



MICHIGAN DEPARTMENT OF
ENVIRONMENT, GREAT LAKES, AND ENERGY

Preliminary Investigation of 6PPD-Quinone in Surface Water and Standing Road Water in Michigan

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Background

What is 6PPD-quinone and why do we care?



6PPD-quinone History

- Mysterious **urban runoff mortality syndrome**: up to 90% of migrating coho salmon would die after rainstorms prior to spawning in NW United States
- Mortality due to runoff of tire wear particles (TWP)
- Tian et al. 2021 – identifies 6PPD-quinone, LC50 = 95 ng/L



A coho salmon gapes for air, one of the symptoms of "urban runoff mortality syndrome," in Miller Creek in Normandy Park, Washington. Screenshot from University of Washington video

What is 6PPD-quinone?

- 6PPD oxidizes quickly to 6PPD-quinone
- 6PPD is an antioxidant chemical used in tire rubber – used in all road-worthy tires.
- 6PPD a short half life: 2.9 h @ 23°C
- 6PPD-quinone more stable, half-life: 33 h at 23°C



LC50's show immediate acute toxicity

Species	LC50 (ug/L)	Reference
Coho Salmon	0.095	Tian et al. 2021, 2022
Brook Trout	0.59	Brinkmann et al. 2022
Rainbow Trout	1.0	Brinkmann et al. 2022
White Sturgeon	>14.2	Brinkmann et al. 2022
Zebrafish (larvae)	132.92	Varshney et al. 2022
Water flea	>100	Hiki et al. 2021
Scud	>100	Hiki et al. 2021

Scrap tire reuse a potential source?

- Michigan grants fund innovative scrap tire reuses – paving projects
- Scrap tires are classified ‘inert’ and ‘beneficial reuse’ products
- Crumb rubber modified asphalt 4% of tire re-use in United States in 2018



Sampling Plan and Results

How did we monitor for 6PPD-quinone and what
did we find?

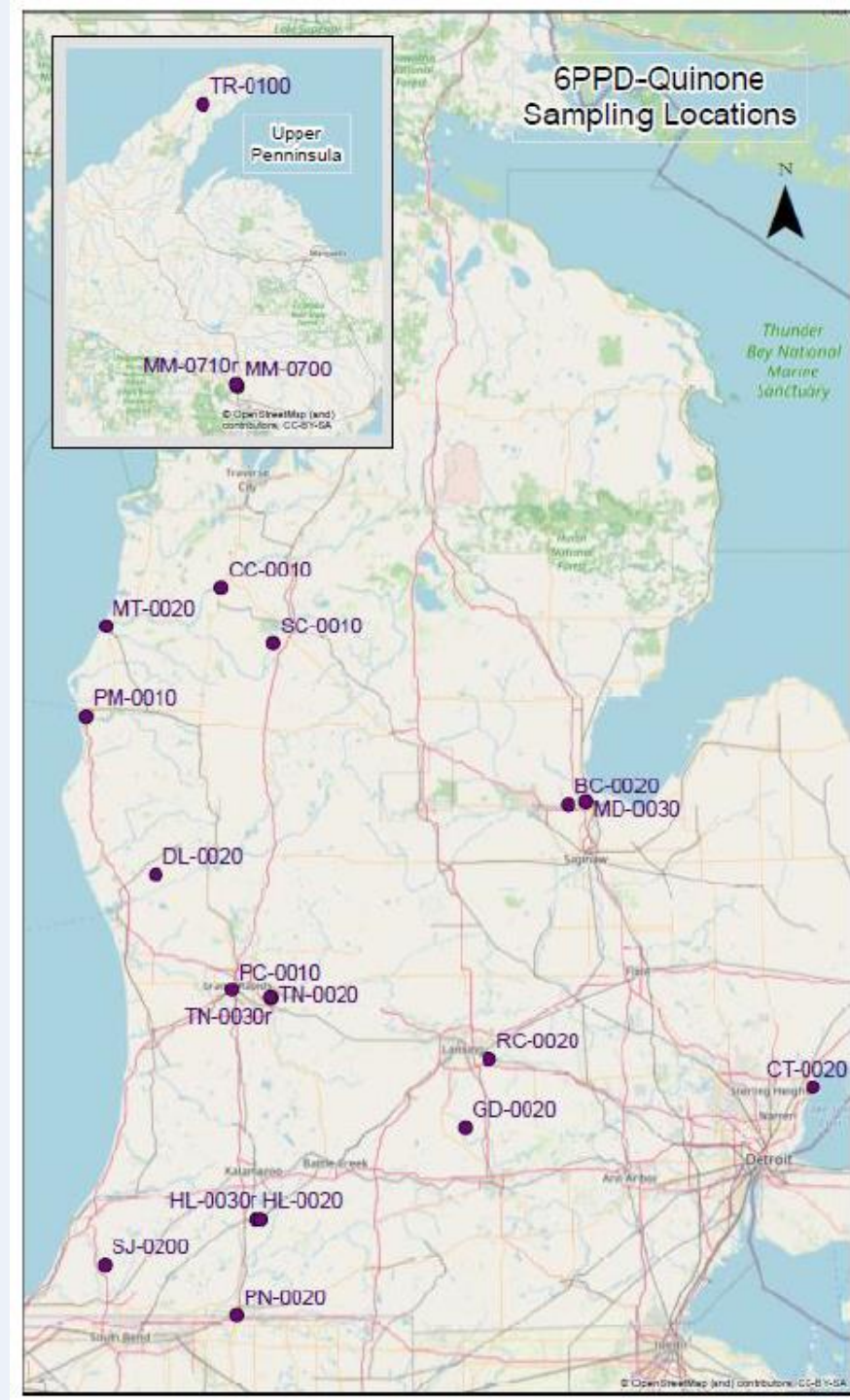


Research Questions for MI Study

Site Category	Question
All Sites	Is 6PPD-q present in Michigan surface waters at concentrations that are negatively impacting aquatic life?
Industrial	Do industrial sources of crumb rubber have releases of 6PPD-q into surface waters?
Crumb Rubber	Do recycled crumb rubber products in paving projects increase release of 6PPD-q into surface waters?
Exposure	Is 6PPD-q present in trout spawning rivers?

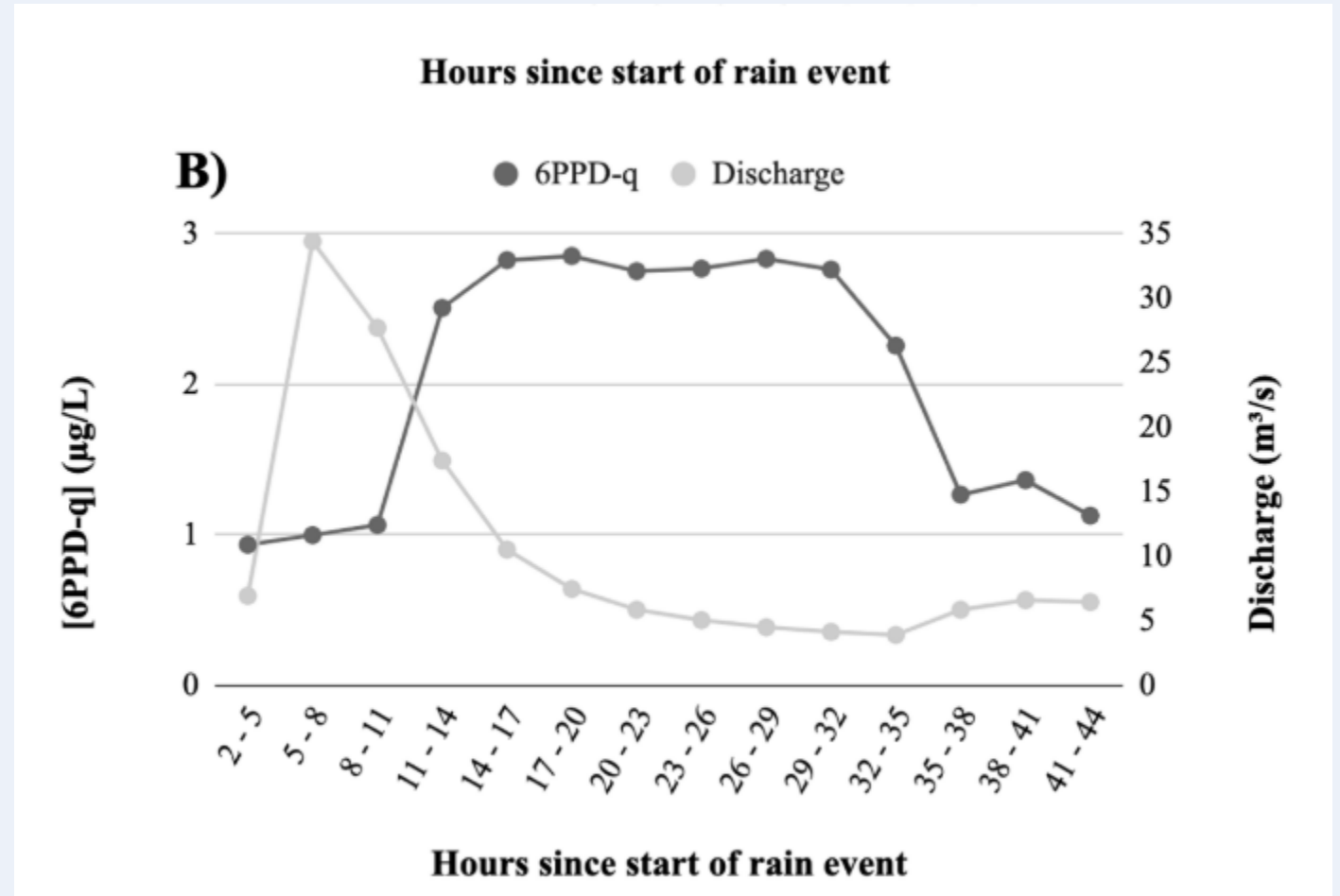
Sampling Plan Design

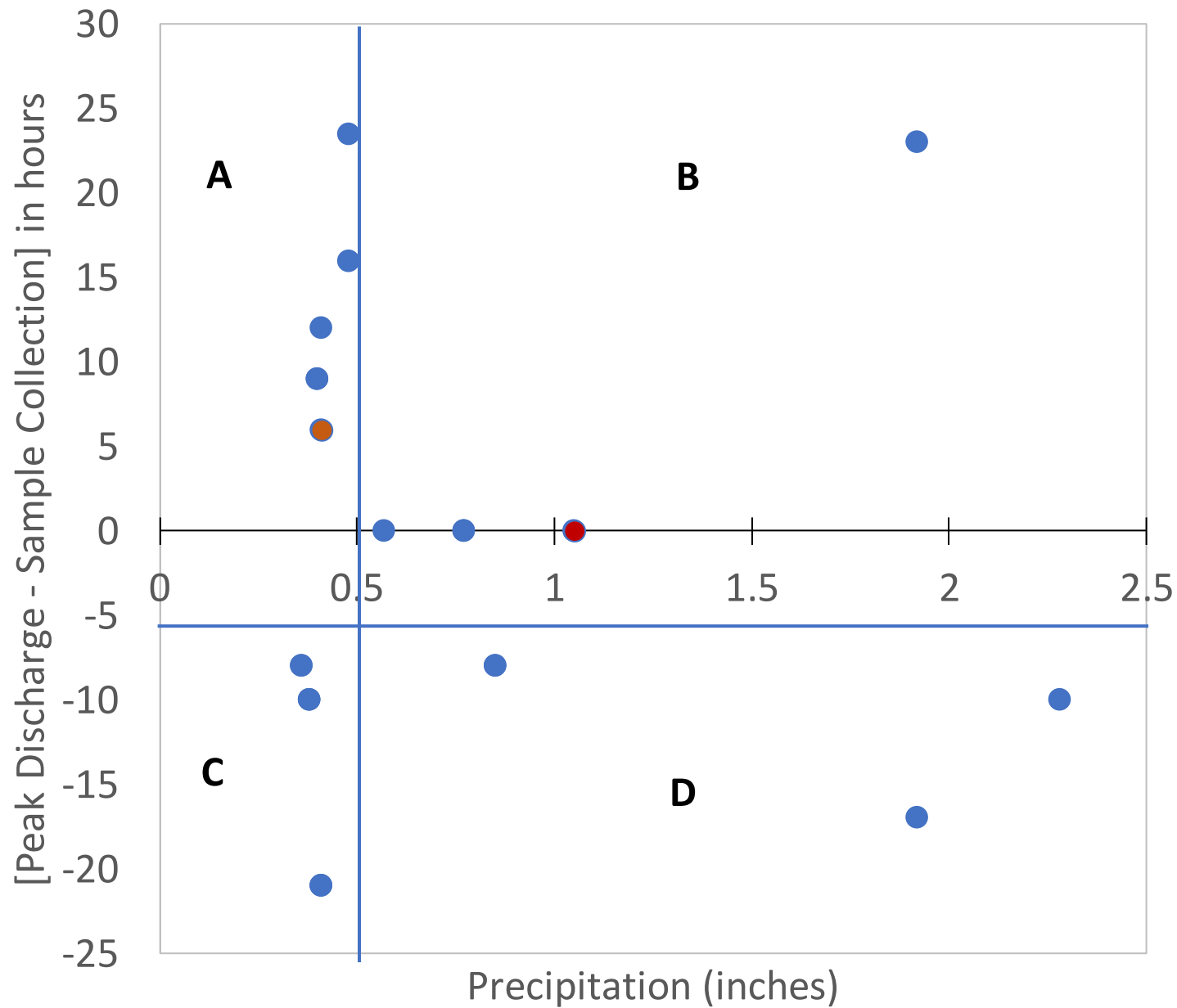
- Surface water (SW) grab samples - 12 watersheds
 - 17 SW samples perpendicular or parallel to roadways
- 3-4 sites per category:
 - Historic crumb rubber paved
 - Recent crumb rubber paved + reference
 - Before and after crumb rubber paving
 - Exposure – trout spawning river
 - Industrial – crumb rubber stockpile
- 5 standing road water (puddle) samples
- 5-minute informal car counts



Catching the perfect storm...Sample Collection Design

- From Cassandra Johannessen, master's thesis
- Toronto, CA into Lake Ontario
- Sample 11-35 hrs. after rain
- Sample 6-30 hrs. after peak discharge
- Storm event >0.5"





Sampling recommendations (either/or):

- Within 11-35 hrs of $\geq 0.5''$ precipitation event
- Between 6 and 30 hours after peak discharge

A = met neither

B = met 1 of 2

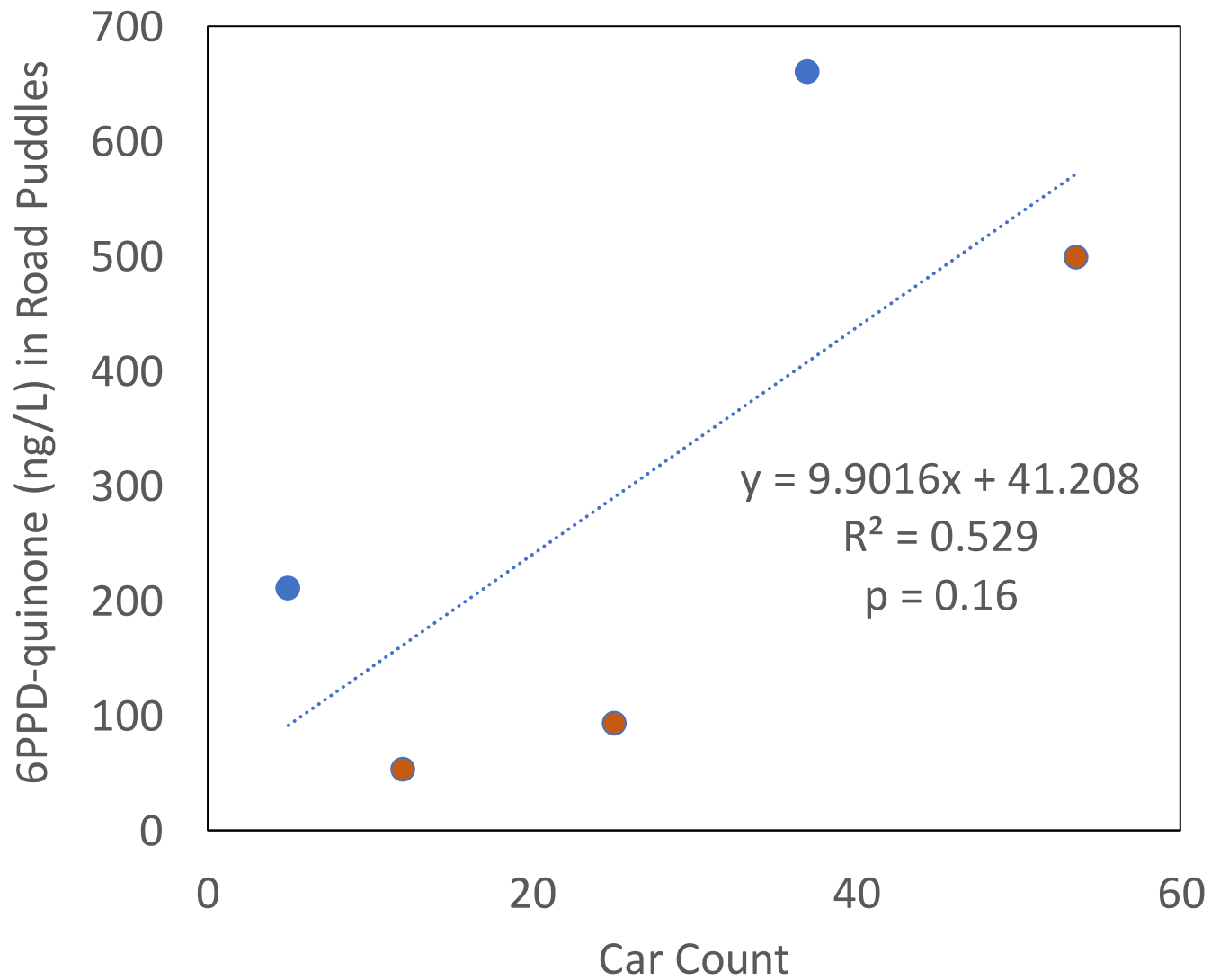
C = met 1 of 2

D = met both

~70% of sites met at least one recommendation

Roadway Standing Water (i.e. Puddles) show elevated 6PPD-q concentrations





Moderate, positive correlation between road traffic and 6PPD-q concentrations in standing road water

Data shows more data is needed...

Question	Data Suggests...
Is 6PPD-q present in Michigan surface waters at concentrations that are negatively impacting aquatic life?	Possibly. Preliminary data detected at lower concentrations than expected.
Do industrial sources of crumb rubber have releases of 6PPD-q into surface waters?	Preliminary evidence suggests more sampling needed.
Do recycled crumb rubber products in paving projects increase release of 6PPD-q into surface waters?	No evidence crumb rubber increases 6PPD-q release. All impacted sites were ND.
Is 6PPD-q present in trout spawning rivers?	All were ND. More study needed.

Summary and Next steps

Summary

- 6PPD-quinone is short-lived in aquatic systems. Time sequence data is needed with implementation of autosamplers.
- 6PPD-quinone is being released from roadways (see puddle samples) at elevated concentrations.
- Acute effects of 6PPD-quinone continues to be a concern to aquatic life in Michigan.

Next Steps...

- Watershed scale study for 6PPD-quinone with autosamplers – targeted focus on important spawning rivers along heavy traffic corridors
- Tire re-use study comparing runoff from traditional asphalt and crumb rubber overlays

Report & References

Michigan's Report: <http://dx.doi.org/10.13140/RG.2.2.34478.59204>

References:

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- Tian et al., 2021. A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon. Science (80-.). 371, 185–189. <https://doi.org/10.1126/science.abd6951>
- Tian, Z., Gonzalez, M., Rideout, C.A., Zhao, H.N., Hu, X., Mudrock, E., James, C.A., McIntyre, J.K., Kolodziej, E.P., 2022. 6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard. Environ. Sci. Technol. 1–10.
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