2023 ITRC Project Team Final Proposal

Proposed Project Title

Tire Chemicals of Emerging Concern: Use and Fate of Tire Anti-Degradants

Proposal Contacts

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Abstract

Tire anti-degradants are used to extend the life of tires, and 6PPD is currently the most prevalent chemical used for this purpose. A quinone transformation product of 6PPD has been detected in roadway runoff, and is acutely toxic to aquatic organisms. This is especially true for Coho salmon, where the quinone is acutely toxic at multiple life stages. This project will consolidate available information about the use of anti-degradants in tires as well as fate, transport, stormwater treatment, and analytical methods. Fact sheets, guidance documents, a web tool, and training will help raise awareness of this issue and shed light on unanswered questions.

Problem Statement:

The recently-discovered 6PPD-quinone, a transformation product of the tire ingredient 6PPD, is the second most toxic aquatic contaminant known at this time. This compound is acutely lethal to coho salmon, rainbow trout, and brook trout, and additional research is underway to understand concern for additional species as well as sub-lethal impacts. 6PPD-quinone appears to be ubiquitous in highly trafficked areas around the world and is being hailed as the DDT of this generation.

The discovery of 6PPD-quinone began with the discovery of Urban Runoff Mortality Syndrome (URMS). Also known as Coho pre-spawn mortality, URMS a condition first identified on the west coast of the United States where adult Coho salmon die when returning to freshwater streams before spawning. URMS is associated with lethargy, surface swimming, gaping, and loss of equilibrium, in addition to mortality.

Coho salmon are a traditional part of the economy and culture of the west coast and are widely distributed from Northern California to British Columbia. Pacific Northwest tribal groups have been very involved in initial discussions around this issue, with concern that inaction would infringe on their treaty rights. Several Coho populations have declined both in range and abundance in recent years, and many are listed as threatened or endangered under the Endangered Species Act. URMS has been documented mostly in the Pacific Northwest, however ongoing research may reveal additional occurrences.

In December 2020, researchers identified 6PPD-quinone (6PPD-q), a transformation product of the tire anti-degradant 6PPD, as the chemical responsible for URMS (Tian et. al, 2021). Lab studies with 6PPD-q proved the compound to be lethal to 100% of exposed adult Coho salmon in just five hours with an LC50

(concentration at which 50% of the exposed population dies) of ~95 ng/L (Tian et. al, 2022), mimicking previously observed effects of stormwater on Coho, and making it second only to parathion in aquatic toxicity, and twice as toxic as DDT. However, there are many open questions about the specifics of 6PPD-q toxicity. Research is currently underway to provide clarity on the mechanism of mortality, as well as how water quality (i.e., pH, dissolved oxygen) affects 6PPD-quinone toxicity. Road salt has recently been shown to increase the toxicity of the parent compound 6PPD on rotifers (Klauscies and Isanta-Navarro, 2022), suggesting that environmental factors could affect the toxicity of 6PPD-q to other species.

6PPD is used in presumably all vehicle tires to prevent the cracking and breakdown of tire rubber due to reaction with oxygen species – most importantly ozone. 6PPD slowly migrates to the surface of the tire over time where it reacts with ozone and forms a protective barrier. This function is a critical part to ensure the safety and durability of tires.

While the understanding of the reaction of 6PPD to form 6PPD-q is still preliminary, it appears to occur on the surface of the tire or tire fragments (tire wear particles) generated on the road surface once released to the environment. These tire wear particles containing 6PPD and 6PPD-q can then be flushed into streams during storm events. Due to the ubiquity of tire wear particles in aquatic environments (up to 4.6 kg of tire wear particles released per person per year in the United States), 6PPD-q is almost certainly widespread in water bodies across the country. 6PPD and 6PPD-q have been detected in water, sediment, road dust, and air samples worldwide (Hiki and Yamamoto 2022, Zhang et al. 2021, Cao et al. 2022).

Climate change has the potential to worsen the effects of tire antidegradants. Climate change will likely increase ozone concentrations, causing increased reaction of 6PPD to form 6PPD-q. Additionally, in an effort to address climate change, the use of electric vehicles, which are generally heavier, may increase tire wear and the creation of tire wear particles.

The presence of 6PPD-q in multiple media indicates the potential for exposure to a wide variety of aquatic organisms. While URMS is a relatively new phenomenon with relatively few documented instances, 6PPD-q has been detected in California streams and urban runoff at concentrations above the LC50. Exposure of vulnerable populations of Coho to 6PPD-q, including the numerous populations listed as threatened or endangered under the Endangered Species Act, may impede the considerable efforts and money spent by states and tribal governments to rehabilitate these populations. While Coho salmon have been the focus of the URMS research to date, preliminary evidence suggests that the toxic impacts of 6PPD-q are not limited to Coho salmon. Salmonids that are closely related to Coho such as steelhead and chinook salmon are also adversely impacted by exposure to 6PPD-q, even if not to the same extreme degree as is seen for Coho salmon. Additionally, a recent publication revealed 6PPD-quinone to be lethal to rainbow trout and brook trout, although they do not appear to be as sensitive as Coho salmon (LC50 values of ~.59 µg/L and 1 µg/L respectively) (Brinkmann et al., 2022).

Toxicity to trout shows that 6PPD and 6PPD-q contamination of stormwater could be affecting important aquatic species nationwide, given the prevalence of trout as hatchery-reared recreational fish. Stormwater has been shown to have an adverse effect on trout populations in locations such as Minnesota and North Carolina, and 6PPD-quinone may be contributing to these problems. Other species such as arctic char, white sturgeon, and zebrafish seem to be much less susceptible to 6PPD-q toxicity (Brinkmann et al., 2022), but there are likely also as-yet identified impacts to non-salmonid aquatic organisms. Therefore, the presence of 6PPD-q in waterbodies presents a clear and present danger for aquatic life across the country.

There has been research into other anti-ozonants that can be used in tires as anti-degradants besides 6PPD. Other p-phenylenediamines (PPDs) have historically been used for this purpose, including IPPD, 7PPD, and 77PD. In addition, a wide variety of chemicals have been tested for anti-ozonant properties in rubber,

such as styrenated phenols, trimethylquinoline polymers, diphenylamine derivatives, and bisphenol/monophenol derivatives. Many of these potential alternatives showed similar or superior performance in the lab as an anti-ozonant. However, 6PPD has emerged as the anti-ozonant of choice by the industry due to a wide variety of factors, including migration time, molecular weight, melting point, and compatibility with rubber formulations. Other PPDs and their quinone transformation products have also been detected in environmental samples, showing that they still have widespread use (Cao et al. 2022), most likely in products other than tires. There is limited toxicological information available on many of these alternatives, especially PPDs, and whether their quinone transformation products can also cause URMS is unknown.

Limited research has shown that certain forms of green stormwater infrastructure may be effective at treating roadway runoff to prevent URMS. A column of soil, sand, and bark reduced deaths from stormwater that was otherwise fatal to Coho salmon. However, there are many open questions with regard to stormwater treatment, such as the effectiveness and lifetime of other types of treatment.

The parent compound 6PPD has known human health concerns, including reproductive toxicity and skin sensitization. Researchers as well as members of the public have expressed interest in more information about potential risks to human health from tire use. There has been significant research into risks from crumb rubber use in applications such as synthetic turf recreation fields, and the contribution of 6PPD and 6PPD-q to potential hazards associated with the use of crumb rubber is unknown. Further consolidation of 6PPD, other PPD, and anti-ozonant toxicity information as a whole would shed light on this area of interest.

Addressing Technical and Regulatory Barriers*:* Since identification of 6PPD-q as the causal agent in URMS, a wide variety of states, manufacturers, NGOs, tribal governments, and environmental laboratories have expressed interest in the problem. Given the newness of the topic and lack of data, there is a strong need for material that provides the basics of the issue in a way that is approachable to a diverse audience.

Research efforts to better understand the toxicological hazards of 6PPD or 6PPD-q have just begun. Tire anti-degradants in general are an unexplored source of potential toxicity to the environment and humans as they are intended to be reactive. Other anti-degradants, including other p-phenylenediamines (PPDs), have been used historically in tires and are still used today. The toxicity of these other compounds and how they compare to 6PPD is still largely unknown. Alternative anti-degradants are under investigation for both toxicity and performance. A wide-ranging amount of research presumably began in December of 2020 or early 2021 to better understand this emerging issue. Keeping apprised of this literature will be a formidable undertaking for all who are interested in this topic. While efforts to consolidate this research are underway locally in Washington, there is no larger, nation-wide effort.

Methods to quantify 6PPD and 6PPD-q in products and in the environment are still in development. A small number of contract and government labs are just beginning to offer analysis of 6PPD-q to those interested in the topic, but this number is expected to grow. Awareness of these services is critical for those seeking to better understand the presence of 6PPD and 6PPD-q in the environment. Future efforts to expand these methods to include other anti-degradants would provide much-needed insight into the environmental implications of tire rubber derived pollutants.

One critical finding of the URMS research has been that green stormwater infrastructure is effective at preventing URMS in treated roadway runoff. Those tasked with mitigating the impacts of 6PPD-q from stormwater will need best management practices and training on how to implement these treatments as well as an understanding of their limitations.

ITRC Innovative Solutions: Although many state agencies and other groups are pursuing the latest science on 6PPD and other tire related anti-degradants, there is no national group serving as a central location for sharing of information and coordination among the states. ITRC will provide this function, as well as consolidating the limited available knowledge in this area, informing the interested public as to the science behind this problem, and informing efforts to manage the harm to aquatic life. Given the newness of the topic, we anticipate that the working group for this project may be small. Therefore, we propose a smaller set of project deliverables. This project will serve to provide valuable information to states and the public, facilitate information gathering and sharing beyond the initial project scope, and may inform future projects related to 6PPD and tire related contaminants.

Fact Sheets - Fact sheets will be developed to provide an overview of 6PPD-q and urban runoff mortality syndrome, including the history and use of 6PPD, analytical methods for measuring 6PPD and 6PPD-q concentrations, stormwater treatment BMPs and effectiveness, and the known physical and chemical properties, fate, and transport of 6PPD and 6PPD-q. These fact sheets will be instrumental in helping states get up to speed on this issue and assess the relevance to their local environments.

Training – A series of short videos based on the Fact Sheets will be developed that environmental professionals can use to get up to speed on the 6PPD topic. These videos, in combination with the fact sheets, will provide two tools for learning the basics of 6PPD and sharing the information with the general public.

A wide variety of stakeholders have expressed interest in 6PPD, 6PPD-q, and anti-degradants in general since the association with URMS was discovered. Webinars discussing the subject regularly have representation from municipal, state, and federal agencies working on subjects including stormwater, wastewater, transportation, human health, and consumer products. In addition, many NGOs have proposed and advocated for legislative action and further public information. Both Washington and Minnesota state have proposed or adopted legislative agendas to further investigate the health and environmental risk of tire anti-ozonants, and California has proposed regulating the presence of 6PPD in motor vehicle tires. The tire industry has been very involved in initial discussions, and the Tire Industry Project, a research arm of the tire industry, has several research efforts aimed at clarifying information related to possible effects and composition of tire and road wear particles.

Project Deliverables

- A Fact Sheet that summarizes the available information on 6PPD-q and urban runoff mortality syndrome, including the history and use of 6PPD, analytical methods for measuring 6PPD and 6PPD-q concentrations, and physical and chemical properties, fate, and transport of 6PPD and 6PPD-q in the environment.
- A series of short videos based on the Fact Sheets that can be used for training on the topic.

State Team Leader

Which, if any, states have indicated an interest in leading the team and providing a Team Leader:

1. Main Lead - Washington Ecology: 6PPD Coordinator (in the hiring process now)

2. Secondary Lead - California DTSC: Anne-Cooper Doherty

Additional Information

Other groups that have expressed interest in participating on the team:

Oregon Department of Environmental Quality: Kevin Masterson, kevin.masterson@deq.state.or.us

Minnesota Pollution Control Agency: Mark Ferry, mark.ferrey@state.mn.us

Massachusetts Department of Environmental Protection, Office of Research and Standards: C. Mark Smith Ph.D., M.S. Director, Office of Research and Standards, c.mark.smith@mass.gov

Washington State Dept. of Ecology: Samuel Iwenofu, siwe461@ecy.wa.gov (ITRC Board)

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Dan Kent, Salmon Safe, dan@salmonsafe.org

Dylan Ahearn, Herrera, dahearn@herrerainc.com (a geodatabase for 6PPDq field data)

Shelly Keding, Eastman Chemical Company, SRKEDI@eastman.com as a resource for the team-not a full participant

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