

Organic contaminants in tire and crumb rubber: 6PPD-quinone and beyond

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Northeastern University

Outline

- Acknowledgements
- Coho salmon mortality and tire rubber chemicals
- Crumb rubber chemicals: ongoing research

Acknowledgements

UW Center for Urban Waters:

Christopher Wu, Rachel Hettinger, Rachel Lundeen, Alex Gipe, Craig Rideout, Allan Cortina, Fan Hou, Andy James, Joel Baker

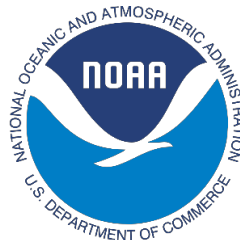
WSU-Puyallup (McIntyre group)

Jen McIntyre, Jill Wetzel, Emma Mudrock, Jasmine Prat

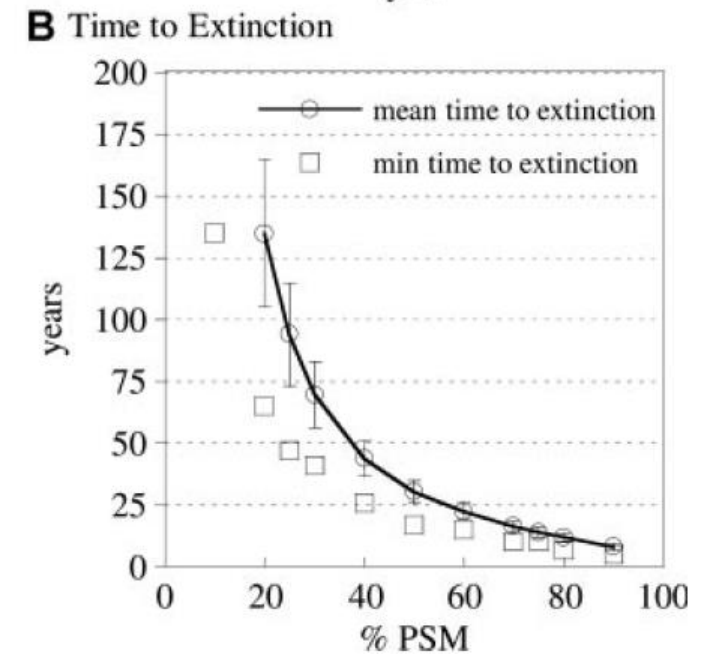
Other collaborators:

UW-Seattle (Mike Dodd, Huan He, Scott Edgar, Dale Whittington), U Toronto (Andre Simpson Group), SFEI, SCCWRP, NOAA, NWFSC, Citizen Science Teams

Funding sources:



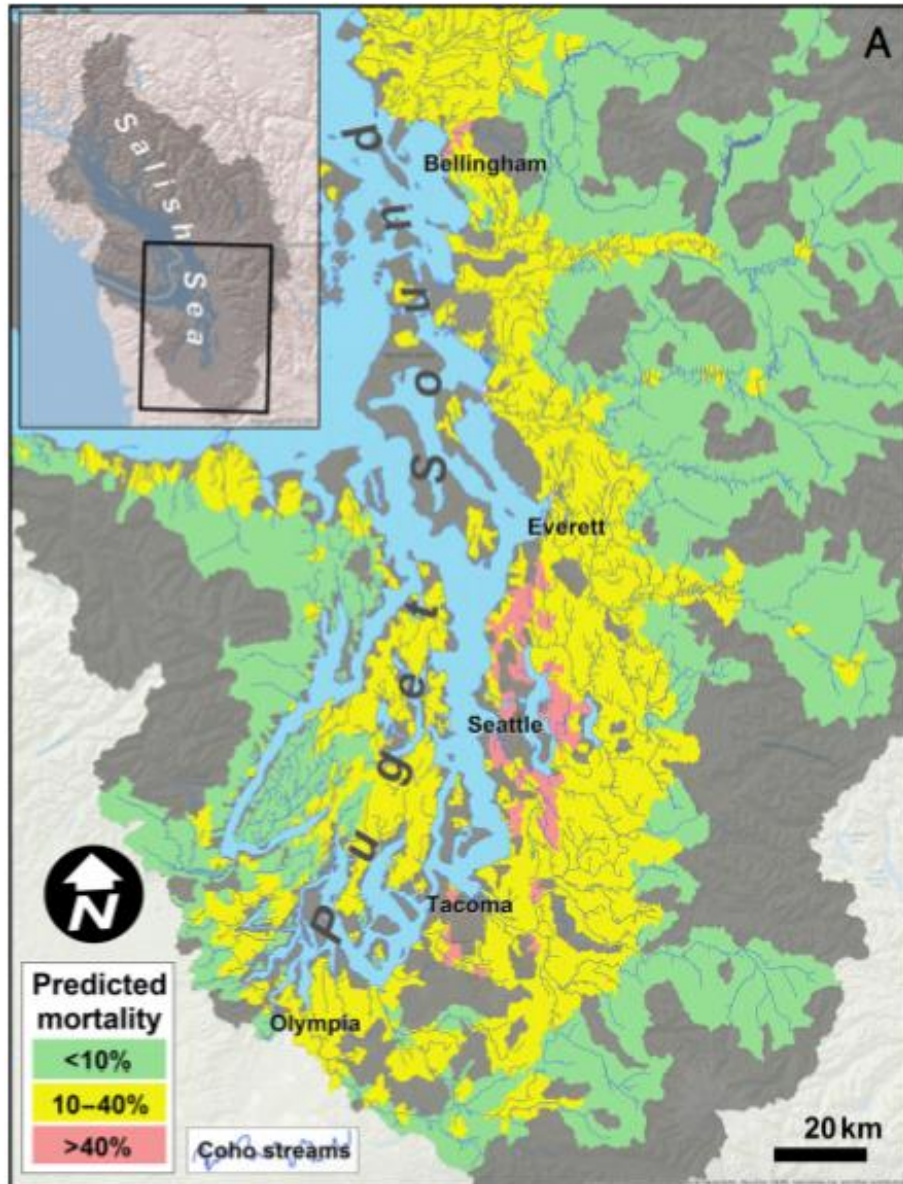
Fall Stormwater kills spawning coho salmon: “Urban Runoff Mortality Syndrome” (URMS)



Coho mortality at Miller Creek, Oct 30th, 2018

- PNW, every year after fall storms (Oct- Nov)
- Symptoms: losing equilibrium, gaping, circling
- Killed in hours, many died before spawning
- Species specific (not chum salmon)

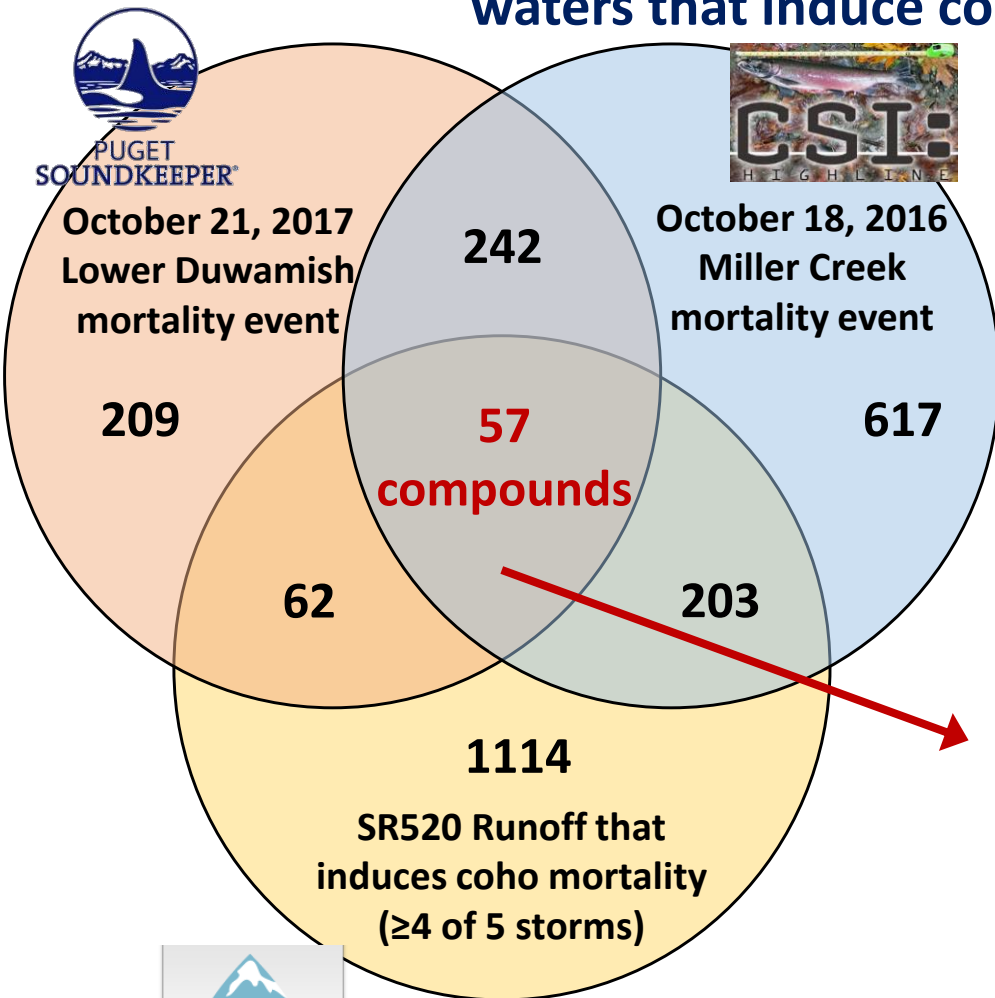
Coho mortality syndrome is linked to urbanization and traffic intensity



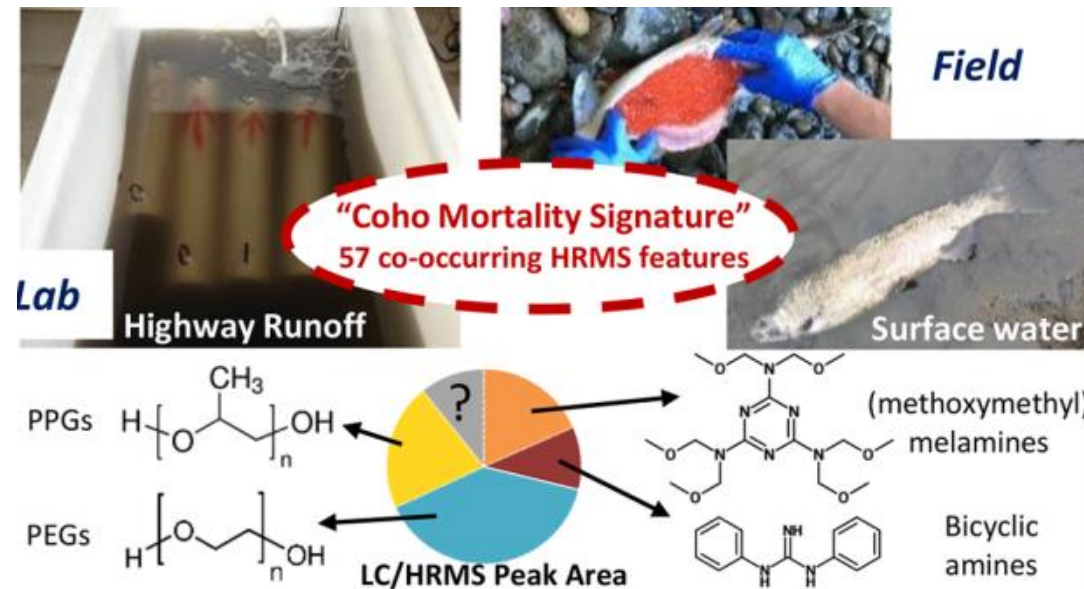
- “Urbanization gradient” predicts coho mortality risk
- Road runoff kills coho, same symptoms as in creeks
- Toxicant(s) currently unknown; likely related to road/cars

What chemicals are in every water sample where coho mortality occurred?

Concept: define a “chemical signature” that appears in all lab & field waters that induce coho mortality (using HRMS)



HRMS: high-resolution mass spectrometry



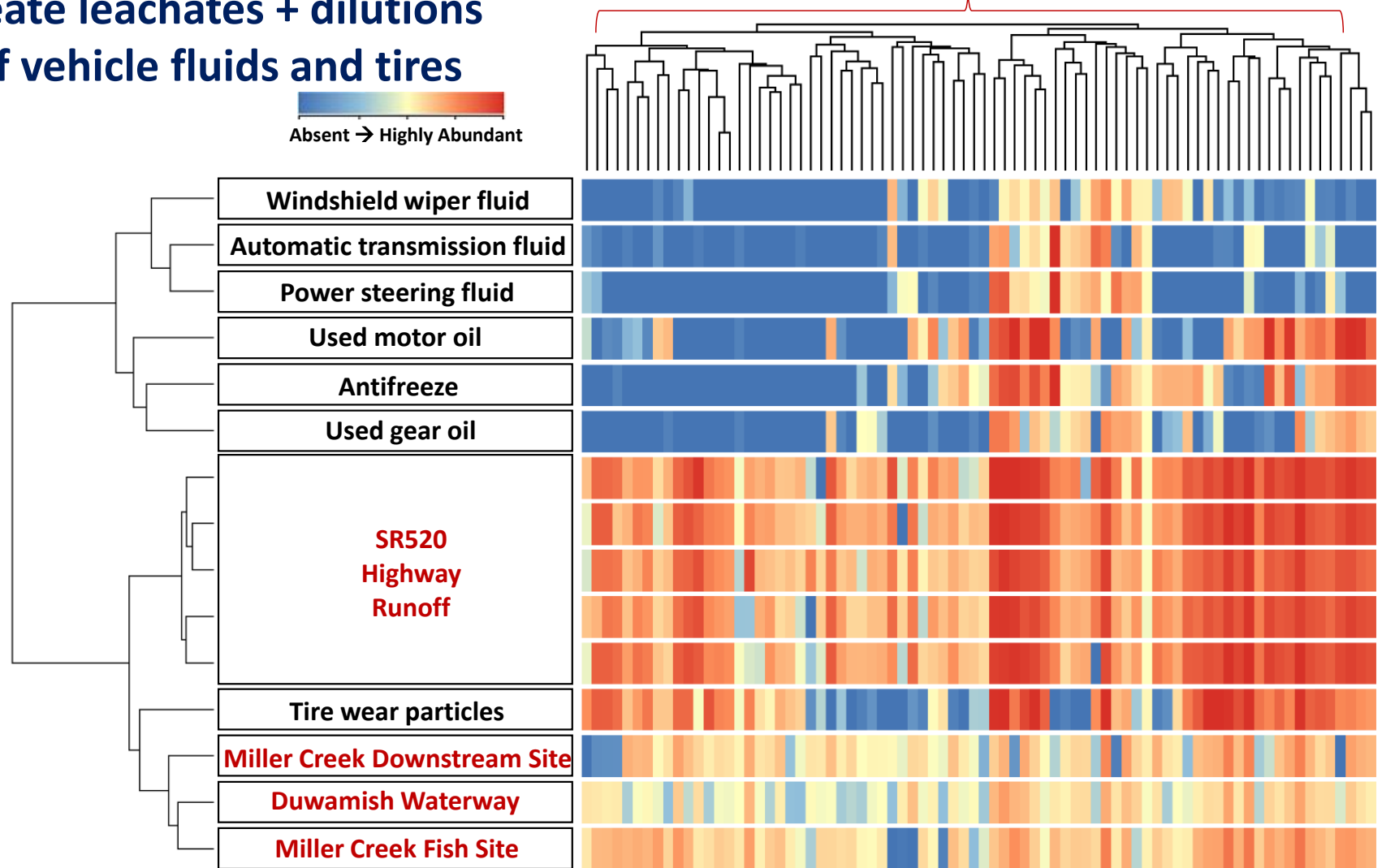
- Track signature in treatment systems
- Track contamination sources

HRMS: Compare the mortality signature to different vehicle-related sources

Create leachates + dilutions of vehicle fluids and tires

Absent → Highly Abundant

Each column = 1 of the features in the signature



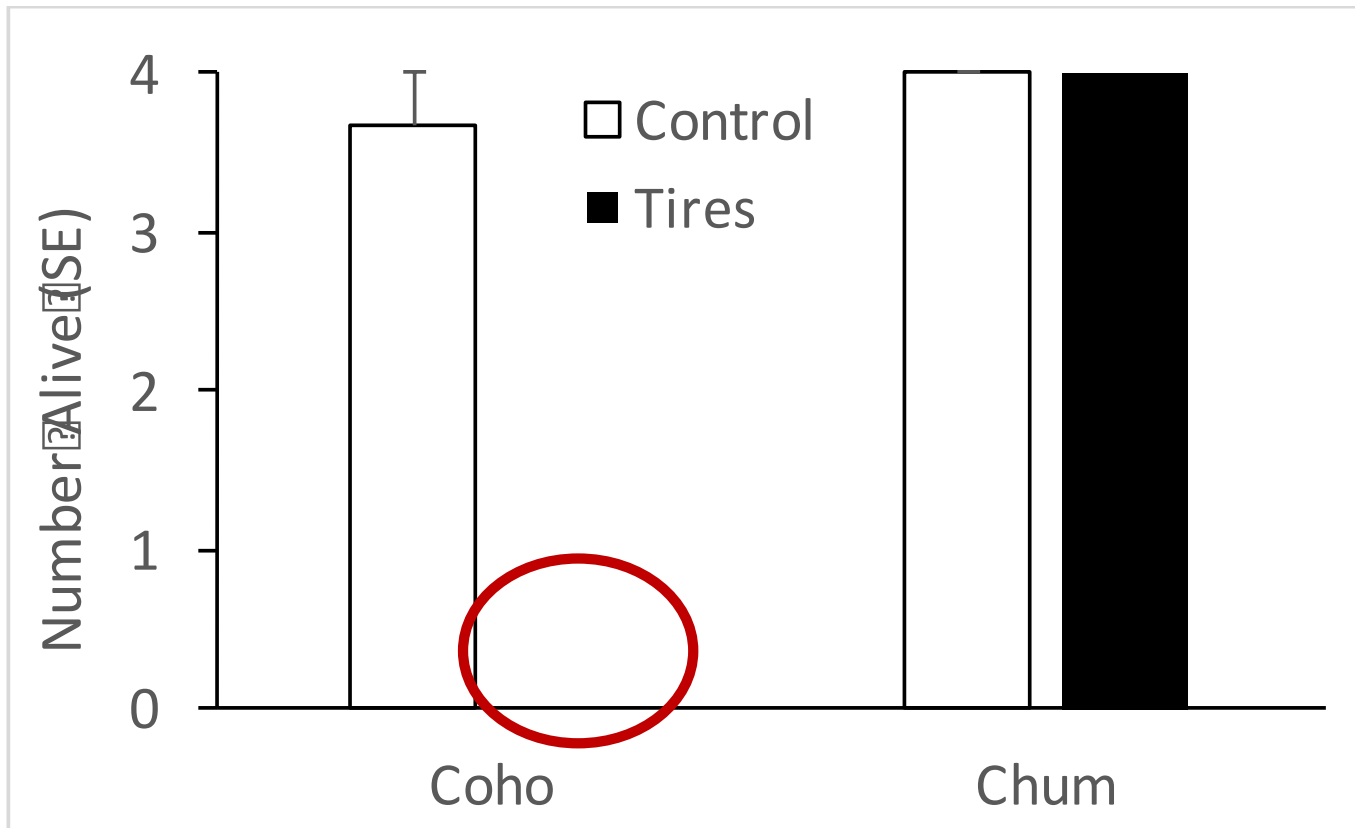
Tire wear particle leachates cluster with waters from coho mortality events

Tire wear particle leachate kills coho

~320 mg/L tire rubber (HRMS: more like ~200 mg/L)

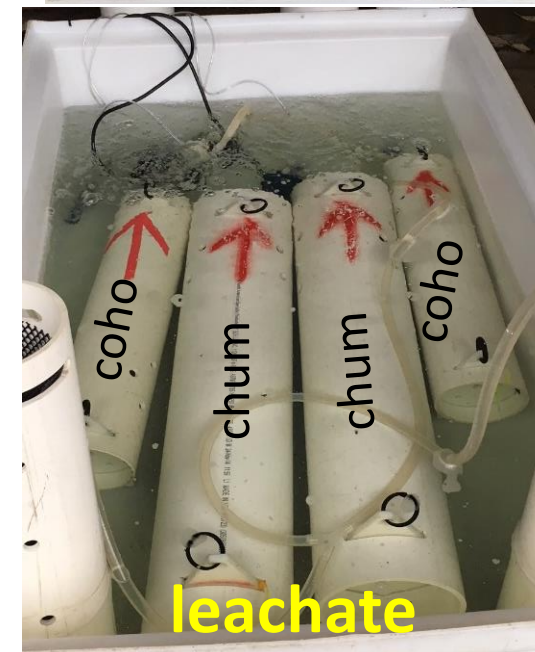
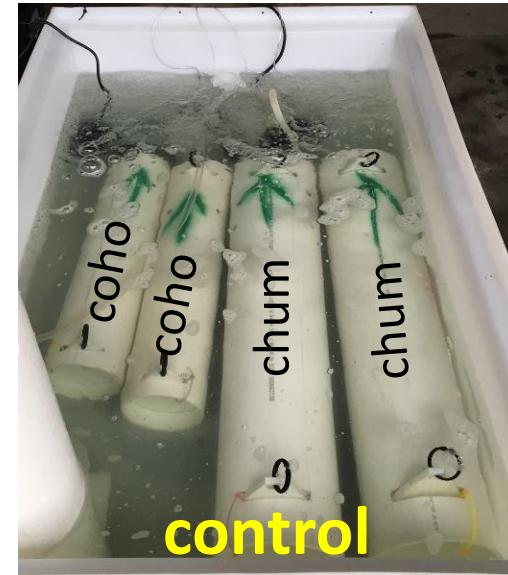
Leaching: 24 h at 8 °C

Expose fish up to 24 h, Repeated 4X (64 fish total)

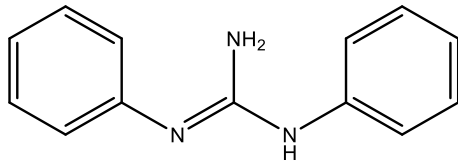


16/16 exposed coho died, 16/16 exposed chum lived

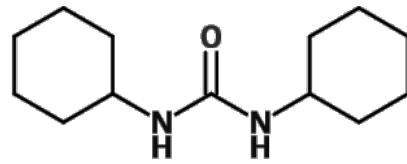
What are the lethal toxicant(s) in tire ??



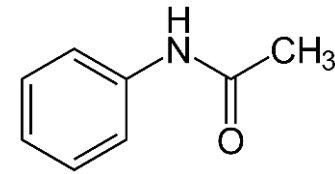
“Homerun” mixtures did not kill coho



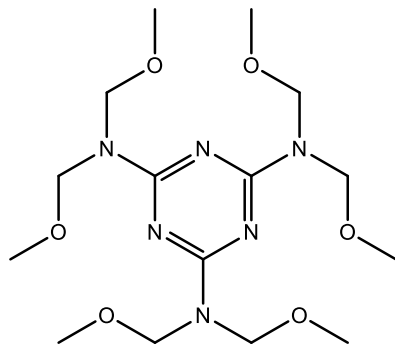
1,3-diphenyl guanidine
(DPG)



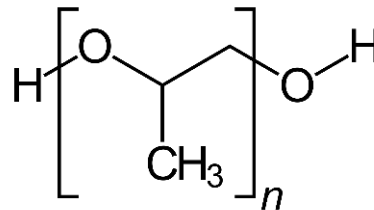
dicyclohexyl urea



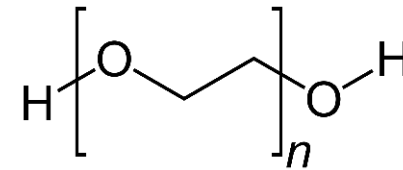
acetanilide



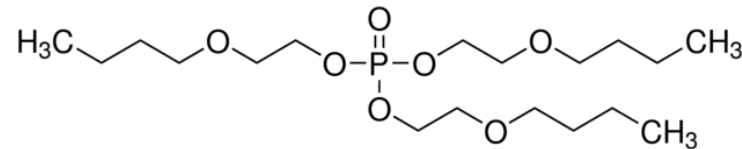
hexa(methoxymethyl)
melamine (HMMM)



Polyethylene glycols (PEG)



Polyethylene glycols (PPG)

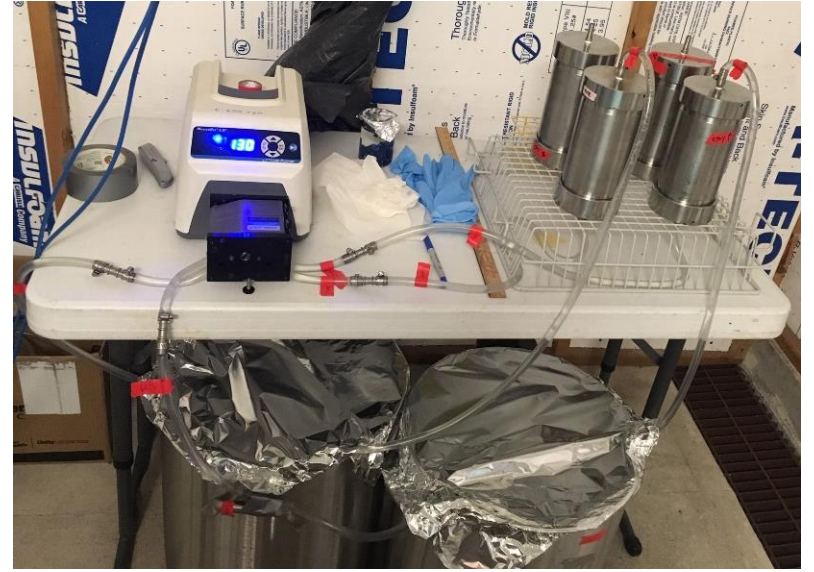


Tris(2-butoxyethyl) phosphate (TBOEP)

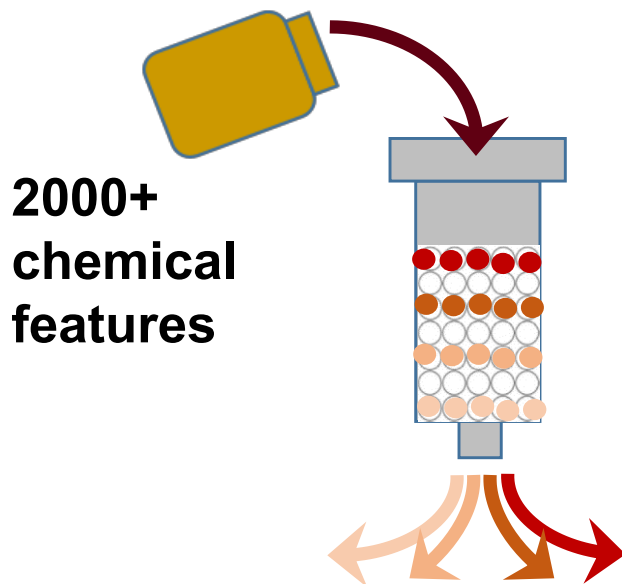
- Made a mixture from the “mortality signature” compounds (20/57), 1x & 10x concentration relative to SR520 runoff
- **Did not kill** coho. The toxicant isn't in the signature (or not standard available)!

Identify the toxicant(s): tire leachate fractionation

Leach tire particles into water



Fractionate tire leachate & expose juvenile coho

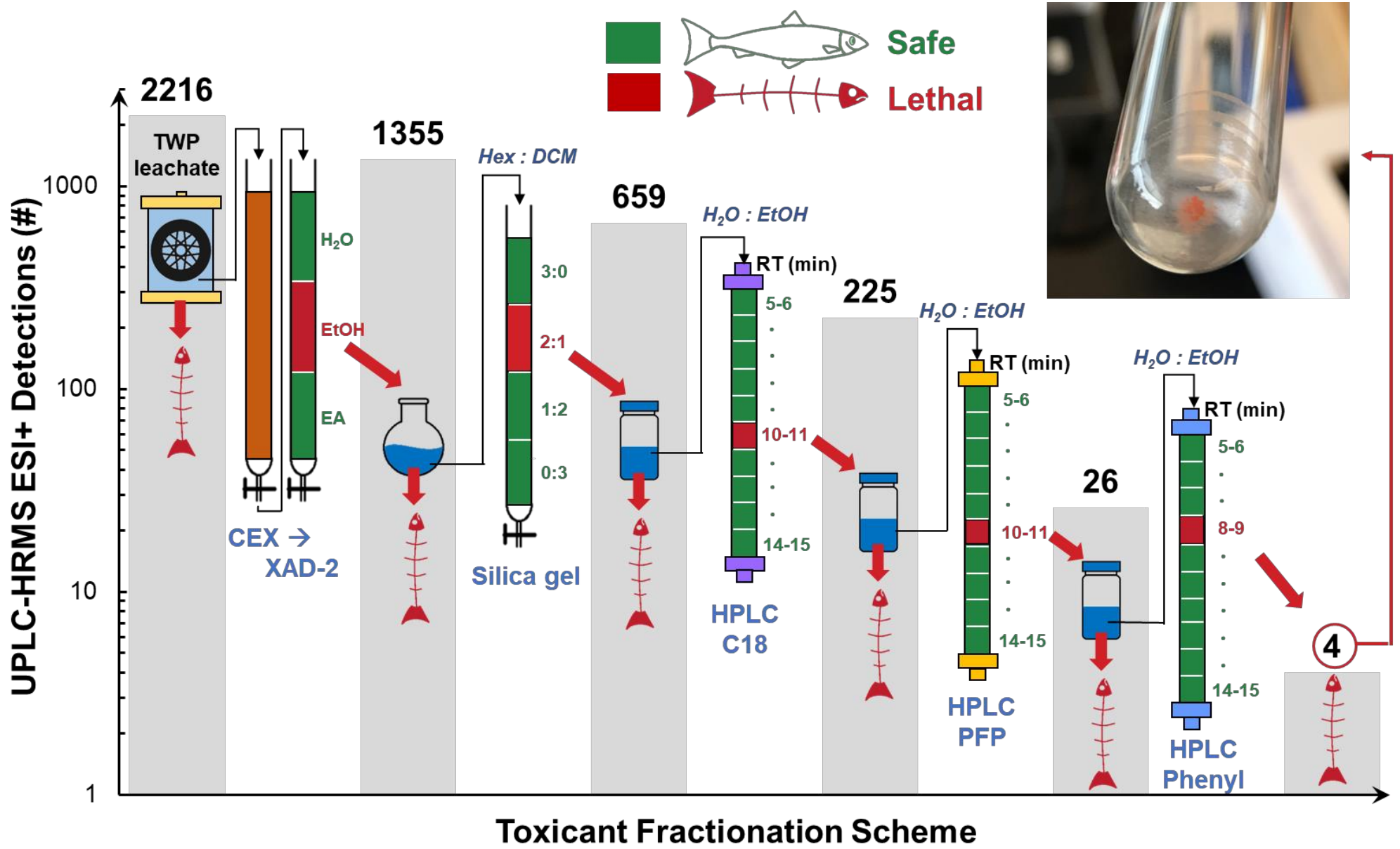


Which part is
toxic?



Toxic fraction go to HRMS for identification

Fractionation of tire wear particle leachate



Purified pink-magenta solid ($C_{18}H_{22}N_2O_2$) acutely lethal to coho in hours

Linking the toxicant to industrial chemical

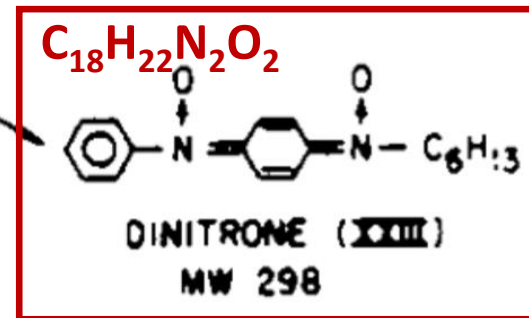
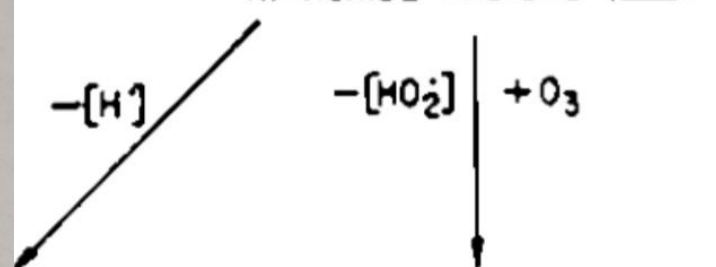
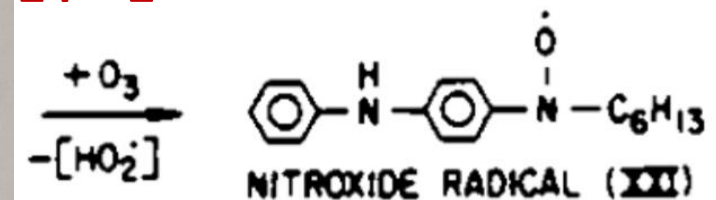
- $C_{18}H_{22}N_2O_2$ NOT found in literature/database about tire rubber chemicals: “True Unknown”
- Assuming transference of H and O but same C and N

changed H and
 $24N_2$ (“6PPD”)



6ppd Rubber Chemical 6ppd Ex-factory Price Rubber Chemicals Antioxidant

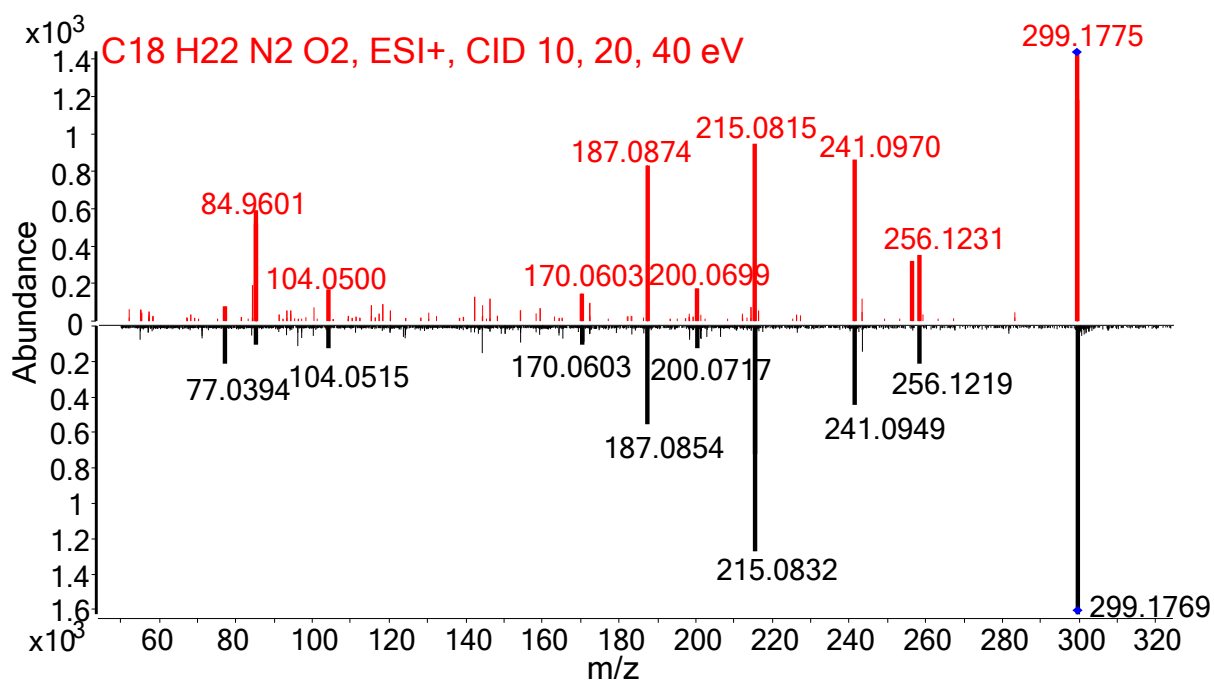
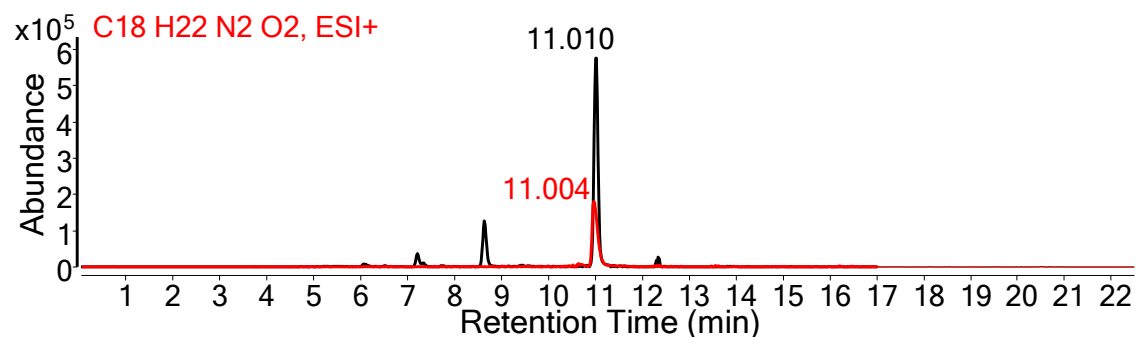
US \$2450-\$2900 / Ton
 1 Ton (Min. Order)



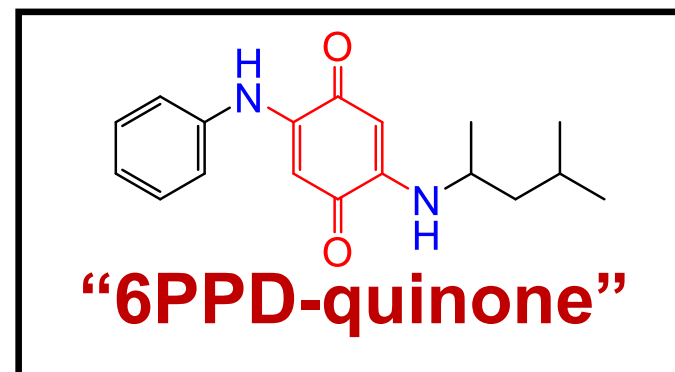
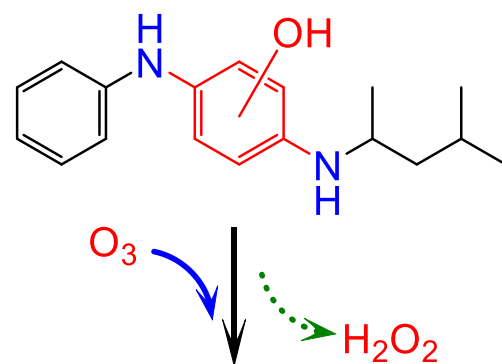
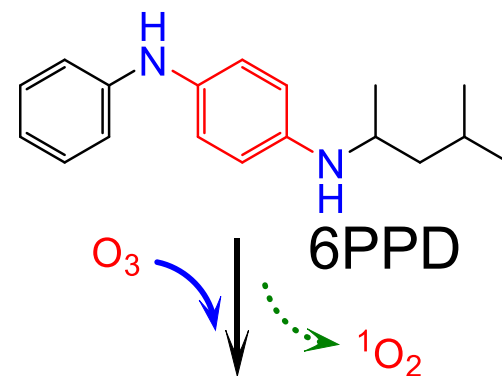
Confirmation and structure elucidation

HRMS & NMR: same compound

Tire leachate | 6PPD ozonation



NMR: identify structure





Field URMS
(Longfellow Creek,
2014)



Lab exposure with
6PPD-quinone

**Same symptoms
before death**

Prevalent occurrences of 6PPD-Q

ENVIRONMENTAL
Science & Technology **LETTERS**

pubs.acs.org/journal/estlcu Letter

Occurrences of Tire Rubber-Derived Contaminants in Cold-Climatic Urban Runoff

J. K. Challis, H. Popick, S. Prajapati, P. Harder, J. P. Giesy, K. McPhedran, and M. Brinkmann*

ENVIRONMENTAL
Science & Technology **LETTERS**

pubs.acs.org/journal/estlcu Letter

Occurrence of Substituted *p*-Phenylenediamine Antioxidants in Dusts

Wei Huang, Yumeng Shi, Jialing Huang, Chengliang Deng, Shuqin Tang, Xiaotu Liu, and Da Chen*

Contents lists available at [ScienceDirect](#)

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Detection of selected tire wear compounds in urban receiving waters[☆]

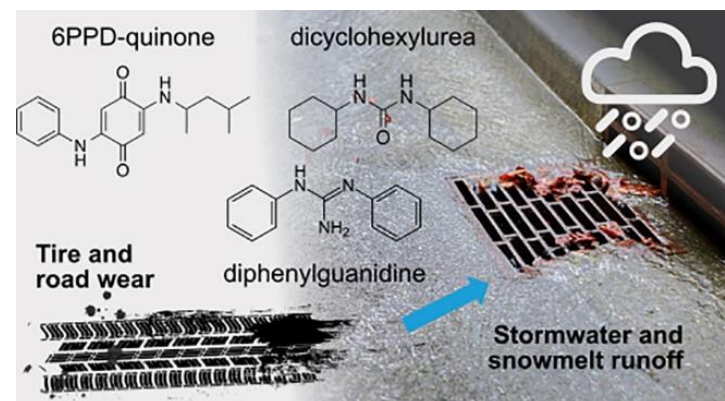
Cassandra Johannessen^{a,*}, Paul Helm^b, Chris D. Metcalfe^a

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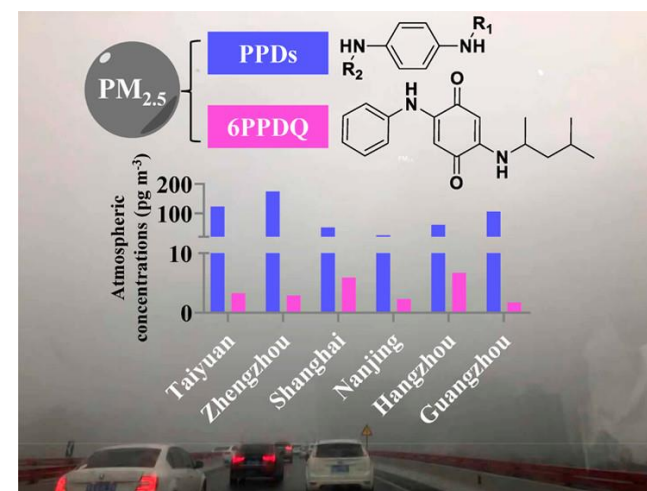
pubs.acs.org/est Article

p-Phenylenediamine Antioxidants in PM_{2.5}: The Underestimated Urban Air Pollutants

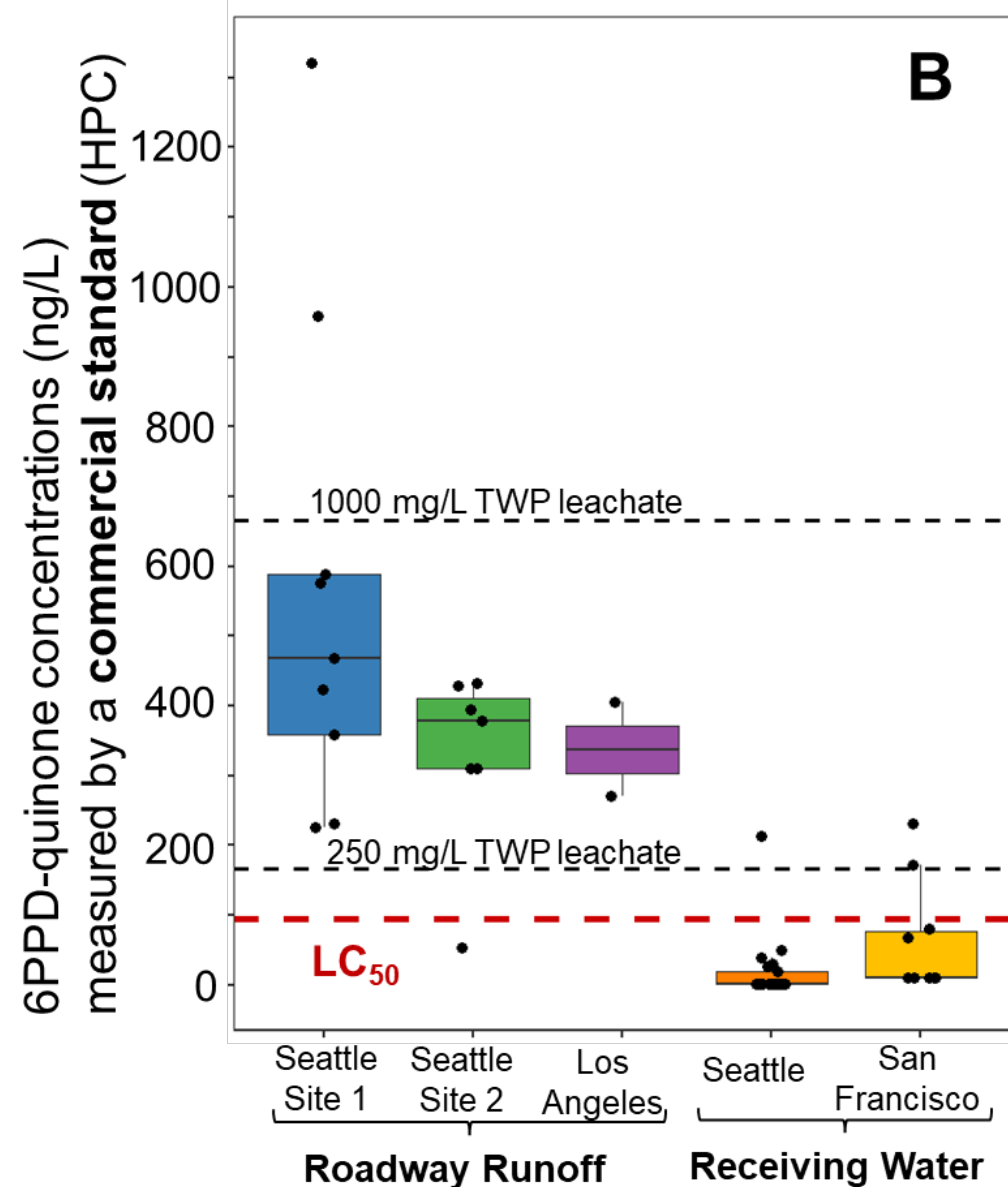
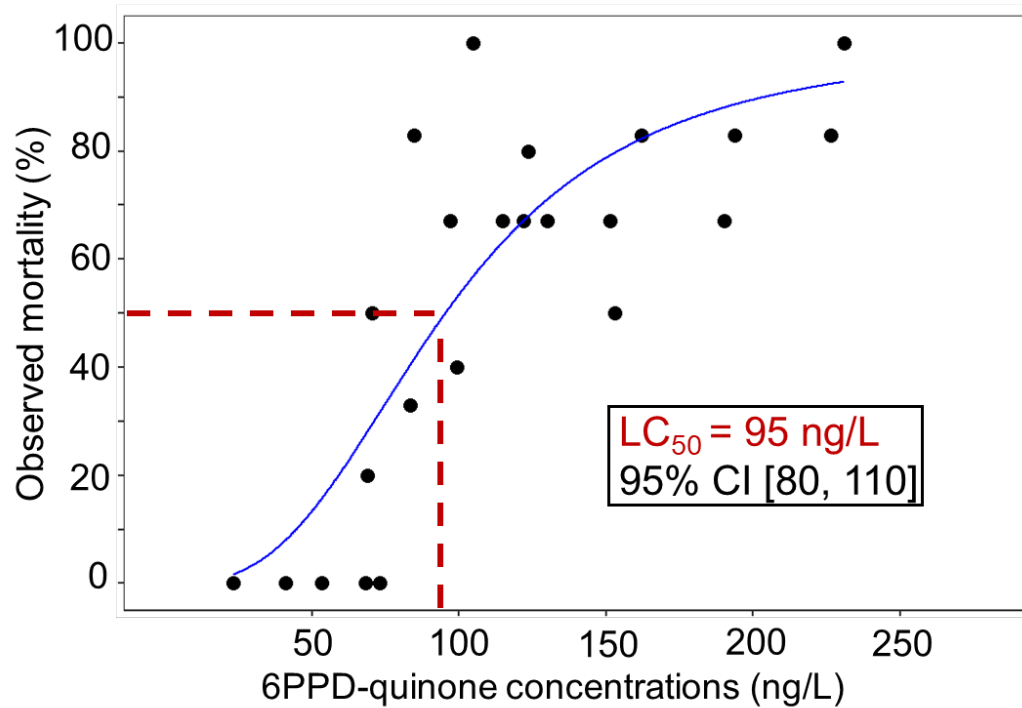
Yanhao Zhang, Caihong Xu, Wenfen Zhang, Zenghua Qi, Yuanyuan Song, Lin Zhu, Chuan Dong, Jianmin Chen, and Zongwei Cai*



compound	road dust (N = 20)	
	range	median
6PPD	4.1–238	52.5
77PD	<LOQ–38.5	<LOQ
DNPD	1.5–35.9	3.4
DPPD	5.8–126	34.9
IPPD	<LOQ–321	55
CPPD	3.4–190	50.2
total PPDs	20.3–543	226
6PPD-Q^b	3.0–88.1	32.2



Updated toxicity with a commercial standard



Lower LC₅₀, lower enviro conc.
More toxic than expected

6PPD-Q toxicity to other aquatic species ?



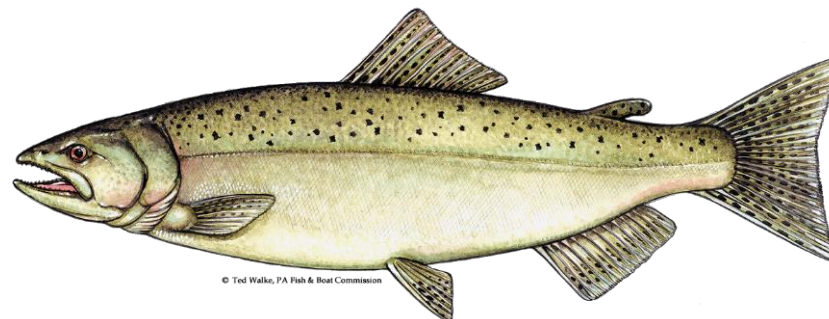
Acute Toxicity of a Tire Rubber-Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species

Kyoshiro Hiki,* Kenta Asahina, Kota Kato, Takahiro Yamagishi, Ryo Omagari, Yuichi Iwasaki, Haruna Watanabe, and Hiroshi Yamamoto

Toxicity to other salmon and trout?

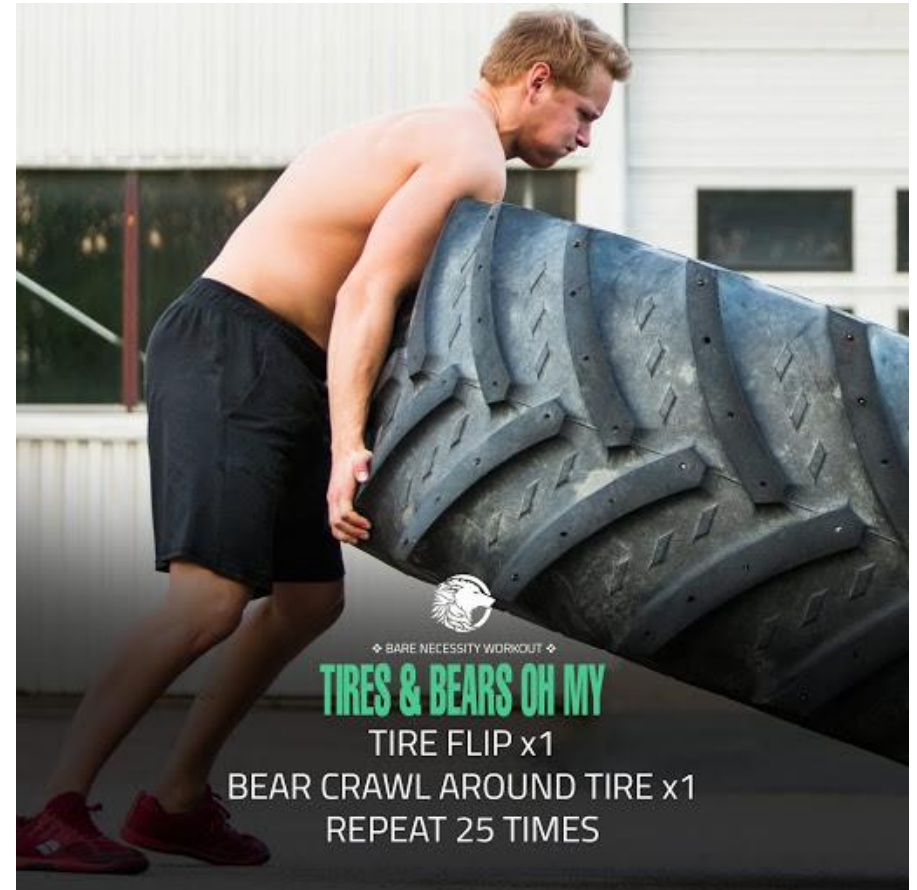


Rainbow trout



Chinook salmon

Crumb rubbers? Human exposure?



- Crumb rubber in artificial fields made from used tires
 - What are the chemical profiles? Similar with tires?
 - Are those tire chemicals toxic to human beings?

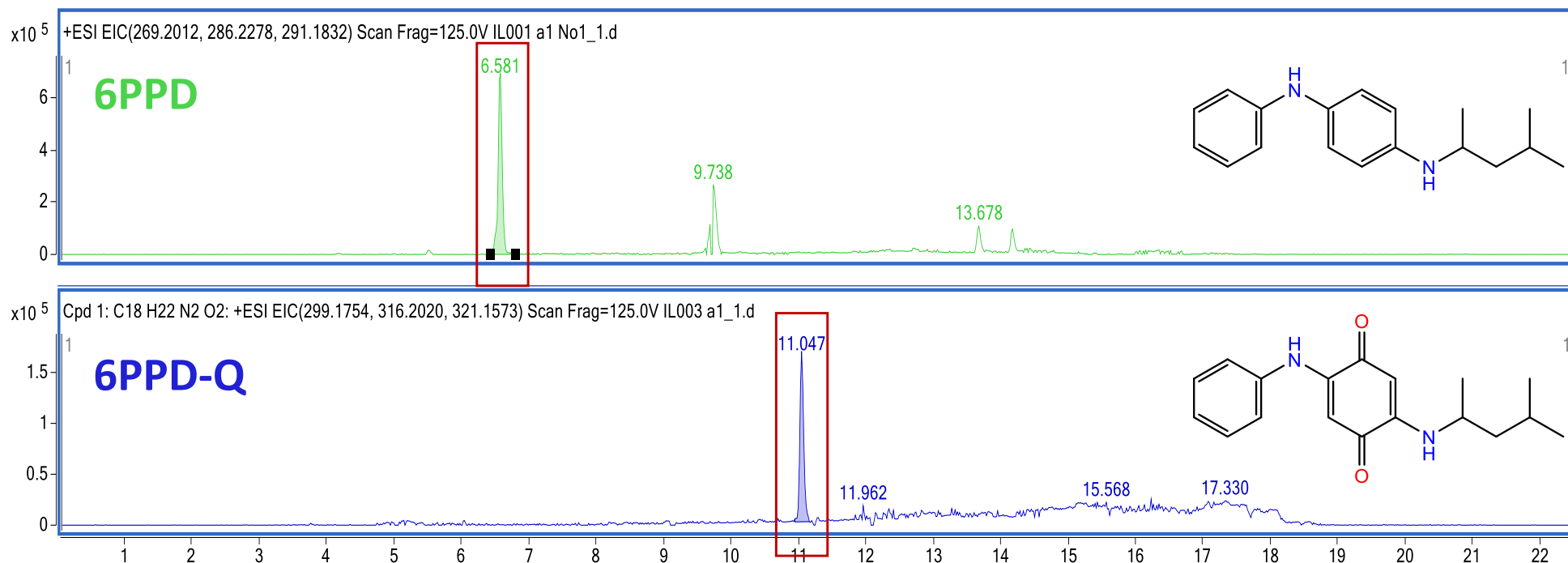
Preliminary work on crumb rubbers



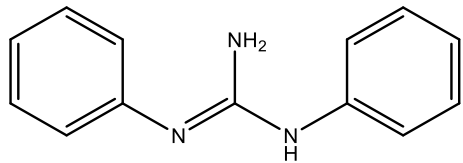
- Collected samples from 6 artificial turf fields
- Solvent extraction and suspect screening

Preliminary analysis on crumb rubbers

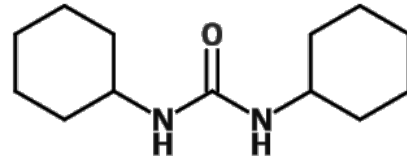
- 6PPD-Q and 6PPD detected in crumb rubbers
 - 6PPD-Q median conc.: 13 $\mu\text{g/g}$ (tire rubber 15 $\mu\text{g/g}$)
- Other typical tire chemicals also identified



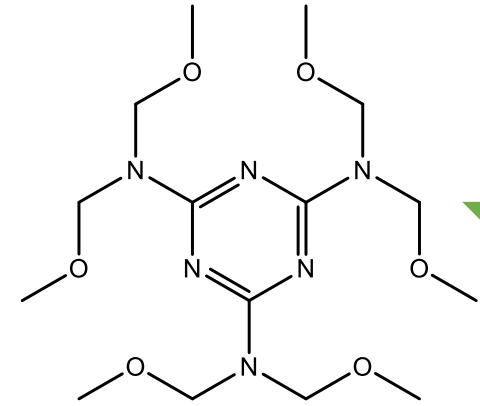
Other chemicals detected in crumb rubbers



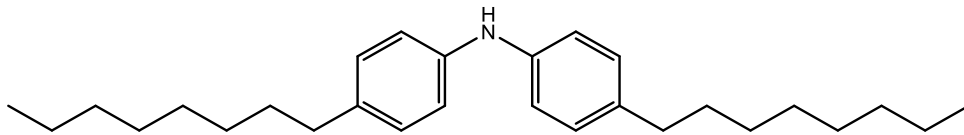
1,3-diphenyl guanidine (DPG)



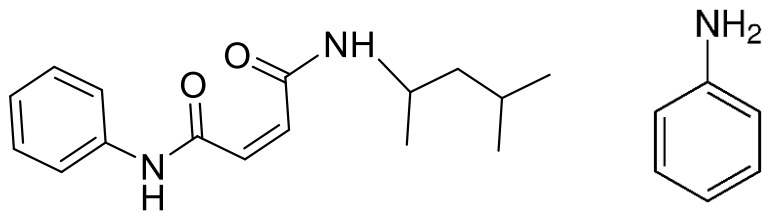
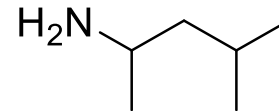
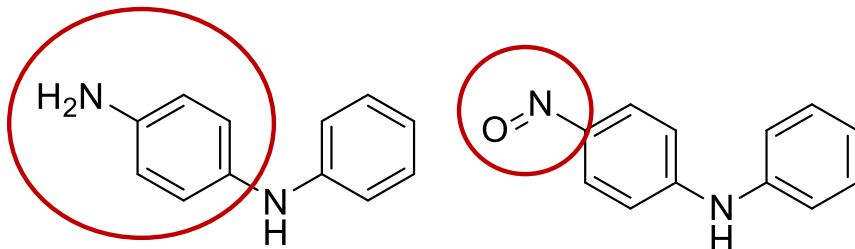
1,3-dicyclohexyl urea



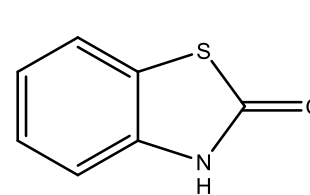
hexa(methoxymethyl) melamine (HMMM)



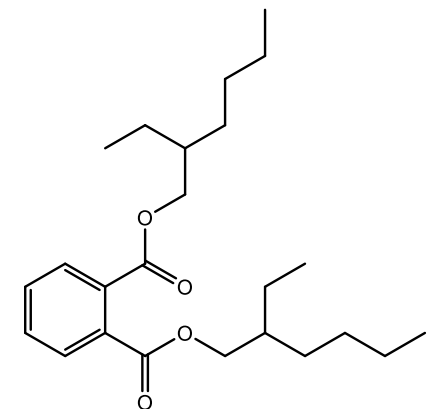
Substituted Diphenylamine Antioxidants (SDPA)



Various transformation products



2-hydroxy-benzothiazole



phthalates

Need for future research

- “Emerging” and unknown contaminants
 - Many contaminants/TPs don’t have analytical standard or toxicology data
- Whole mixture toxicity assessment is needed

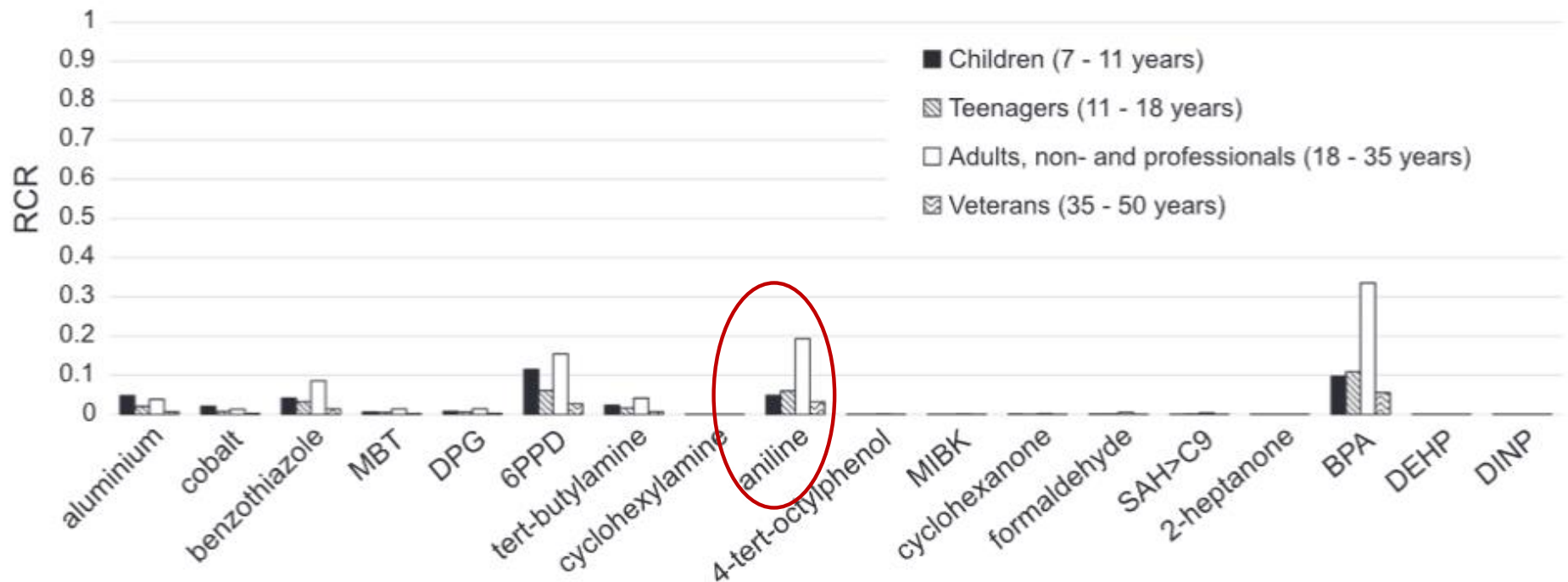
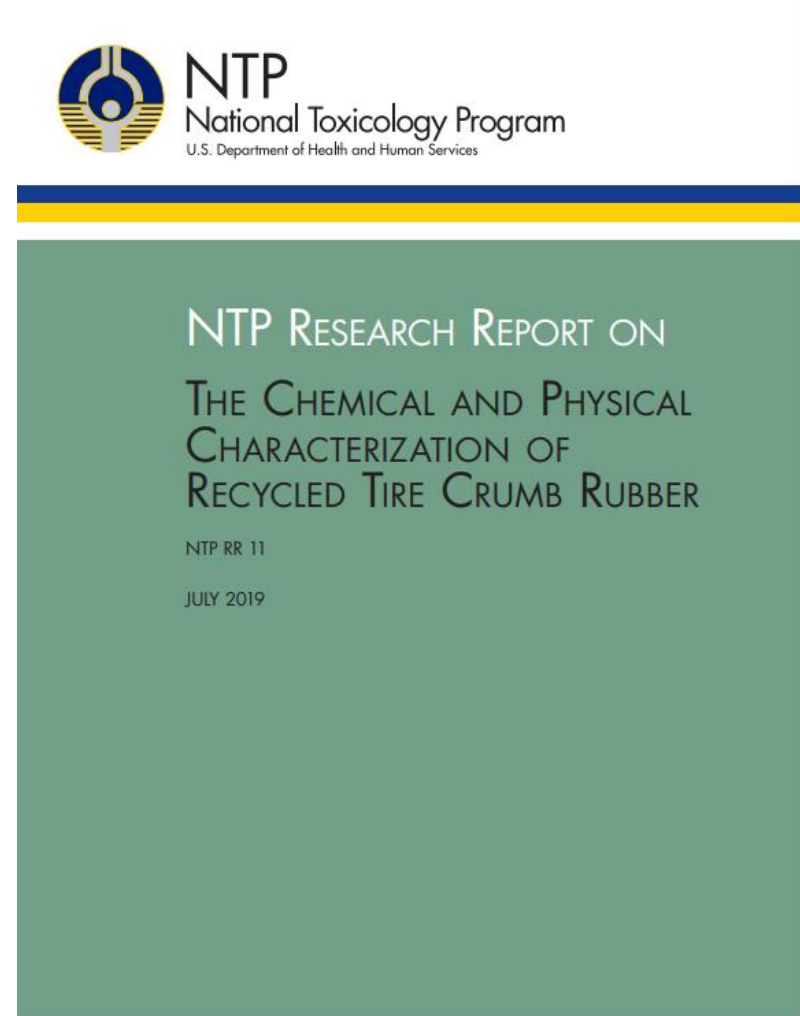
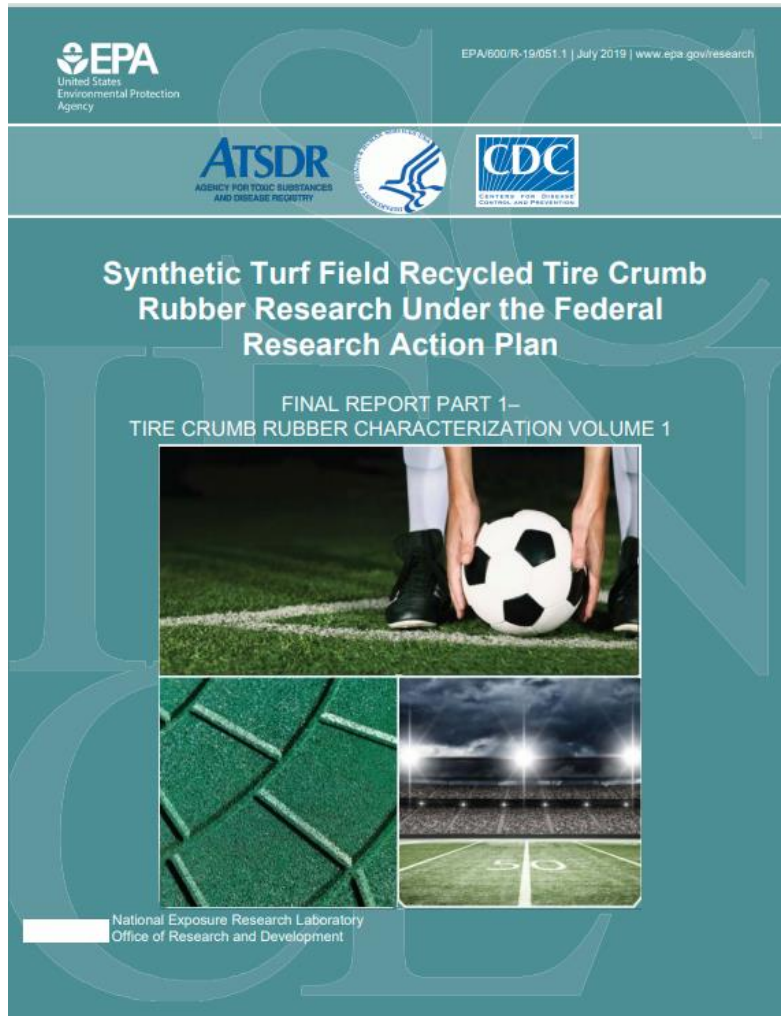


Fig. 3. Combined RCRs for goalkeepers

EPA & NTP reports as good resources



*“...are **not** sufficient by themselves, to directly answer questions about potential health risks.”*

Thanks for your attentions!
Any questions?



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