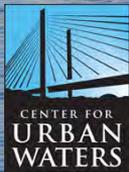


Using HRMS to Identify Organic Contaminants Linked to Urban Stormwater Mortality Syndrome

Edward P. Kolodziej, Katherine Peter, Zhenyu Tian,
Christopher Wu, Fan Hou, Jen McIntyre, Nat Scholz,
and many others at WSU-Puyallup and NOAA-NMFS!



New Tools: High Resolution Mass Spectrometry

So many chemicals: How do we decide which ones are important??



High Resolution Mass Spectrometry (HRMS):
-Identify novel compounds, holistic screening for chemicals

Detect it “all”, then figure out what’s there.

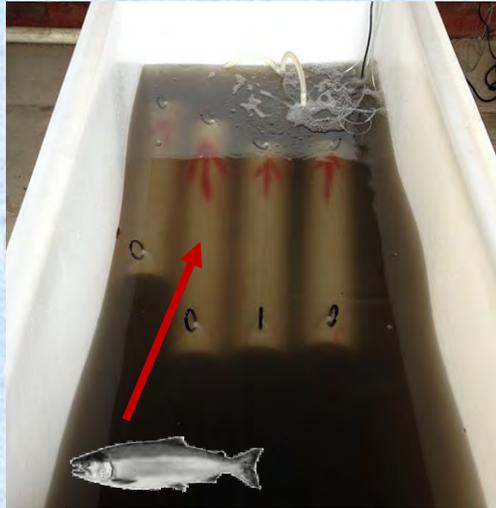
- Fewer assumptions about what is going on



Which chemicals and sources are most important?

Salmon Ecotoxicology In the Lab and Field

Effort to find biological mechanism of toxicity & symptomatic salmon in the field help us to understand URMS



- WSU-Puyallup, NOAA, Grover's Creek Hatchery
- SR 520 highway runoff vs. well water (control)



Miller-Walker
Community Salmon
Investigation



Daily volunteer surveys of urban creeks to count spawning fish, salmon redds, and document URMS



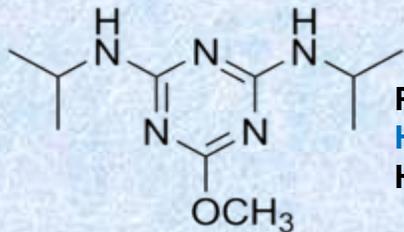
PUGET
SOUNDKEEPER®

Longfellow Creek coho
monitoring

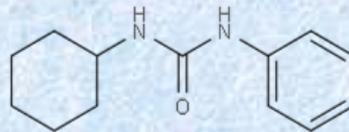


Example Identifications in Urban Stormwater

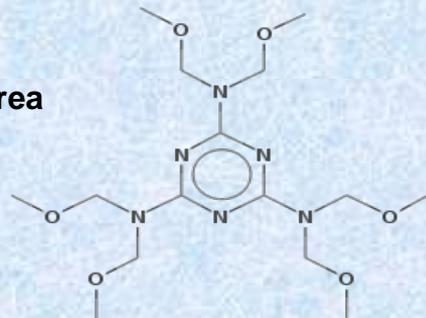
Every stormwater sample has hundred to thousands of chemicals in it..



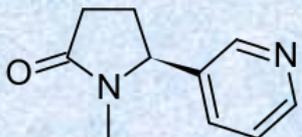
Prometon
Herbicide
Highway runoff (S1)



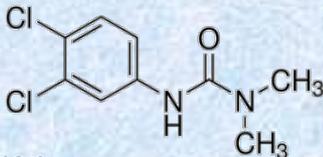
1-cyclohexyl-3-phenylurea
(tire rubbers)
Highway runoff (S1)
Miller Creek (S1)



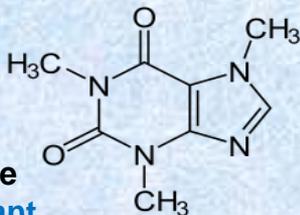
Hexa(methoxymethyl)melamine (HMMM) family
>6 chemicals, tire rubber, automotive plastics
Up to 20 ug/L in runoff, receiving waters
Highway runoff (S1)
Miller Creek (S1)



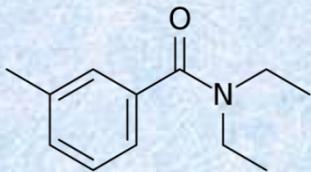
Cotinine
Nicotine metabolite
Highway runoff (S1)



Diuron
Herbicide, paint biocide
Highway runoff (S1)
Miller Creek (S1)

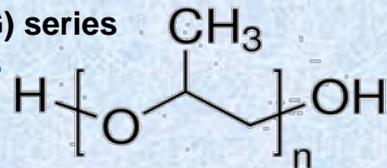


Caffeine
Stimulant
Highway runoff (S1)
Miller Creek (S1)

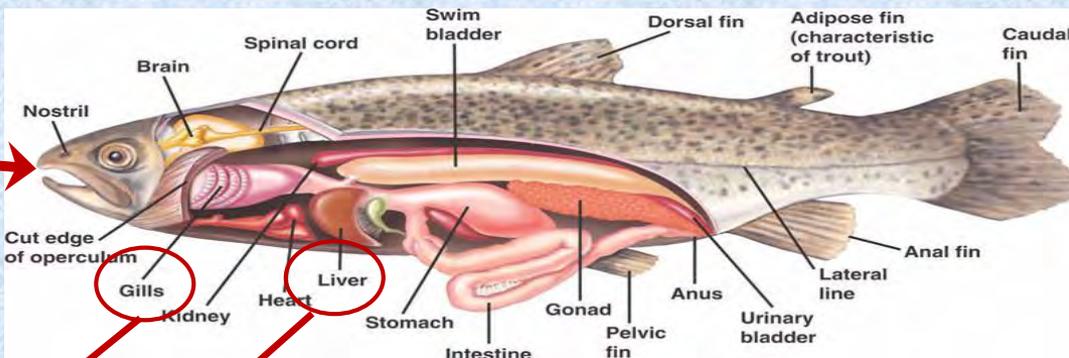
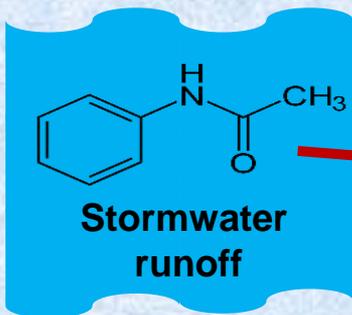


DEET
Insect repellent
Highway runoff (S1)

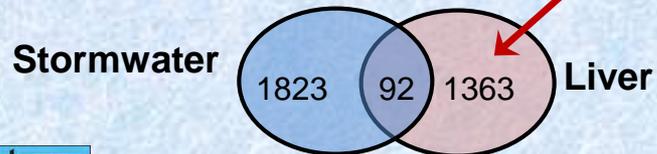
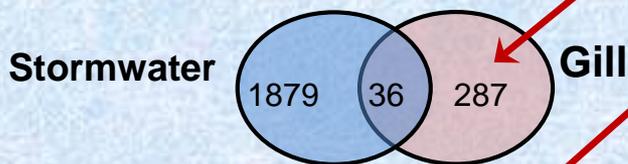
Polypropylene glycol (PPG) series
>22 chemicals, surfactants
Highway runoff (S1)
Miller Creek (S1)



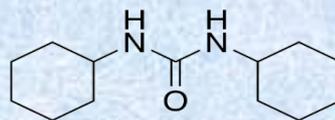
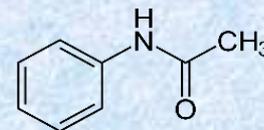
Tire Rubber Chemicals Also Detected in Coho Tissue



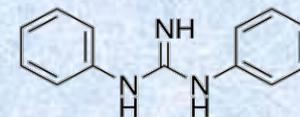
Adult Coho Lab Exposures



Acetanilide (S1)
(tire rubbers)
runoff, liver, gill



1,3-dicyclohexylurea (S1)
(plastics, tires)
runoff, liver, gill

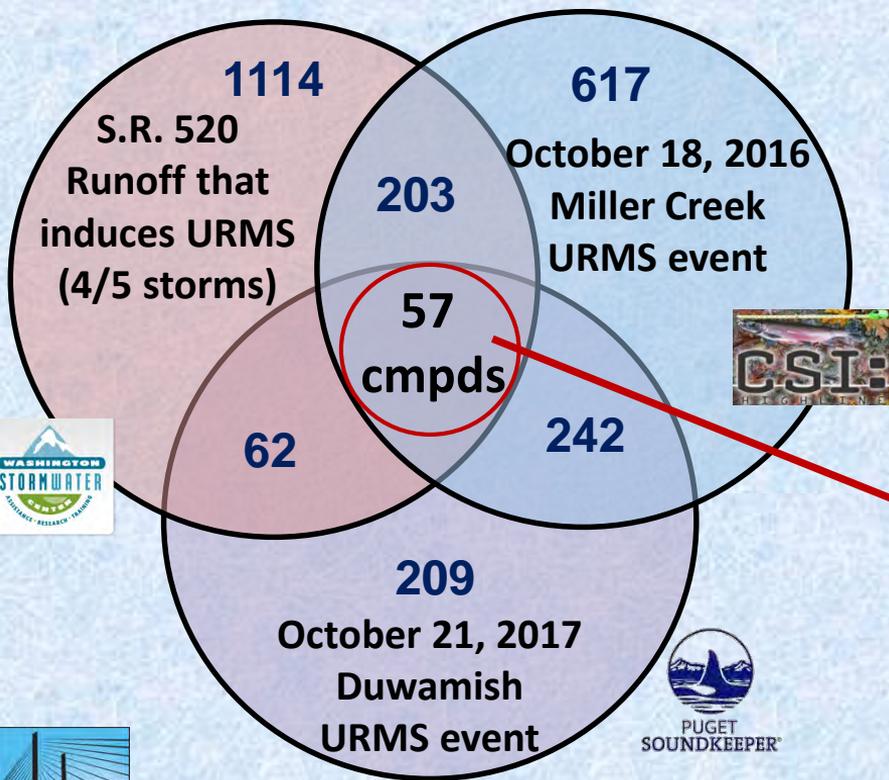


1,3-diphenylguanidine (S1)
(vulcanization accelerator)
runoff, liver

**Chemicals from tires detected in both stormwater and URMS coho;
-rapid uptake (2-3 hrs) of chemicals into fish**

Which Chemicals are Always Present If Salmon Die?

This “toxicant signature” helps us understand why coho died.

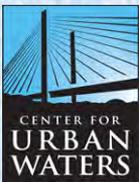


Can compare “new” waters to the waters that we know induced URMS

- Track chemical sources in creeks
- Track signature in treatment systems
- Optimize treatment for signature removal

Blue = # Chemicals detected

Peter et al. 2018 ES&T

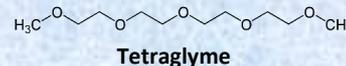
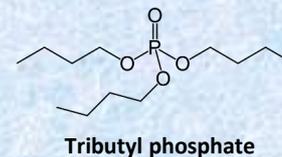
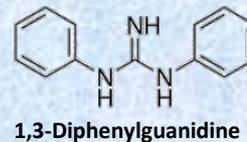
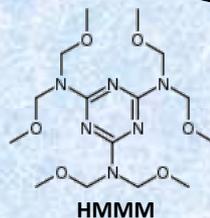
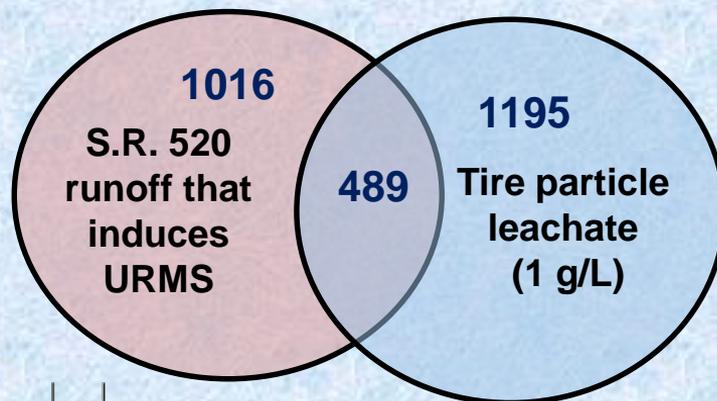


Tire Rubber Chemicals are Especially Common in Urban Stormwaters

**Identified: 29 of 57 detections
Explain ~75-90% of peak area**

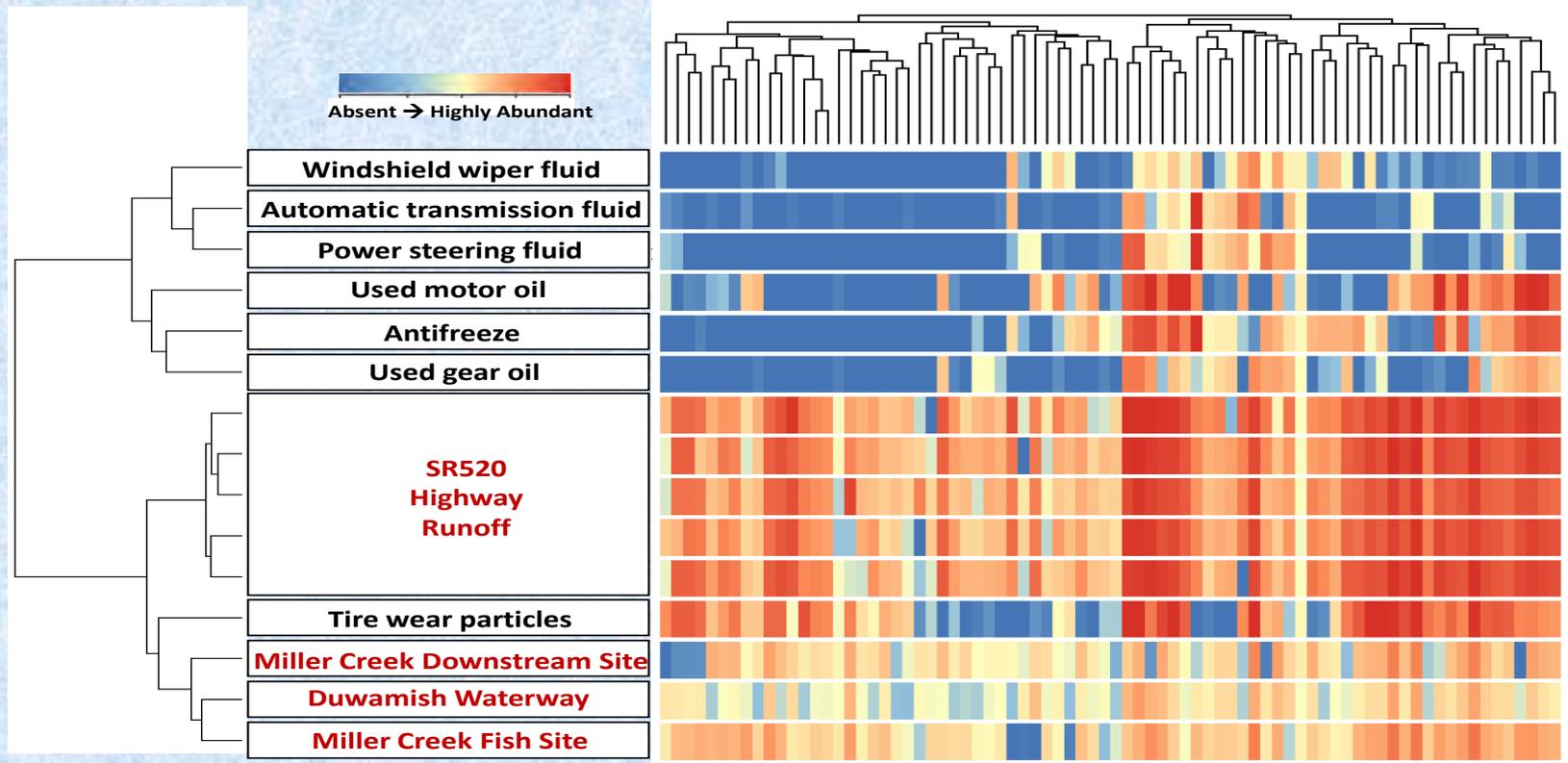
Top Peak Area Detections

| Compound | Peak Area (Miller Creek) | In Tire Leachate? |
|------------------------------------|--------------------------|-------------------|
| Hexa(methoxymethyl)melamine (HMMM) | 2,301,632 | Yes |
| 1,3 Diphenylguanidine | 1,825,652 | Yes |
| C19H28N2O3 @ 10.5 min | 990,915 | Yes |
| Heptapropylene glycol | 696,585 | Yes |
| Nonapropylene glycol | 681,805 | Yes |
| Decapropylene glycol | 619,912 | Yes |
| Tetraglyme | 533,753 | Yes |
| Dicyclohexylurea | 523,377 | Yes |
| Undecapropylene glycol | 434,070 | Yes |
| 312.1575 @ 5.72 min | 395,524 | |



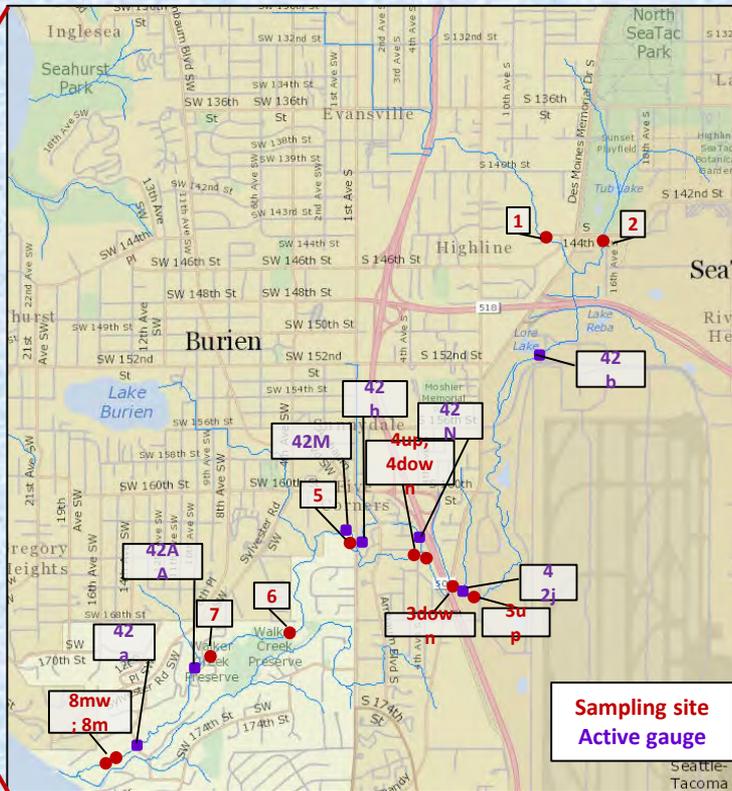
Comparison of “URMS Toxicant Signature” to Different Vehicle Sources

Hierarchical Cluster Analysis (chemical #, intensity, and ratios) of URMS signature detections across different URMS events and automotive chemical sources



Tire leachates cluster with chemical signatures from URMS events

“In Watershed” Spatial Survey to Identify Important Stormwater Sources



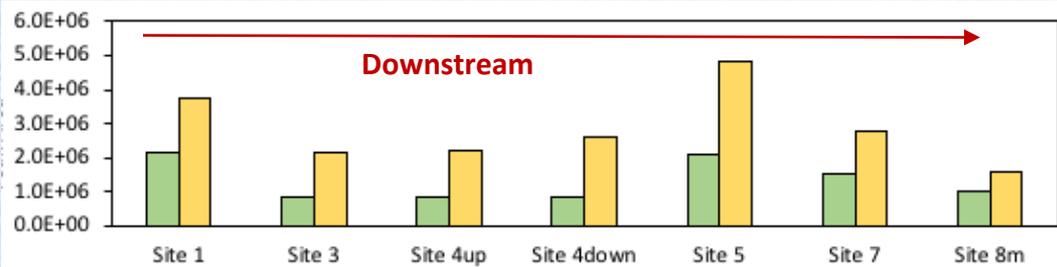
- Study Design:**
- Sample from headwaters (Sites 1,2) to estuary (Site 8)
 - Sample above/below key sources
 - Collection during summer baseflow and fall storms

Miller Creek, Burien/Normandy Park

Can We Prioritize Specific Locations for Management?

Detect and track the appearance of URMS mortality signature in Miller Creek..

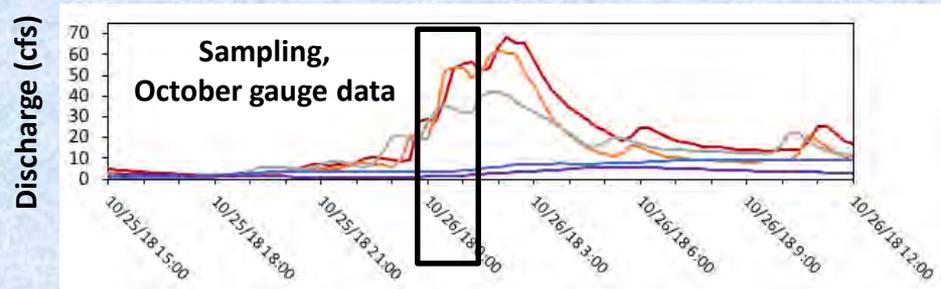
Total mortality
signature peak area



July 11 baseflow
October 22 baseflow

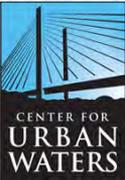


October 25 storm

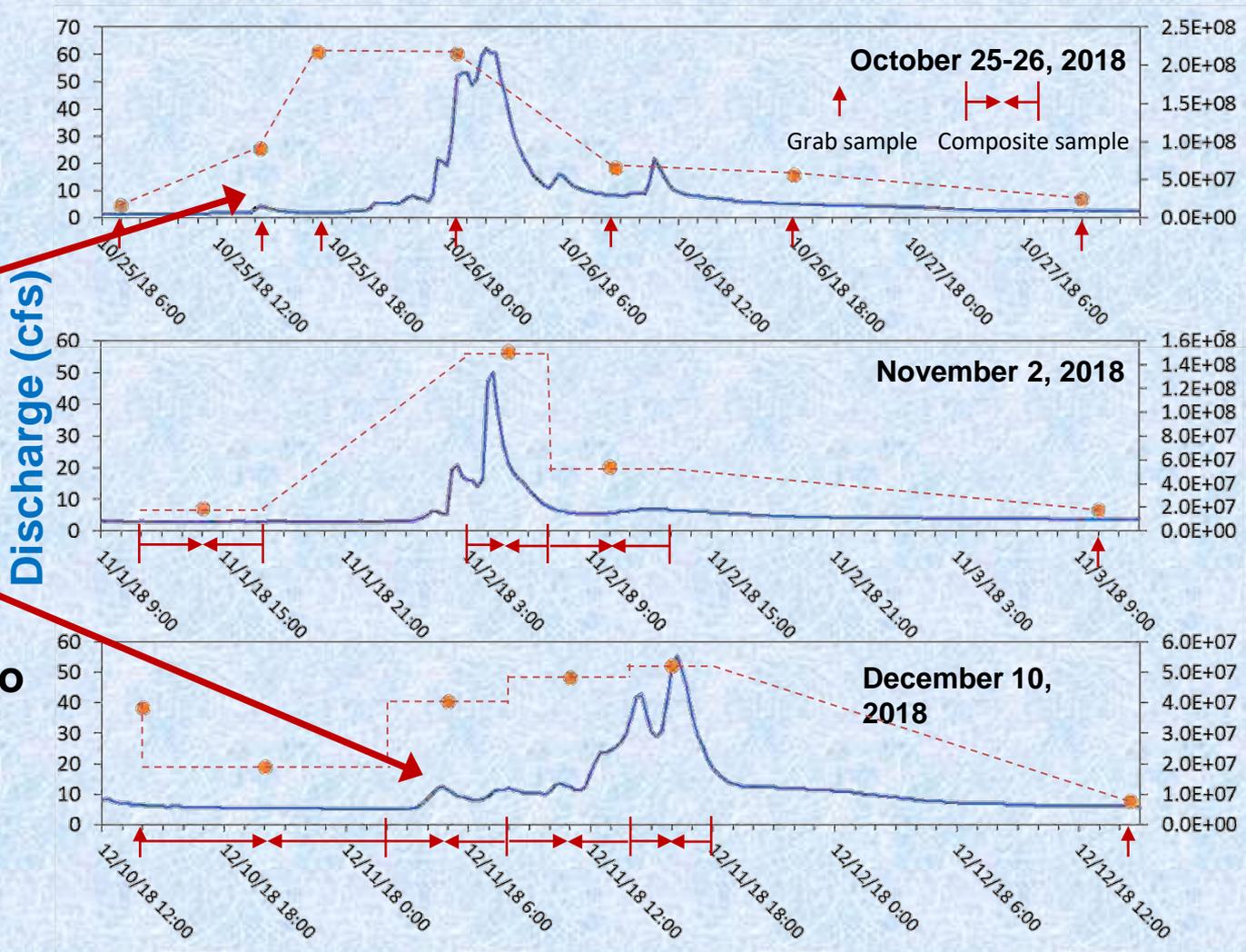


-Higher mortality signature occurrence in fall vs. summer

-URMS mortality signature appears at "Site 4"



Miller Creek



“Killer Drizzle”??

-Up to 7-8 hrs of bad water quality, no real flow increase

-Strong, stagnant chemical source?

Total Mortality Signature Peak Area

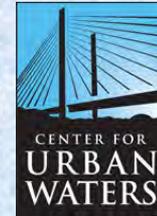
Study Outcomes

- Strong pollution signal from roadways and highways in urban creeks exhibiting URMS symptomology. Also within URMS coho salmon!
- HRMS is detecting pervasive tire rubber chemicals (and others) associated with URMS in Seattle area urban creeks
- URMS mortality signature used to identify specific locations and storm events where water quality degradation occurs
- Small, low intensity rain events may be enough to cause URMS in some urban systems

Acknowledgements and Thanks

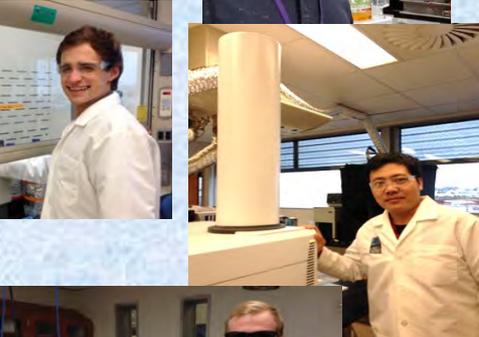
Center for Urban Waters (UW-Tacoma)

- Kathy Peter, Zhenyu Tian, Christopher Wu



Collaborators, Funders, & Citizen Science Teams

- NOAA NWFSC – Nat Scholz, James Cameron, Jessica Lundin (and many others)
- WSU-Puyallup Stormwater Center – Jen McIntyre, John Stark (and many others)
- US Fish & Wildlife Service – Jay Davis, Ken King
- National Science Foundation
- WSDOT – Alex Nguyen, Fred Bergdolt
- EPA-National Estuary Program and WA Dept of Ecology
- FHWA – Cindy Callahan
- SPU – Katherine Lynch, Steve Damm
- Suquamish Tribe
- Miller Walker Community Salmon Investigation, Puget Soundkeeper, Thornton Creek Alliance



References and Technical Details

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Article

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Using High-Resolution Mass Spectrometry to Identify Organic Contaminants Linked to Urban Stormwater Mortality Syndrome in Coho Salmon

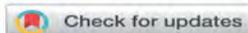
Katherine T. Peter,^{*,†,‡,§} Zhenyu Tian,^{†,‡,§} Christopher Wu,[‡] Peter Lin,[‡] Sarah White,[‡] Bowen Du,^{||} Jenifer K. McIntyre,[⊥] Nathaniel L. Scholz,[#] and Edward P. Kolodziej^{†,‡,§}

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Development of suspect and non-target screening methods for detection of organic contaminants in highway runoff and fish tissue with high-resolution time-of-flight mass spectrometry^{†,‡}

Bowen Du,[Ⓜ] ^{*,a} Jonathan M. Lofton,^a Katherine T. Peter,[Ⓜ] ^a Alexander D. Gipe,^a C. Andrew James,^a Jenifer K. McIntyre,^b Nathaniel L. Scholz,^c Joel E. Baker^a and Edward P. Kolodziej[Ⓜ] ^{ad}

Questions?

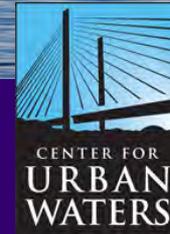
koloj@uw.edu



Center for Urban Waters, Tacoma, WA

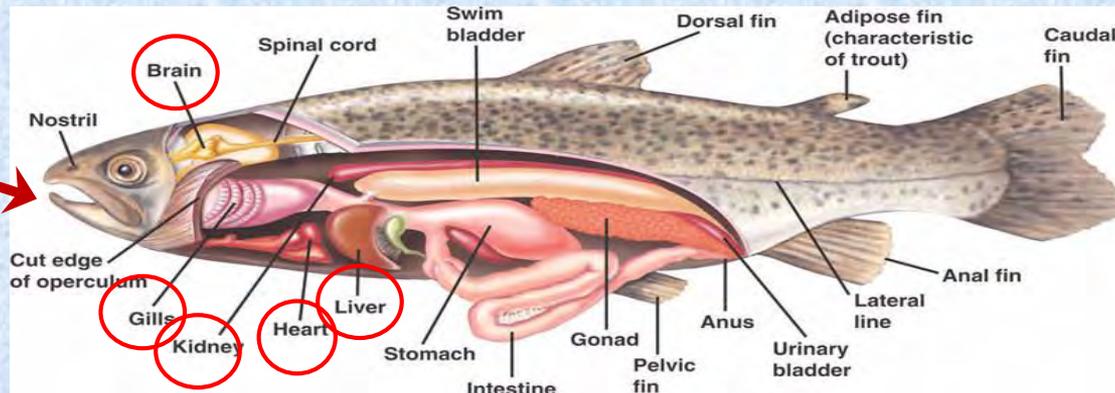
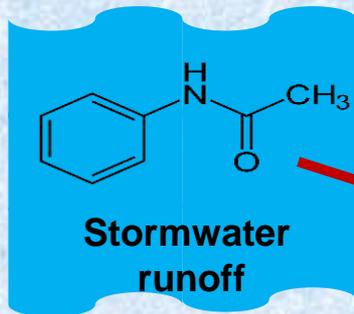
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TACOMA



Understanding Urban Runoff Mortality Syndrome (URMS) with HRMS

URMS cause unknown. CUW: Look for possible toxic chemicals in paired stormwater and coho tissue samples and find their sources.



Toxicant Assumptions:

- Gill uptake
- Dissolved phase
- Polar? LC amenable?
- Conc. ~ug/L?

Water

Gill

Kidney

Liver

Heart

Brain

Study Design: Sample Along Exposure Pathway

Chemical Uptake from Highway Runoff into Exposed Fish

Prioritizing HRMS detections for identification: Hierarchical Cluster Analysis (HCA) to isolate chemical co-occurrence in runoff and tissue samples

