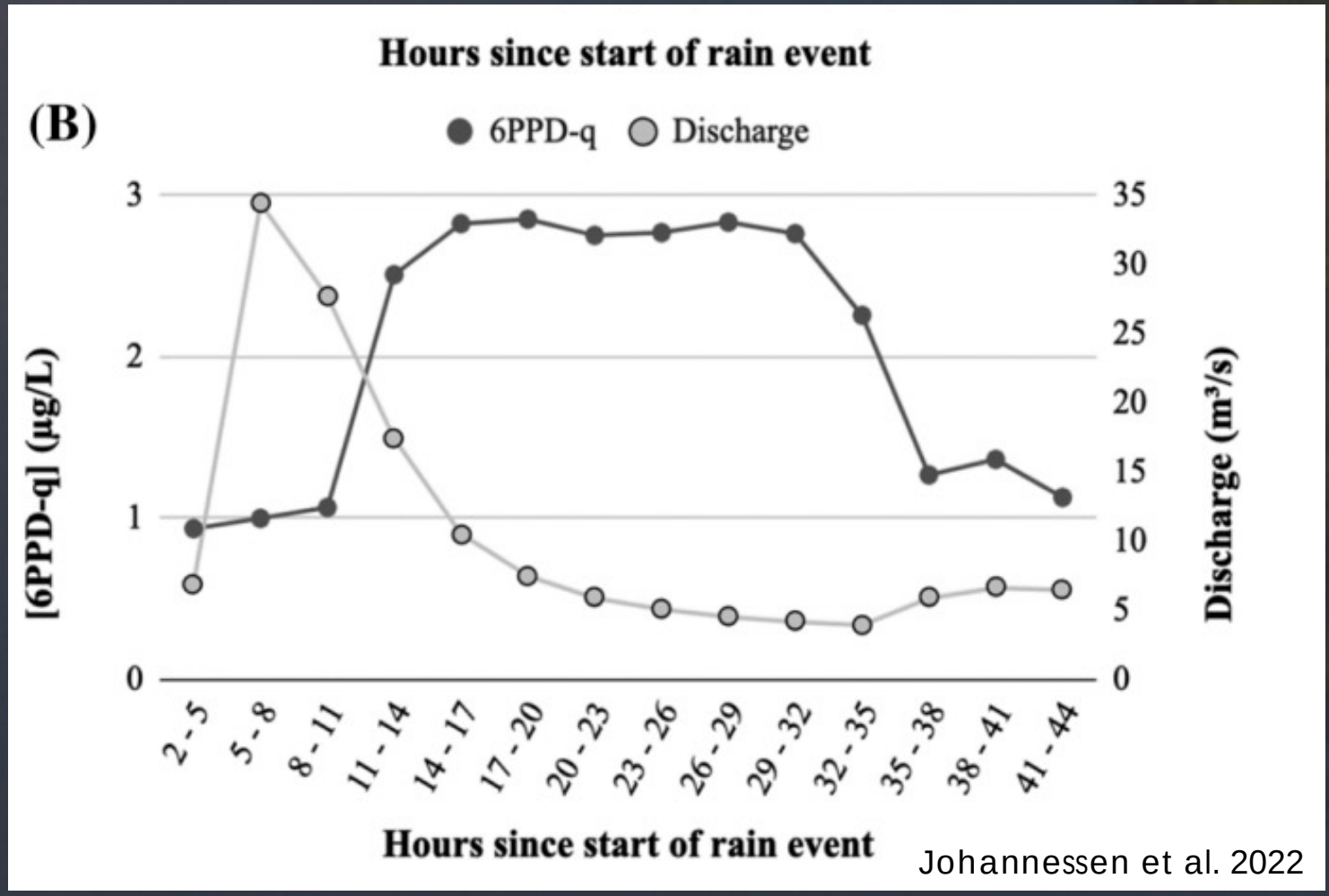
CONCENTRATIONS IN THE DON RIVER

- Concentrations in highly polluted watersheds are toxic to local salmonids
- 6PPD-Q stays at elevated level well after discharge of 6-PPD into river
- 6PPD decreases show formation of 6PPD-Q



Johannessen et al. 2022

PILOT STUDIES

- Investigations of different media within Canada
  - Surface water
  - Soils
  - Biosolids and Effluent

- Investigated presence of 6PPD and 6PPD-Q based on proximity to potential source and seasonal effects

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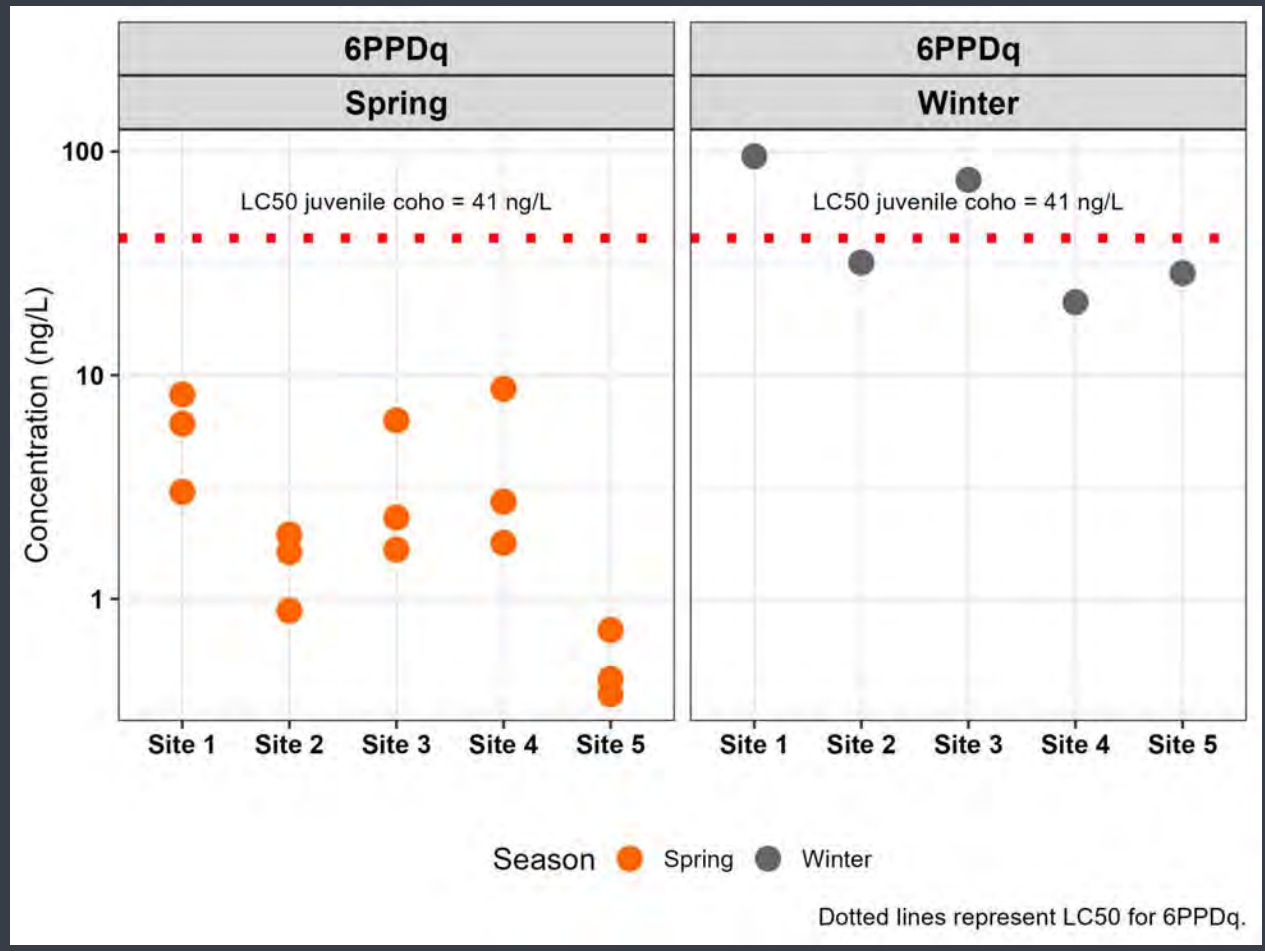
PILOT STUDIES – SURFACE WATER

- Collected from Victoria, BC
- These samples are from relatively clean creeks and rivers
- Winter samples collected during first rain events show effects of rain-runoff
- Spring concentrations lower, measured during period of low runoff



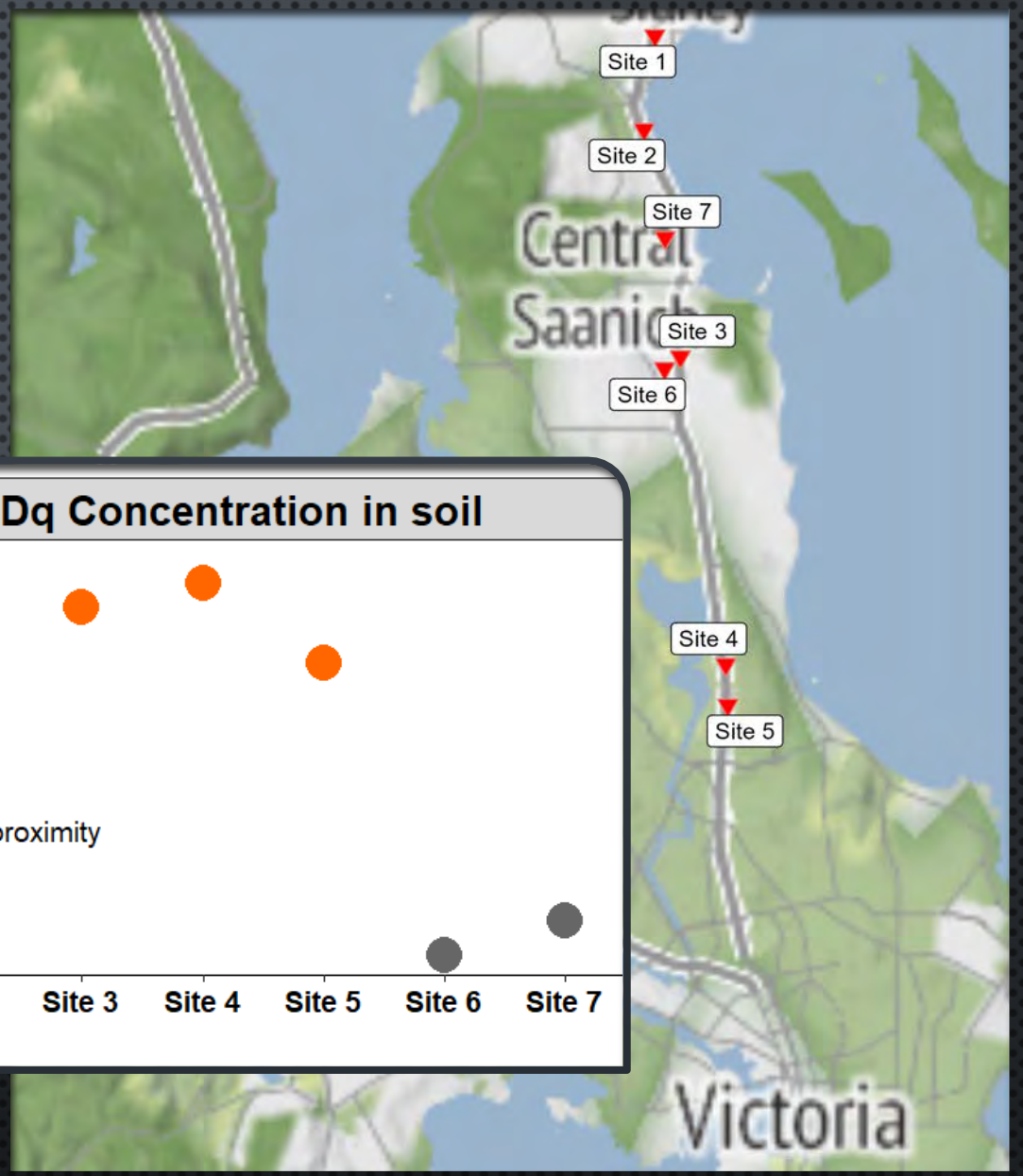
PILOT STUDIES – SOILS

6PPD-Q was detected in all soil samples collected near roads

Samples close to highway [site 1-5] show significantly higher concentrations compared with local roads [site 6 & 7]

6PPD-Q log K_{OC} = 3.928

Indicates high partitioning to Soil/Sediment



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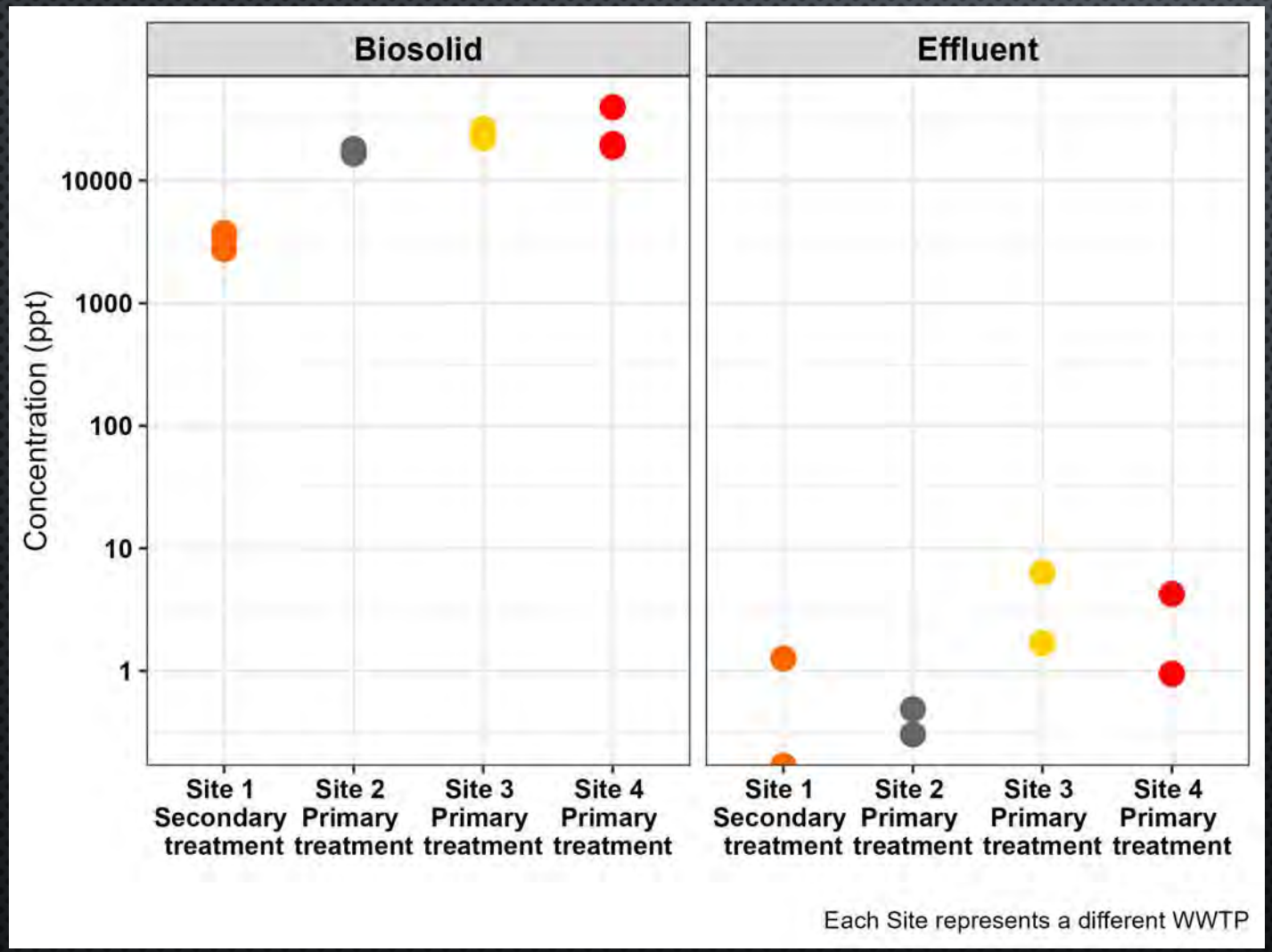
PILOT STUDIES – BIOSOLIDS AND EFFLUENT



6PPD-Q was detected in all biosolid samples analyzed

6PPD-Q was detected in nearly all archived effluent samples

6PPD-Q concentration in biosolids were greater than those in the effluent

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REGULATORY LANDSCAPE

- Regulations pertaining to 6PPD have started coming into force
- Mostly pertain to understanding 6PPD properties
- Commitments to search for 6PPD alternatives with rubber and tire industry

DTSC
Department of Toxic Substances Control

DEPARTMENT OF ECOLOGY
State of Washington

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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REGULATORY LANDSCAPE

Washington, USA

DEPARTMENT OF ECOLOGY
State of Washington

Identified 6PPD as a "Priority Toxic Chemical"

Persistence, Bioaccumulative, Toxicity

Includes PFAS, PCBs, Phthalates, Flame Retardants

Three key efforts underway

Understand the problem

Reduce stormwater pollution

Reduce sources of 6PPD

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REGULATORY LANDSCAPE

California, USA

DTSC
Department of Toxic Substances Control

Tires containing 6PPD are a "Priority Product"

Safer Consumer Products Regulations

October 1, 2023

Onus placed on manufacturers

Manufacturers obliged to declare intent to remove or replace use of 6PPD in tires (March 2024)

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REGULATORY LANDSCAPE

United States (Federal)

Committed to addressing 6PPD issues

Must respond to petition from several Indigenous tribes to address use of 6PPD (November 2023)

Research and Grants

Develop standard analytical method

Develop screening values for aquatic life

Supporting ITRC

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REGULATORY LANDSCAPE

European Union

Proposed tighter limits on vehicle emissions

Particulate and microplastics from brakes and tires in November 2022

Research into 6PPD properties

Review of persistence and bioaccumulation

No restrictions are planned

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REGULATORY LANDSCAPE

Tire Industry

U.S. TIRE MANUFACTURERS ASSOCIATION

Tire Industry Project

Research into new technology

Bioretention, storm water infrastructure, bioswales

6PPD alternatives

Research into tire emissions and life cycle

Researching TWP, emissions, end-of-life management, sustainability

Planning a global conference on tire emissions including TWP

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WHAT'S NEXT?

Research into 6PPD and 6PPD-Q remains in its infancy but there is increasing interest from regulators, industry, and the public

- Mitigation strategies and Best Management Practices
  - Opportunities for Green Infrastructure
- Toxicity, measurement, occurrence of 6PPD and 6PPD-Q
- Replacement of 6PPD in tire and rubber manufacturing
  - Nine potential alternatives identified by Washington Dept. of Ecology

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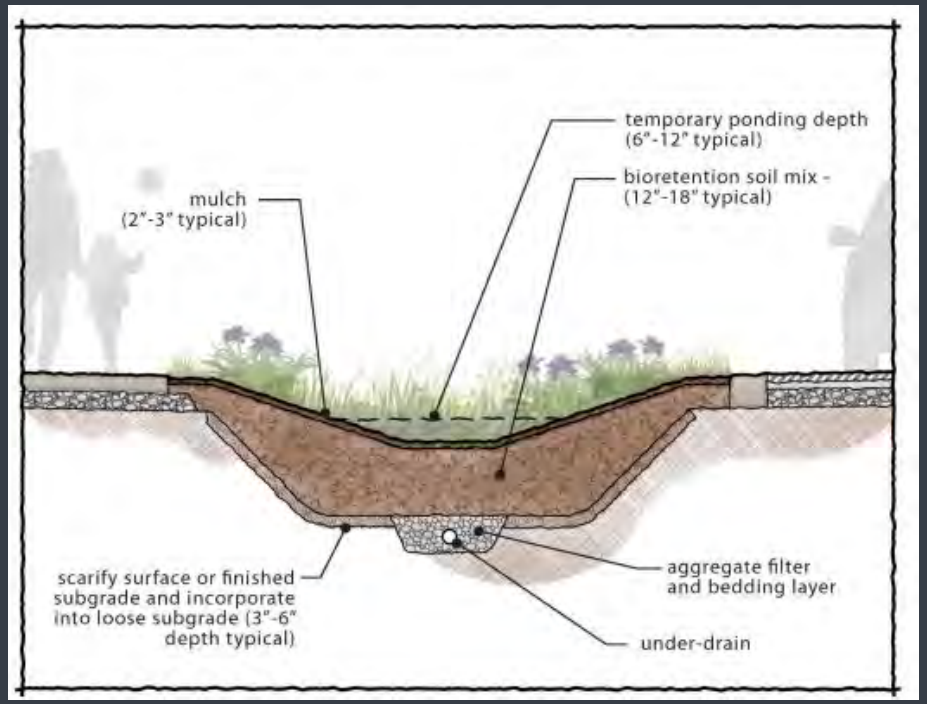
WHAT'S NEXT?

How can we mitigate the effects of 6PPD in stormwater?

- Evidence that bioretention prevents sensitive species mortality
- Potential that "Green" Street Infrastructure can reduce contaminant load in surface water
- The design of urban stormwater treatment systems should consider these emerging contaminants



ITRC 6-PPD Factsheet, 2023

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WHAT'S NEXT?

Is 6PPD-Q just the tip of the iceberg?

- 6PPD and 6PPD-Q are only two of many tire wear compounds found in road runoff and particulate matter
- Could this change how we evaluate vehicle emissions?

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WHAT'S NEXT?

What are other contaminants of concern with tire wear?

- Tirewear particles are the largest single source of microplastics in the urban environment (SFEI 2021)
- Crosslinking agents such as Hexamethoxymethyl melamine (HMMM) and many other chemicals also present
  - Recent internal method can measure to 10 ng/L
- Benzothiazoles and other additives

Tires contain more than rubber

Compound Type	Content
Rubber	40-60%
Fillers/reinforcing agents	20-35%
Process/extender oils	12-15%
Additives (preservatives, plasticizers, etc.)	5-10%
Vulcanization agents	1-2%

Adapted from Wagner et al. 2018

PowerPoint Presentation (sfei.org)

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WHAT'S NEXT?

- It is unclear if 6PPD and 6PPD-q have the potential to contaminate lands over the longer term
  - Analytical methods have only recently been developed
  - What are baseline concentrations in soil and groundwater?
  - Could soil and groundwater act as a secondary source of tire wear leachate?

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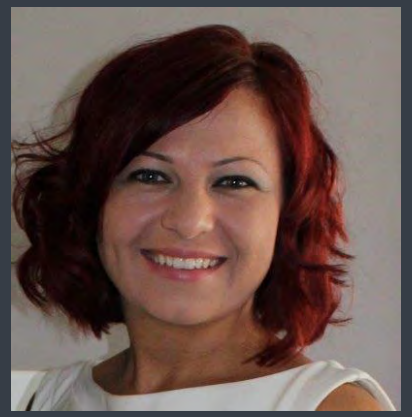

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