6PPD-Q Spatial PAC agenda March 30th, 2022

Where should we focus our resources first?
When, where and how does 6PPD-Quinone and Aquatic Life Converge?
Acute toxicity to several fish species has been shown, what other aquatic species are impacted?
Tire Wear Particles are persistent microplastics that are bioaccumulated

Note: Today's meeting is a little larger on the invitee list to allow others to hear some of the speakers today.

9:00 Thorsten Reemsta

Head of the Department of Analytical Chemistry
Helmholtz-Centre for Environmental Research – UFZ, Germany

Tire wear particles and associated chemicals in the environment

Thorsten Reemsta specializes in development of analytical methods for organic and polar contaminants in environmental systems, and behavior of trace pollutants in natural and engineered systems. Dr. Reemsta is a member of the Division of Environmental Chemistry and Ecotoxicology of the German Society. Thorsten has authored hundreds of peer-reviewed papers, including several recent papers on TRWP and associated organic contaminants in the environment.

Aging of tire and road wear particles in terrestrial and freshwater environments

Notes:

(presentation links provided on EZview)

This is a large publically funded research center. 6PPD is part of the class of chemicals phenylendiamines, but there are lots of other classes of chemicals in tires which are found in environment as well as their transformation products. Tire additives are 3-10% of tire make up. Image shows particle is a mixture of tire particle and road wear particles are intimately mixed. The alternative chemicals are not known but not suspected to have a better environmental profile. All these protective additives will be transformed if they fulfill their function.

Wagner et al 2019 Water Research gives tire wear rates for US and Germany. If assume 1% 6PPD in rubber, then …
How do these 11,000 tons/a spread on roads compare to 95 ng/L of 6-PPDq? TRWPs are difficult to detect in lab. Pyrolosis GCMS, single particle analysis, Zn after density separation, organic markers, but challenges with each surrogate, and costly. While the zinc surrogate approach is initially promising, the aging of rubber particles changes the relationship and has limited sensitivity. Other organic chemicals, once released move in the environment differently.

6PPDq isn't the only transformation product and it can further transform – lab study (Seiwert et al 2022). Therefore 6PPD cannot be transferred to load 1:1 for 6PPDq, it is a fraction of many 6PPD transformation products.

Leaching of chemicals from tire particles…study from fresh tire tread cryo-milled (Muller et al 2022) Sci Tot Env. 4 fold range of leaching of chemicals from tires and somewhat depends on the polarity of the chemicals, (low MW and polar will leach more), and heavier less polar leach less. **UFZ (2022) unpublish - most of the 6PPD and 6PPDq stay in the particles and are not leached into the environment.** Snow collected in urban environment (Seiwert et al 2022) aqueous portion of melted snow vs majority in particles, most of the load of the snow was in the particle fraction.

Aging of tire and the tire particles; photooxidation, thermooxidation, shear stress, microbial degradation, ozonenation, volatilization, leaching, deposition etc….limited understanding at the moment.
Processes affecting 6PPDq…while still in the boundary layer there is likely an equilibrium between diffusion, oxidation, transformation….so 6PPD is going down in boundary layer and 6PPDq is going up until it is washed off, phase transfer of 6PPDq to water from rubber phase. We need to understand the influencing factors rate of transformations……

Possible solutions

substitutions of chemical **(beware regrettable substitutions)**. **Street cleaning, runoff treatment, sedimentation – burial of TRWPs in sediments should slow down the formation and the release of 6PPDq,**

Conclusion

Most transport of chemicals of TRWPS with road runoff occurs with the particulate phase and not dissolved in water. Importance of dissolved for more polar. 6PPD in TRPWs are partially transformed when deposited on road surface.

Questions

Q: Relative importance of PSD of the particles (Kelly-CA)?

A: There is little to no ability to measure how far down the particle sizes go, in Germany we are looking at aerosols but methods to measure these sizes are limited.

Q: How does temperature affect leaching rates?

A: photochemistry is relatively important and of course temperature would affect rates. But quantitative impacts are not know and not sure if possible to quantify because of how many processes going on. We didn't see a particularly strong result or haven't evaluated the importance of salinity/salt in kinetics.

Q: buried legacy contaminants and flooding, are these a re-mobilization concern?

A: Yes, would think so but would anticipate that would be in particulate form and not expected to be in aqueous phase.

Q: Is there enough ozone in air to form 6PPDq in new products?

A: Unknown

Q: Air chemistry expected to be different than boundary chemistry?
A: We suspect not.

9:20 Markus Hecker

Professor & Canada Research Chair
University of Saskatchewan
Toxicology Centre and School of the Environment & Sustainability

Occurrence of 6PPD-quinone in cold-climate urban runoff and acute toxicity to four fishes of commercial, recreational and cultural relevance

Markus Hecker is a Professor and Canada Research Chair in Predictive Aquatic Toxicology, with 25 years of experience in conducting research in ecotoxicology and chemical hazard assessment. He is considered a global expert in environmental risk assessment, ecotoxicogenomics, hazard characterization of contaminants in native fishes and amphibians, and development of alternatives to live animal testing. Dr. Hecker is a member of the College of the Royal Society of Canada, and a visiting/guest professor at Xiamen University, China. He is the co-Editor-in-Chief of Aquatic Toxicology and serves/served as an advisor/expert to several national and international organizations including Environment and Climate Change Canada, Health Canada, the U.S. Environmental Protection Agency, the European Food Security Agency and the Organization for Economic Cooperation and Development. Markus has authored or co-authored over 200 peer-reviewed papers, review articles, editorials and book chapters over his career.
Including the recent paper "Acute Toxicity of the Tire Rubber-Derived Chemical 6PPD-Quinone to Four Fishes of Commercial, Cultural, and Ecological Importance".

Notes: Canadian researchers are expanding information on fish toxicity in North American prairies environments and cold climates. Research area is characterized by sporatic rain events and very cold winters. The group assessed water samples for DPG, DCA, DCU, CPU, 6PPDq using LC-orbitrap HRMS for chemicals in water and is direct injection (more chemical concentration retention). Saskatoon stormwater runoff was collected from mixed land uses including residential/industrial with four sampling events. **6ppdq found most in the first big rain event (took more than a drizzle) in June but no DPG was detected and samples were collected early in the event.** 1.3-1.4 ug/L. Later rain events shifted to DPG away from 6PPDq. Differences in mass loadings DPG has most mass loading but others are 1-2 orders of magnitude or so below. Roads and residential areas were the most significance land use (linear regression) direct correlation with road surface being a major correlation for other tire chemicals (didn't show 6PPDq). Snowmelt concentrations were releasing 6PPDq early on and were 3-60times less in concentration than direct road runoff during rain events. Latest publication rainbow trout, brook trout, arctic char, white sturgeon ranks sensitivities to 6PPDq (standard static renewal 24hr test) dose response experiments. Brook and rainbow trout maximum mortality within

24hrs and 60hrs respectively. Both displayed same behavioral changes as coho gasping, spiraling, loss of equilibrium. Biologically they observed an increase in glucose and hematocrit affecting energy metabolism as suggested in earlier research.

LC50s: coho 0.095, brook trout 0.59, rainbow 1-2, arctic char, white sturgeon, Japanese medaka zebrafish all >12.7ug/L. Insect results (standard ecotox tests acute/chronic) are being conducted now, but no effects thus far, well above max water solubility.

Questions

Q: Are these dissolved concentrations?

A: Yes they were filtered over glass fiber filter before extraction but only the standard size to get rid of particles. Could easily include nanoparticles. Also, they looked at stability in sediment and didn't see much loss of 6PPDq especially in the higher concentrations. The lower concentrations in the lab 'systems' did go down a little.

Data gap (post meeting followup): what filter size should we be using for cross lab, interstate and international comparisons? Standard is GFF 0.45 µm, should we go smaller? Microbial studies use much smaller pore sizes, and what about the stickiness factor, is 6PPDq sticking to the filters?

Q: Are you looking at sublethal effects?

A: No data yet but this chemical's toxic effects are like a light switch on/off, sensitive or tolerant

Q: How does the fate and transport of DPG vs 6PPDq compare?

A: **the DPG is likely more tightly bound to the particles so some soaking may be needed.** This is just thoughts/guess. Seems to be that the DPG needs a wetting period with TRWP before it desorbs. 6PPDq seems to desorb more quickly. Not sure how much the climate affects these results, not many studies on it. These concentrations are higher than other published runoff studies.
From the chat: Ed K - I think timing of sampling during storms is important.. there are compound specific transport effect that become evident in the data. **Tian Z also about the logKow... polar compounds like DPG will have a broader pollutograph and linger longer in water, while 6PPD-Q is more "flashy" with narrower pollutograph peak.**

9:40 Chad Larson
Washington State Department of Ecology

Examining the direct and indirect impacts of anthropogenic stressors on stream macroinvertebrate communities at multiple spatial scales: a structural equation modeling approach.

Natural Resource Scientist in the Environmental Assessment Program and project lead for biological monitoring for several stream monitoring studies occurring throughout the state

Stream Biological Monitoring

Notes: What is known right now about the stressors to macroinvertebrates from a broad swath overview? Biological metric strategies for measuring the health of a stream, will be useful for context when we begin to evaluate the chemical exposures from emerging chemicals like 6PPDq. Statewide assessments are conducted probabilistically (Larson et al 2019).

Ecological indicators 102: 175-185; **about 30% are impaired for benthic environments and went up for Puget Sound watersheds to ~40%**. Top stressors to BIBI statewide are relative bed stability, percent sand & fines, total N, DO, embeddedness. Relative risk showed that 4x lower BIBI scores due to **% sand & fines**. Next relative risks were **lead and canopy**, and embeddedness causing 3x lower BIBI scores. Attributable risk further tells us how to bring up the BIBI scores across Washington (brings back in the number of locations impacted this way). Lead falls off because it was relevant for only a very small number of sites in WA.

The highest Attributable Risk was % Sand &Fines, RBS, and embeddedness **all has to do with the habitat degradation** prevalence for BIBI across the state. Looking out at landscape likely loss of watershed function is caused by a combination of deforestation, channel alteration, hardened surfaces. In general, it is difficult to pin-point just one culprit.

Biological invertebrate taxa communities shifts in response to altered habitat. The BIBI score is heavily structured on existence of sensitive insect taxa. Used structural equation models to see what is impacting the PS Region so heavily. **BIBI sampling works best for structurally degraded habitats rather than chemically degraded habitats. And it becomes complicated to tease apart what drives the more sensitive species away, we just know that the aquatic site has more tolerant species.**

Statewide: Studies found **% forest cover** going down with **% agriculture and % urban cover** and that impact on BIBI via increased % sand fines most dominantly, followed by conductivity, temperature on par with % agriculture and % urban cover. When look at SEM for just EPT was less conductivity and more temperature.

Puget Sound Region: BIBI what was different is that % sand fines conductivity and % urban cover all equal. There is less agricultural influence. Was still roughly equal when looking at SEM for just EPT. When SEM was done for how different the taxonomic communities were, the line from urban cover goes straight to Vd and not through % sand fines (was this true before?)

10:00 Coffee Break

10:45 Christy Rains
Fish Passage Section Manager
Washington State Fish & Wildlife

WDFW's Fish Passage Barrier Inventory & Assessment Program – An Overview

Fish passage inventory, assessment, and prioritization

Notes: Consideration for this ~30 year program are likely to overlap with considerations for this 6PPD/Q spatial prioritization effort. Barrier assessments is focused on adult fish return obstacles that preclude migration barriers at typical travel times. By count culverts are most numerous followed by "other" barriers and then dams across the landscapes. "Others" includes flumes for example. Our database is called the Fish Passage & Diversion Screening Inventory (FPDSI) available to public on WDFW website along with the manual used for training as they rely on lots of partners to gather this data. Barriers are assessed by water surface drop height, shallow water depth and high water velocity. For water surface drop height is gaged by a 6" trout swimmer, and shallow water depth is the big bodied chinook.

Culvert assessment methods use slope as surrogate for depth and velocity or a hydraulic analysis to determine depth and velocity. Other barrier conditions include sediment depth, trash racks or gates (tide/flood), pipe/culvert damage and deterioration. Most work is with state and local government – fairly externally funded – which means missing barriers on private lands. Federal lands? Partners help get data from different lands. Inventory helps understand the magnitude of the problem. geodataservices.wdfwa.gov/hp/fish passage

We mainly collect instream habitat surveys (physical features) not water quality. Goal really is to inform and get sites improved because when opened up the fish will come. We really don't need to create the fish habitat, it is usually already there.

Q: How can Ecology and WDFW coordinate to get WQ habitat 'chapter' added to this effort so that we are fixing chemical and physical barrier?

A: area of interest and want to keep talking (We have already had some great initial discussions, but need to assess resources and feasibility).

10:30 Braeden Van Deynze
Postdoctural Research Associate
University of Washington School of Marine and Environmental Affairs

Analyzing and applying cost information in restoration planning

Dr. Braeden's research applies econometric and microeconomic methods to better inform conservation planning, with a recent focus on fish passage issues in the Pacific Northwest.

Notes: Theory and conceptual ideas on costs and conservation planning are so important. Everyone wants most bang for the buck and that requires knowledge of the benefits as well as the costs. **Science tends to focus on benefits, and not enough attention given to understanding costs of conservation planning.** Planners might prioritize cost first or benefit first and independently they'll pick different projects. **If we integrate cost and benefit then find the more optimal project for both goals.**

Variability in costs or variability in benefits really impact usefulness of an integrated approach. Focus on cost side for rest of talk. Cost for planning, construction, and opportunity. Planners can integrate costs directly or separate them in a parallel analysis. WDFW's prioritization efforts for culverts (prior speaker) cost are being included in prioritizations. Planners should aim to match the methods for estimating costs to the project needs. Optimize needed precision of data needs e.g. prelim designs and anticipated variability e.g. historical vs current pricing.

Case Study: Culvert correction costs for WA and OR. 15yrs of data from Pacific NW Salmon Habitat Project. Reported costs vs predicted costs; multiple linear regression and boosted regression analysis approaches. Cost driving variables explored (higher or lower).

Thoughts on how to prioritize 6PPDq mitigation costs. While there isn't much data from historical projects…so there may not be established best practices (variability will be very high). Suggest borrowing cost drivers from culvert replacement and road construction, **build ballpark estimates for a handful of situations, and ask folks to track costs in a consistent and transparent manner.**

Questions

Q: Perhaps we should consider reduced cost for placement for simultaneous 6PPD-Q treatment when and where other restoration is planned, e.g., culverts. May also influence design?

10:50 Robert McKane & Jonathan Halama (Speakers)
Environmental Protection Agency & Oregon State University
Additional Authors: Vivian Phan, Allen Brookes, Kevin Djang, Edward Kolodziej, Katherine Peter, Zhenyu Tian.

VELMA model green infrastructure applications for reducing 6PPD-quinone concentrations in Puget Sound urban streams.

VELMA

Notes: Corvallis lab of EPA developed VELMA (grid model 5-10meter) that links hydrology and biogeochemistry and was adapted to include contaminant transport. Using VELMA to evaluate LID in Seattle. Bioswales, pervious pavements, rain gardens and other green insfrastructure. Where should BMPs be located to most effectively remove 6PPD prior to making it to streams. Framing costs are very important to stormwater managers. Ultimately EPA would like to add other contaminants. There are layers of precip, imperviousness, soil layer (4) and the confining bedrock. Can do sensitivity analysis on the fate and transport parameters for 6PPD. Traffic

pattern data is the proxy for deposition in Longfellow creek. Getting hydrology right in this fine system; includes roads as part of hydrology system including buildings. Permeability layer of 0 to 1. Stormwater system is simpler than SWMM, just following the roadways with an in and out.
VELMA performance for hydrology in 2019-2020 pretty good, so adding 6PPDq to hydrology in model and some data on observed instream in creek 6PPDquinone concentrations. VELMA is a daily model so first flush is limited, but is in the 'ballpark' following rain events. 10/26/2020 event well modeled and 11/15/2020 only ~5ng/L off on peak but fairly close in time to model output. Have looked at where the higher input is happening based on traffic pattern inputs. This can help locate where to put LID. Modelling how much LID to use to remove 6PPD-quinone for coho currently and working on sensitivity analysis. We should be finished next month or so. Will be developing models for Miller, Piper, Taylor in Seattle but haven't added 6PPDq to these models yet.

Questions

Q: Can VELMA help figure out more than hotspot inputs, but also existing load in the streambed to make sure the stream supports the fishery?

A: The verification side of modeling is important and users will need to do iterative models when they have a chance to implement and iterate this model.

Q: Samples were grab right, not really spikes or zero as shown.

A: Right, should probably be fixed, we only have point data provided by UWT.

Q: Given the domain that this group is interested in – statewide, and given that VELMA is focused on small and fine scales, how do we use it?

A: UW (Seattle?) has new grant to address nutrient loading in stormwater and scale up to find high priority areas in nearshore systems/ areas of high urbanization pressure.

Q: there is very detailed PM2.5 data in state that tracks tire wear, how can that data be added to VELMA deposition?

A: Could use data like that for deposition. We built a script to translate traffic load x tire wear = deposit on cell by cell. Could replace this approach with atmospheric data. However, VELMA is a daily model, not hourly like atmospheric models, we would have to adjust the model if needed.

Q: SFEI is looking to further refine models and PSD from tires is that most mass is 10-100 um and likely to deposit in first 10m of road but don't know where most surface area (aka contam) is. … trying to sort this out.

A: no but they want to add more BMPs into the model. Ecology is contracting for a broad BMP review for green or gray infrastructure that may work for capturing particulate and the

dissolved contaminant as a starting place on best professional judgement for design and verification monitoring moving forward.

12:00 Wrap up
Rhea is going to pull together all she's heard for prioritization for the Ecology legislative report due by November 2022.

SAVE THE DATE: May 18th *(Updated Teamvite coming soon)*
NOAA updates
6PPD Proviso updates
Monitoring Strategy & Coordination
Next steps

Link to our shared folder for presentation uploads for those willing to share:
6PPD PAC Folder
Username: ecy-10rheasmith
Password: Ehq#3$4Ap2
(both are case sensitive)

Thank you everyone!