Technical/Regulatory Guidance

6PPD &

6PPD-quinone

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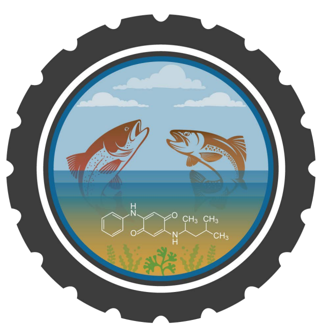

September 2024

Prepared By

The Interstate Technology & Regulatory Council (ITRC)

6PPD and 6PPD-quinone Team

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In 2020, 6PPD-quinone (6PPD-q) was identified as a chemical that is fatal to coho salmon in urbanized areas of the Puget Sound in Washington State (Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. “A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon.” Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.). Since its discovery, 6PPD-q has been found to be acutely toxic to brook, rainbow/steelhead, lake trout, and coastal cutthroat trout, which are important ecological and recreational species throughout the United States (Nair et al. 2023[9V5ES4MI] Nair, Pranav, Jianxian Sun, Linna Xie, Lisa Kennedy, Derek Kozakiewicz, Sonya Kleywegt, Chunyan Hao, et al. 2023. “In Process: Synthesis and Toxicity Evaluation of Tire Rubber–Derived Quinones.” Preprint. Chemistry. https://doi.org/10.26434/chemrxiv-2023-pmxvc.Brinkmann et al. 2022[QN6HYEV7] Brinkmann, Markus, David Montgomery, Summer Selinger, Justin G. P. Miller, Eric Stock, Alper James Alcaraz, Jonathan K. Challis, et al. 2022. “Acute Toxicity of the Tire Rubber–Derived Chemical 6PPD-Quinone to Four Fishes of Commercial, Cultural, and Ecological Importance.” Environmental Science & Technology Letters, March, acs.estlett.2c00050. https://doi.org/10.1021/acs.estlett.2c00050.Roberts et al. 2024[FMG8VP7Y] Roberts, Catherine, Junyi Lin, Evan Kohlman, Niteesh Jain, Mawuli Amekor, Alper James Alcaraz, Natacha Hogan, Markus Hecker, and Markus Brinkmann. 2024. “Acute and Sub-Chronic Toxicity of 6PPD-Quinone to Early-Life Stage Lake Trout (Salvelinus namaycush).” bioRxiv. https://doi.org/10.1101/2024.03.26.586843.Di et al. 2022[BLEFEP7S] Di, Shanshan, Zhenzhen Liu, Huiyu Zhao, Ying Li, Peipei Qi, Zhiwei Wang, Hao Xu, Yuanxiang Jin, and Xinquan Wang. 2022. “Chiral Perspective Evaluations: Enantioselective Hydrolysis of 6PPD and 6PPD-Quinone in Water and Enantioselective Toxicity to Gobiocypris Rarus and Oncorhynchus Mykiss.” Environment International 166 (August):107374. https://doi.org/10.1016/j.envint.2022.107374.). Studies have shown that 6PPD-q is not lethal to several other aquatic species, including, but not limited to Atlantic and sockeye salmon (Foldvik et al. 2022[LQWXZHJA] Foldvik, Anders, Fedor Kryuchkov, Roar Sandodden, and Silvio Uhlig. 2022. “Acute Toxicity Testing of the Tire Rubber–Derived Chemical 6PPD-Quinone on Atlantic Salmon (Salmo Salar) and Brown Trout (Salmo Trutta).” Environmental Toxicology and Chemistry 41 (12): 3041–45. https://doi.org/10.1002/etc.5487.Greer et al. 2023[P6RF5UFR] Greer, Justin B., Ellie M. Dalsky, Rachael F. Lane, and John D. Hansen. 2023. “Establishing an In Vitro Model to Assess the Toxicity of 6PPD-Quinone and Other Tire Wear Transformation Products.” Environmental Science & Technology Letters, May. https://doi.org/10.1021/acs.estlett.3c00196.).

6PPD-q is now recognized as a global contaminant (Tian et al. 2022[BICQHLBC] Tian, Zhenyu, Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C. Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej. 2022. “6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard.” Environmental Science & Technology Letters, January, acs.estlett.1c00910. https://doi.org/10.1021/acs.estlett.1c00910.). To put 6PPD-q toxicity into context, in June 2024, the United States Environmental Protection Agency (USEPA) issued non-regulatory and non-binding screening levels for 6PPD-q that provide information to states and tribes for their water quality protection programs. These screening levels are intended to serve as values that are protective of aquatic life, including sensitive species like coho salmon. USEPA set the screening level for 6PPD-q at 11 nanograms per liter (ng/L), or 11 parts per trillion, for acute (1-hour) exposure.

Mammalian studies have found that 6PPD-q can pass through the placenta to a fetal mouse (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. “Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear

Receptor Pathways." Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.), damage rodent liver and other organs (He, Gu, and Wang 2023[6MPWVZGE] He, Wenmiao, Aihua Gu, and Dayong Wang. 2023. "Four-Week Repeated Exposure to Tire-Derived 6-PPD Quinone Causes Multiple Organ Injury in Male BALB/c Mice." Science of the Total Environment 894 (October):164842. https://doi.org/10.1016/j.scitotenv.2023.164842.), and primarily distribute in mice adipose tissue (Zhang et al. 2024[BZQEGEXI] Zhang, Jing, Guodong Cao, Wei Wang, Han Qiao, Yi Chen, Xiaoxiao Wang, Fuyue Wang, Wenlan Liu, and Zongwei Cai. 2024. "Stable Isotope-Assisted Mass Spectrometry Reveals in Vivo Distribution, Metabolism, and Excretion of Tire Rubber-Derived 6PPD-Quinone in Mice." Science of the Total Environment 912 (February):169291. https://doi.org/10.1016/j.scitotenv.2023.169291.). Data on human toxicity is lacking for 6PPD-q; however, human biomonitoring has measured 6PPD-q in human urine (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. "First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China." Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.), serum (Zhang et al. 2024[BZQEGEXI] Zhang, Jing, Guodong Cao, Wei Wang, Han Qiao, Yi Chen, Xiaoxiao Wang, Fuyue Wang, Wenlan Liu, and Zongwei Cai. 2024. "Stable Isotope-Assisted Mass Spectrometry Reveals in Vivo Distribution, Metabolism, and Excretion of Tire Rubber-Derived 6PPD-Quinone in Mice." Science of the Total Environment 912 (February):169291. https://doi.org/10.1016/j.scitotenv.2023.169291.), and cerebrospinal fluid (CSF) (Fang et al. 2024[2L4QI2CG] Fang, Jiacheng, Xiaoxiao Wang, Guodong Cao, Fuyue Wang, Yi Ru, Bolun Wang, Yanhao Zhang, et al. 2024. "6PPD-Quinone Exposure Induces Neuronal Mitochondrial Dysfunction to Exacerbate Lewy Neurites Formation Induced by α-Synuclein Preformed Fibrils Seeding." Journal of Hazardous Materials 465 (March):133312. https://doi.org/10.1016/j.jhazmat.2023.133312.).

6PPD-q is a transformation product of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), the primary anti-degradant added to tires and used to prevent premature weathering and degradation of the rubber from sunlight, oxygen, and ozone damage (Hu et al. 2022[ZYXPMXFA] Hu, Ximin, Haoqi Nina Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2022. "Transformation Product Formation upon Heterogeneous Ozonation of the Tire Rubber Antioxidant 6PPD (N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine)." Environmental Science & Technology Letters, April. https://doi.org/10.1021/acs.estlett.2c00187.Santoso, Giese, and Schuster 2007[GZL3D5KN] Santoso, M., U. Giese, and R.H. Schuster. 2007. "Investigations on Initial Stage of Aging of Tire Rubbers by Chemiluminescence Spectroscopy" 80:762–76. https://hero.epa.gov/hero/index.cfm/reference/details/reference_id/5714930.Rossomme et al. 2023[AXGUT6MJ] Rossomme, Elliot, William M. Hart-Cooper, William J. Orts, Colleen M. McMahan, and Martin Head-Gordon. 2023. "Computational Studies of Rubber Ozonation Explain the Effectiveness of 6PPD as an Antidegradant and the Mechanism of Its Quinone Formation." Environmental Science & Technology, March, acs.est.2c08717. https://doi.org/10.1021/acs.est.2c08717.). 6PPD serves an essential safety function in tires by guaranteeing a tire's integrity and supports driver and passenger safety. 6PPD-q pollution primarily comes from tires containing 6PPD, although other products containing 6PPD may also be sources of 6PPD-q. A well-established route of exposure to 6PPD-q for coho salmon is via roadway runoff transported by stormwater into surface water (Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. "A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon." Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.Tian et al. 2022[BICQHLBC] Tian, Zhenyu, Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C. Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej. 2022. "6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard." Environmental Science & Technology Letters, January, acs.estlett.1c00910. https://doi.org/10.1021/acs.estlett.1c00910.). Tire and road wear particles (TRWP) containing 6PPD, which can transform to 6PPD-q in the environment (USEPA 2023[E43MRZ92] USEPA. 2023. "6PPD-Quinone." Overviews and Factsheets. August 9, 2023. https://www.epa.gov/chemical-research/6ppd-quinone.), are nearly ubiquitous in the urban environment (Wagner et al. 2018[4UCJI65Q] Wagner, Stephan, Thorsten Hüffer, Philipp Klöckner, Maren Wehrhahn, Thilo Hofmann, and Thorsten Reemtsma. 2018. "Tire Wear Particles in the Aquatic Environment — A Review on Generation, Analysis, Occurrence, Fate and Effects." Water Research 139 (August):83–100. https://doi.org/10.1016/j.watres.2018.03.051.Kole et al. 2017[NZZMY6WC] Kole, Pieter Jan, Ansje J. Löhr, Frank G. A. J. Van Belleghem, and Ad M. J. Ragas. 2017. "Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment." International Journal of Environmental Research and Public Health 14 (10): 1265. https://doi.org/10.3390/ijerph14101265.). These TRWP are transported throughout the environment. Research is ongoing to understand transport and the fate of the chemicals.

Removing 6PPD from tires is an identified long-term solution to preventing 6PPD-q pollution. Tire manufacturers, chemical manufacturers, and governments are working to find a safer alternative to 6PPD in tires. The alternative must continue to ensure compliance with Federal Motor Vehicle Safety Standards and other consumer, vehicle, and tire-manufacturer requirements while also meeting hazard criteria that aim to avoid regrettable chemical substitutions and minimize the potential for an alternative that is also highly toxic.

This Interstate Technology and Regulatory Council (ITRC) team convened in January 2023 to provide information to state, tribal, and municipal agencies that may need to learn more about 6PPD and 6PPD-q to pursue their own policies and regulations regarding these chemicals. These agencies include the following:

- departments of transportation and urban planning agencies
- water quality, air quality, and resource agencies
- fish and wildlife departments
- solid waste agencies
- departments of health
- drinking water and wastewater treatment plants
- agencies seeking chemical alternatives

Because 6PPD and 6PPD-q are so tightly linked by fate and transport—and possibly toxicity and hazard—this document discusses both chemicals. In each section, we will explain what is known and unknown about the linkage between the chemicals.

The information provided in this document is current as of March 2024 (with a few exceptions of updated information). Given the active research in this topic, additional studies have been published since the completion of this document. While the intent of this document is to present the most salient and recently available information on 6PPD and 6PPD-q, interested readers are encouraged to search the scientific literature for newly available information. During preparation of this document, the synonym 6PPD-q was consistently and uniformly used throughout. This ITRC Team is aware that some state and federal agencies are in the process of phasing out the 6PPD-q synonym in favor of 6PPD-quinone, 6PPDQ, or 6PPD-Q.

In September 2023, this ITRC team published a focus sheet entitled ***What We Know: 6PPD and 6PPD-quinone***. This focus sheet offered a first look and overview of 6PPD and 6PPD-q using available information through July 2023. This ITRC team also anticipates recording an interactive outreach session where each section of the team's final work product is discussed. Please visit the ITRC Training website in early 2025 to access this recording.

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About ITRC

The Interstate Technology and Regulatory Council (ITRC) is a state-led coalition working to reduce barriers to the use of innovative environmental technologies and approaches so that compliance costs are reduced and cleanup efficacy is maximized. ITRC produces documents and training that broaden and deepen technical knowledge and expedite quality regulatory decision making while protecting human health and the environment. With private and public sector members from all 50 states and the District of Columbia, ITRC truly provides a national perspective. More information on ITRC is available at www.itrcweb.org.

ITRC is a program of the Environmental Research Institute of the States (ERIS), a 501(c)(3) organization incorporated in the District of Columbia and managed by the Environmental Council of the States (ECOS). ECOS is the national, nonprofit, nonpartisan association representing the state and territorial environmental commissioners. Its mission is to serve as a champion for states; to provide a clearinghouse of information for state environmental commissioners; to promote coordination in environmental management; and to articulate state positions on environmental issues to Congress, federal agencies, and the public.

Disclaimer

September 2024

1 Introduction

This section introduces the concerns arising from the 2020 discovery of 6PPD-q. It summarizes the discovery of 6PPD-q and its toxic effects, the identification of vehicle tires as the source of 6PPD-q and reasons for the continued use of 6PPD, transport and exposure pathways, the impacts to both fish and human populations, detection of 6PPD-q in the environment, and solutions and approaches for mitigation, This section also provides an overview of topics for which information is lacking and a summary of how decision-makers might address 6PPD-q and use this document as a resource.

1.1 Summary: What Is 6PPD-q and What Is the Concern?

1.1.1 Overview

For decades, adult coho salmon (*Oncorhynchus kisutch*) in the Pacific Northwest have been dying en masse in urbanized areas when storms coincide with their migration upstream to spawn. Because of the correlation with rain events and a series of insightful investigations, the mortality seemed linked to contamination in stormwater runoff from roads (McIntyre et al. 2018[G7QW7PSD] McIntyre, Jenifer, Jessica Lundin, James Cameron, Michelle Chow, Jay Davis, John Incardona, and Nathaniel Scholz. 2018. “Interspecies Variation in the Susceptibility of Adult Pacific Salmon to Toxic Urban Stormwater Runoff.” Environmental Pollution 238:196–203. https://doi.org/https://doi.org/10.1016/j.envpol.2018.03.012.Chow et al. 2019[7RMZ3UNQ] Chow, Michelle I., Jessica I. Lundin, Chelsea J. Mitchell, Jay W. Davis, Graham Young, Nathaniel L. Scholz, and Jenifer K. McIntyre. 2019. “An Urban Stormwater Runoff Mortality Syndrome in Juvenile Coho Salmon.” Aquatic Toxicology 214 (September):105231. https://doi.org/10.1016/j.aquatox.2019.105231.Spromberg et al. 2016[GI97QYN4] Spromberg, Julann A., David H. Baldwin, Steven E. Damm, Jenifer K. McIntyre, Michael Huff, Catherine A. Sloan, Bernadita F. Anulacion, Jay W. Davis, and Nathaniel L. Scholz. 2016. “Coho Salmon Spawner Mortality in Western US Urban Watersheds: Bioinfiltration Prevents Lethal Storm Water Impacts.” Journal of Applied Ecology 53 (2): 398–407. https://doi.org/https://doi.org/10.1111/1365-2664.12534.). Researchers named the phenomenon urban runoff mortality syndrome (URMS) (McIntyre et al. 2021[MVL2LKBM] McIntyre, Jenifer K., Jasmine Prat, James Cameron, Jillian Wetzel, Emma Mudrock, Katherine T. Peter, Zhenyu Tian, et al. 2021. “Treading Water: Tire Wear Particle Leachate Recreates an Urban Runoff Mortality Syndrome in Coho but Not Chum Salmon.” Environmental Science & Technology 55 (17): 11767–74. https://doi.org/10.1021/acs.est.1c03569.; Huang et al. 2021[EZEWIV8E] Huang, Wei, Yumeng Shi, Jialing Huang, Chengliang Deng, Shuqin Tang, Xiaotu Liu, and Da Chen. 2021. “Occurrence of Substituted p-Phenylenediamine Antioxidants in Dusts.” Environmental Science & Technology Letters 8 (5): 381–85. https://doi.org/10.1021/acs.estlett.1c00148.Jin et al. 2023[P9WXQJUR] Jin, Ruihe, Yan Wu, Qun He, Pei Sun, Qiqing Chen, Chunjie Xia, Ye Huang, Jing Yang, and Min Liu. 2023. “Ubiquity of Amino Accelerators and Antioxidants in Road Dust from Multiple Land Types: Targeted and Nontargeted Analysis.” Environmental Science & Technology 57 (28): 10361–72. https://doi.org/10.1021/acs.est.3c01448.). According to the Washington State Department of Ecology (WA Ecology), “…for over 20 years, scientists faced a mystery: coho salmon (also known as silver salmon) returning to urban streams and rivers in the Puget Sound region were dying before they could lay their eggs. The culprit was unknown, but it seemed linked to toxic chemicals running off our roads and highways” (Flores 2023[KYFH4S96] Flores, Mugdha. 2023. “Saving Washington’s Salmon from Toxic Tire Dust.” January 2023. https://ecology.wa.gov/blog/january-2023/saving-washington-s-salmon-from-toxic-tire-dust.). In some cases, 90% mortality of returning coho salmon was observed (Huang et al. 2021[EZEWIV8E] Huang, Wei, Yumeng Shi, Jialing Huang, Chengliang Deng, Shuqin Tang, Xiaotu Liu, and Da Chen. 2021. “Occurrence of Substituted p-Phenylenediamine Antioxidants in Dusts.” Environmental Science & Technology Letters 8 (5): 381–85. https://doi.org/10.1021/acs.estlett.1c00148.Jin et al. 2023[P9WXQJUR] Jin, Ruihe, Yan Wu, Qun He, Pei Sun, Qiqing Chen, Chunjie Xia, Ye Huang, Jing Yang, and Min Liu. 2023. “Ubiquity of Amino Accelerators and Antioxidants in Road Dust from Multiple Land Types: Targeted and Nontargeted Analysis.” Environmental Science & Technology 57 (28): 10361–72. https://doi.org/10.1021/acs.est.3c01448.).

In 2020, Z. Tian et al. (2021) identified a transformation product of 6PPD (Figure 1-1), 6PPD-q (Figure 1-2), as a causative toxicant of URMS observed in coho salmon in Washington State. 6PPD supports the durability and safety of tires and is used as the primary anti-degradant that prevents the breakdown of rubber resulting from reactions with atmospheric ozone (Rossomme et al. 2023[AXGUT6MJ] Rossomme, Elliot, William M. Hart-Cooper, William J. Orts, Colleen M. McMahan, and Martin Head-Gordon. 2023. “Computational Studies of Rubber Ozonation Explain the Effectiveness of 6PPD as an Antidegradant and the Mechanism of Its Quinone Formation.” Environmental Science & Technology, March, acs.est.2c08717.

https://doi.org/10.1021/acs.est.2c08717.; Tian et al. 2022[BICQHLBC] Tian, Zhenyu, Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C. Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej. 2022. “6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard.” Environmental Science & Technology Letters, January, acs.estlett.1c00910. https://doi.org/10.1021/acs.estlett.1c00910.), oxygen (Santoso, Giese, and Schuster 2007[GZL3D5KN] Santoso, M., U. Giese, and R.H. Schuster. 2007. “Investigations on Initial Stage of Aging of Tire Rubbers by Chemiluminescence Spectroscopy” 80:762–76.

https://hero.epa.gov/hero/index.cfm/reference/details/reference_id/5714930.), and free radicals (Scott 1985[6SJ7VVGU] Scott, Gerald. 1985. “A Review of Recent Developments in the Mechanisms of Antifatigue Agents.” Rubber Chemistry and Technology 58 (2): 269–83. https://doi.org/10.5254/1.3536065.). 6PPD is used in every tire on the road (USTMA 2024[372BNAEP] USTMA. 2024. “USTMA Consortium Preliminary (Stage 1) Alternatives Analysis Report for CA DTSC.” https://www.ustires.org/sites/default/files/2024-03/USTMA%20Consortium%206PPD%20AA%20Preliminary%20Report_3-25-24.pdf.), creating the possibility of widespread contamination by 6PPD and 6PPD-q in every area impacted by roads.

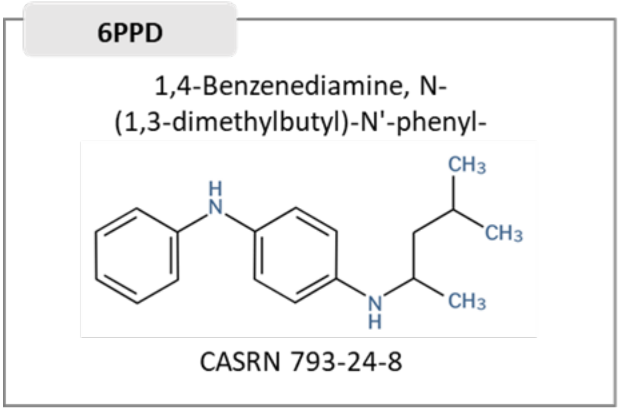


Figure 1-1 Chemical structure of 6PPD

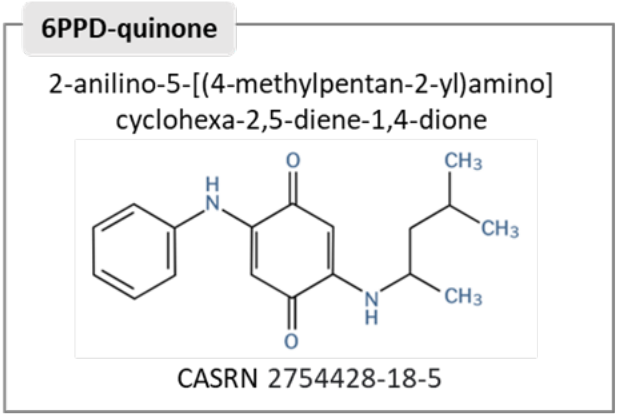


Figure 1-2 Chemical structure of 6PPD-quinone

For more on the discovery of 6PPD-q and how this approach could be used to identify contaminants causing toxic effects, please see the ITRC case study from the Contaminants of Emerging Concern Team.

The identification of 6PPD-q has also generated concerns about the toxicity of the parent 6PPD compound itself. Throughout this document, we will highlight information about each chemical as appropriate (see also Section 3: Chemical Properties. Evaluating both these chemicals is important for estimating and evaluating toxicity and hazard, for understanding environmental fate and transport, and for developing solutions to mitigate the harm caused by 6PPD-q (ITRC 2022[NBCYMAJE] ITRC. 2022. “PFAS Technical and Regulatory Guidance Document and Fact Sheets.” Washington D.C.: Interstate Technology & Regulatory Council, PFAS Team. https://pfas-1.itrcweb.org/.).

In addition to coho (also known as silver) salmon, 6PPD-q has been found to be lethal to brook trout *(Salvelinus fontinalis)* (Brinkmann et al. 2022[QN6HYEV7] Brinkmann, Markus, David Montgomery, Summer Selinger, Justin G. P. Miller, Eric Stock, Alper James Alcaraz, Jonathan K. Challis, et al. 2022. “Acute Toxicity of the Tire Rubber–Derived Chemical 6PPD-Quinone to Four Fishes of Commercial, Cultural, and Ecological Importance.” Environmental Science & Technology Letters, March, acs.estlett.2c00050. https://doi.org/10.1021/acs.estlett.2c00050.); lake trout *(Salvelinus namaycush)* (Roberts et al. 2024[FMG8VP7Y] Roberts, Catherine, Junyi Lin, Evan Kohlman, Niteesh Jain, Mawuli Amekor, Alper James Alcaraz, Natacha Hogan, Markus Hecker, and Markus Brinkmann. 2024. “Acute and Sub-Chronic Toxicity of 6PPD-Quinone to Early-Life Stage Lake Trout (Salvelinus namaycush).” bioRxiv. https://doi.org/10.1101/2024.03.26.586843.); coastal cutthroat trout *(Oncorhynchus clarkii clarkii)* (Shankar et al. 2024[FBNQNIWI] Shankar, Prarthana, Ellie M. Dalsky, Joanne E Salzer, Justin B Greer, Rachael F. Lane, William N Batts, Jacob Gregg, Gael Kurath, Paul K Hershberger, and John D Hansen. 2024. “Evaluation of Lethal and Sublethal Effects of 6PPD-Q on Coastal Cutthroat Trout (Oncorhynchus Clarkii Clarkii).” Csv,xml. U.S. Geological Survey. https://doi.org/10.5066/P16SMKIJ.)*;* rainbow trout *(Oncorhynchus mykiss)* (Nair et al. 2023[9V5ES4MI] Nair, Pranav, Jianxian Sun, Linna Xie, Lisa Kennedy, Derek Kozakiewicz, Sonya Kleywegt, Chunyan Hao, et al. 2023. “In Process: Synthesis and Toxicity Evaluation of Tire Rubber–Derived Quinones.” Preprint. Chemistry. https://doi.org/10.26434/chemrxiv-2023-pmxvc.Brinkmann et al. 2022[QN6HYEV7] Brinkmann, Markus, David Montgomery, Summer Selinger, Justin G. P. Miller, Eric Stock, Alper James Alcaraz, Jonathan K. Challis, et al. 2022. “Acute Toxicity of the Tire Rubber–Derived Chemical 6PPD-Quinone to

Four Fishes of Commercial, Cultural, and Ecological Importance.” Environmental Science & Technology Letters, March, acs.estlett.2c00050. https://doi.org/10.1021/acs.estlett.2c00050.; (Huang et al. 2021[EZEWIV8E] Huang, Wei, Yumeng Shi, Jialing Huang, Chengliang Deng, Shuqin Tang, Xiaotu Liu, and Da Chen. 2021. “Occurrence of Substituted p-Phenylenediamine Antioxidants in Dusts.” Environmental Science & Technology Letters 8 (5): 381–85. https://doi.org/10.1021/acs.estlett.1c00148.Jin et al. 2023[P9WXQJUR] Jin, Ruihe, Yan Wu, Qun He, Pei Sun, Qiqing Chen, Chunjie Xia, Ye Huang, Jing Yang, and Min Liu. 2023. “Ubiquity of Amino Accelerators and Antioxidants in Road Dust from Multiple Land Types: Targeted and Nontargeted Analysis.” Environmental Science & Technology 57 (28): 10361–72. https://doi.org/10.1021/acs.est.3c01448.); and white-spotted char *(Salvelinus leucomaenis),* an Asiatic species (Hiki and Yamamoto 2022[VQE4EZWI] Hiki, Kyoshiro, and Hiroshi Yamamoto. 2022. “The Tire-Derived Chemical 6PPD-Quinone Is Lethally Toxic to the White-Spotted Char Salvelinus leucomaenis pluvius but Not to Two Other Salmonid Species.” Environmental Science & Technology Letters 9 (12): 1050–55. https://doi.org/10.1021/acs.estlett.2c00683.). Steelhead, the ocean-going (or anadromous) form of rainbow trout, have not been specifically tested for toxicity effects when exposed to 6PPD-q, but French et al. (2022) observed mortality in steelhead *(O. mykiss)* treated with roadway runoff. Some acute mortality from 6PPD-q exposure is seen in juvenile Chinook salmon or king salmon *(Oncorhynchus tshawytscha)* (Lo et al. 2023[LA4CEWYX] Lo, Bonnie P., Vicki L. Marlatt, Xiangjun Liao, Sofya Reger, Carys Gallilee, Andrew R.S. Ross, and Tanya M. Brown. 2023. “Acute Toxicity of 6PPD-Quinone to Early Life Stage Juvenile Chinook (Oncorhynchus tshawytscha) and Coho (Oncorhynchus kisutch) Salmon.” Environmental Toxicology and Chemistry 42 (4): 815–22. https://doi.org/10.1002/etc.5568.); however, results are mixed (Montgomery et al. 2023[X3FANIWH] Montgomery, David, Xiaowen Ji, Jenna Cantin, Danielle Philibert, Garrett Foster, Summer Selinger, Niteesh Jain, et al. 2023. “Not Yet Peer Reviewed: Toxicokinetic Characterization of the Inter-Species Differences in 6PPD-Quinone Toxicity Across Seven Fish Species: Metabolite Identification and Semi-Quantification.” bioRxiv. https://doi.org/10.1101/2023.08.18.553920.Greer et al. 2023[P6RF5UFR] Greer, Justin B., Ellie M. Dalsky, Rachael F. Lane, and John D. Hansen. 2023. “Establishing an In Vitro Model to Assess the Toxicity of 6PPD-Quinone and Other Tire Wear Transformation Products.” Environmental Science & Technology Letters, May. https://doi.org/10.1021/acs.estlett.3c00196.), and effects have not been observed at environmentally relevant concentrations (see Section 4: Occurrence, Fate, Transport, and Exposure Pathways). Table 1-1 summarizes acute toxicities for some salmonids.[1] Additional details on toxicity research is available in Section 2: Effects Characterization and Toxicity of this document.

Table 1-1. Acute toxicity of 6PPD-quinone to various salmonids

Species	LC_{50} (µg/L)	Test duration (hours)	Toxicity key
Coho salmon (*Oncorhynchus kisutch*)	0.04 (Lo et al. 2023) 0.08 (Greer et al. 2023a) 0.095 (Z. Tian et al. 2022)	24	Higher
Brook trout (*Salvelinus fontinalis*)	0.2 [fry], 0.5 [fingerlings] (Philibert et al. 2024) 0.59 (Brinkmann et al. 2022)	24	
Lake trout (*Salvelinus namaycush*)	0.51 (Roberts et al. 2024)	24	
White-spotted char (*Salvelinus leucomaenis pluvius*)	0.51 (Hiki and Yamamoto 2022b)	24	
Rainbow trout/steelhead (*Oncorhynchus mykiss*)	0.64 (Nair et al. 2023) 1.0 (Brinkmann et al. 2022) 2.26 (Di et al. 2022)	96	
Chinook salmon (*Oncorhynchus tshawytscha*)	67.3 (Lo et al. 2023), 82.1 (Greer et al. 2023a)	24	
Sockeye salmon (*Oncorhynchus nerka*)	Not acutely toxic at 50 (Greer et al. 2023a)	24	
Atlantic salmon (*Salmo salar*)	Not acutely toxic at 12.2 (Foldvik et al. 2022)	48	
Brown trout (*Salmo trutta*)	Not acutely toxic at 12.2 (Foldvik et al. 2022)	48	
Arctic char (*Salvelinus alpinus*)	Not acutely toxic at 12.7 (Brinkmann et al. 2022)	24	
Westslope cutthroat trout (*Oncorhynchus clarkii lewisi*)	Not acutely toxic at 10 (Montgomery et al. 2023a)	24	
Pink salmon (*Oncorhynchus gorbuscha*)	Not acutely toxic at 12.8 (Foldvik et al. 2024)	48	Lower

Notes: µg/L=micrograms per liter. Selected salmonid species in the table are listed from very high to low across a toxicity gradient based on the LC_{50} value, with the following ratings: coho=very high; brook trout, lake trout, and white-spotted char=high; rainbow trout / steelhead=medium high; Chinook salmon, sockeye salmon, Atlantic salmon, brown trout, Arctic char, Western cutthroat trout, and pink salmon=low. For the sake of brevity, tolerant salmonids not native to North America were excluded from this table. For reference, 6PPD-q has been measured as high as 2.85 µg/L in surface water (

Johannessen et al. 2022[E9K7U5U3] Johannessen, Cassandra, Paul Helm, Brent Lashuk, Viviane Yargeau, and Chris D. Metcalfe. 2022. "The Tire Wear Compounds 6PPD-Quinone and 1,3-Diphenylguanidine in an Urban Watershed." Archives of Environmental Contamination and Toxicology 82 (2): 171–79. https://doi.org/10.1007/s00244-021-00878-4.). For a complete list, please see Table 2-1 and Table 2-2. The LC_{50} for coastal cutthroat trout (*Oncorhynchus clarkii clarkii*) has not yet been released, but quality-assured data showing significant toxicity was released by Shankar et al. (Shankar et al. 2024[FBNQNIWI] Shankar, Prarthana, Ellie M. Dalsky, Joanne E Salzer, Justin B Greer, Rachael F. Lane, William N Batts, Jacob Gregg, Gael Kurath, Paul K Hershberger, and John D Hansen. 2024. “Evaluation of Lethal and Sublethal Effects of 6PPD-Q on Coastal Cutthroat Trout (Oncorhynchus Clarkii Clarkii).” Csv,xml. U.S. Geological Survey. https://doi.org/10.5066/P16SMKIJ.).

Habitats for known sensitive fish species (for example, *O. kisutch*, *O. mykiss, O. clarkii clarkii**, S. fontinalis, and S. namaycush*) are geographically dispersed across the United States. The composite map (Figure 1-3) shows native habitats for four of the fish species in blue, and non-native (i.e., introduced) habitats are shown as rust colored. It is important to note that while this map represents the nationwide distribution of sensitive fish species, the amount of chemical in the local waterway will determine whether there are effects on fishes in these habitats. See Section 5: Measuring, Mapping, and Modeling for more information.

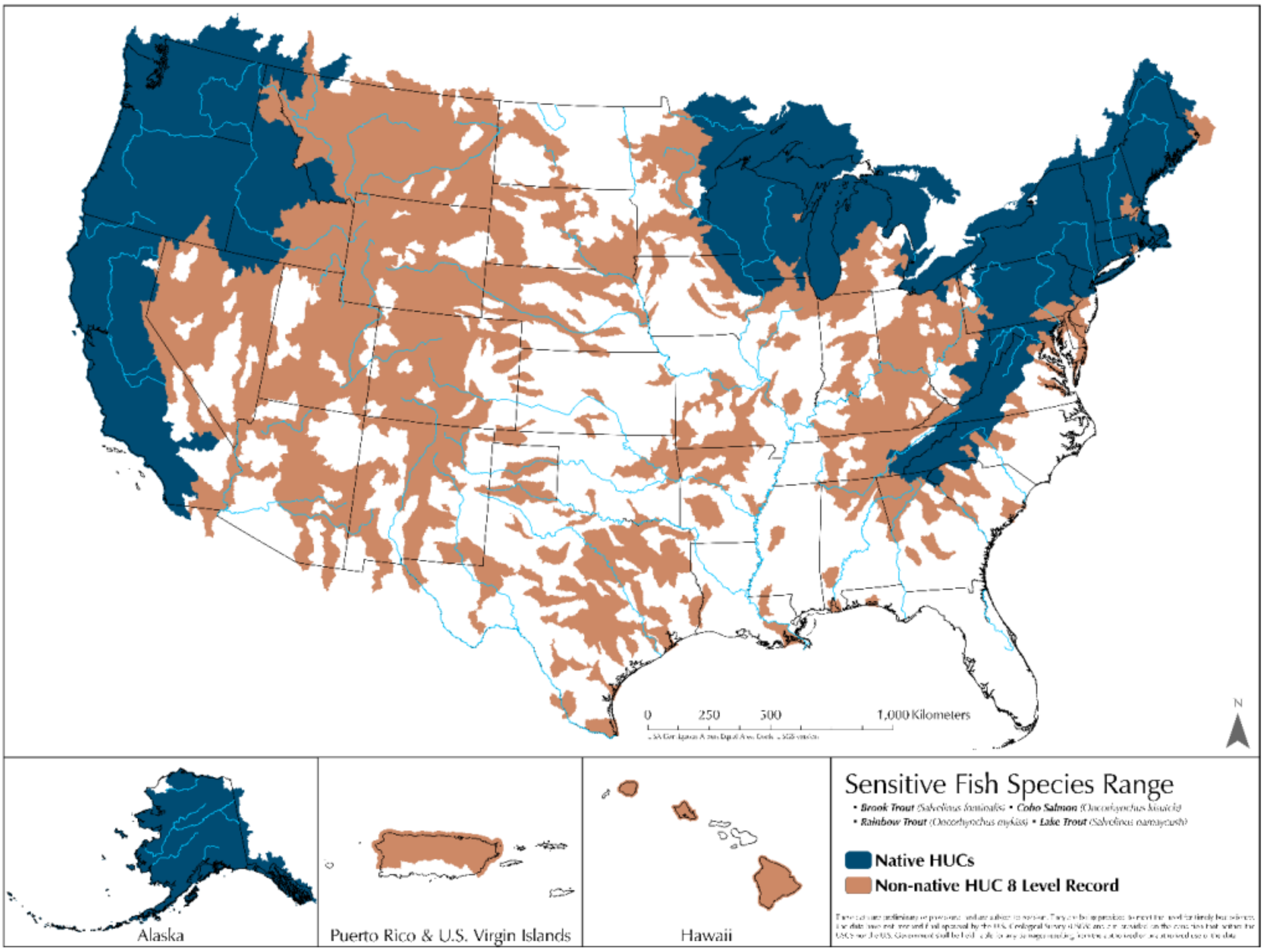


Figure 1-3. Aggregated range for 6PPD-q sensitive fish species: coho salmon (*Oncorhynchus kisutch*), rainbow trout/steelhead *(Oncorhynchus mykiss)*, brook trout *(Salvelinus fontinalis)* and lake trout *(Salvelinus namaycush)*. When native and non-native habitat overlap for the different species, the native habitat is indicated. Habitats are organized by hydrologic unit code (HUC), which indicates nested watersheds that are categorized by the U.S. Geological Survey (USGS). *Coastal cutthroat trout *(Oncorhynchus clarkii clarkii)* range was not specifically included in this map because the data indicating their sensitivity to 6PPD-q became available late in the production of this document (Shankar et al. 2024[FBNQNIWI] Shankar, Prarthana, Ellie M. Dalsky, Joanne E Salzer, Justin B Greer, Rachael F. Lane, William N Batts, Jacob Gregg, Gael Kurath, Paul K Hershberger, and John D Hansen. 2024. “Evaluation of Lethal and Sublethal Effects of 6PPD-Q on Coastal Cutthroat Trout (Oncorhynchus Clarkii Clarkii).” Csv,xml. U.S. Geological Survey. https://doi.org/10.5066/P16SMKIJ.). Their native range largely occurs within the native ranges of coho and rainbow trout/steelhead.

1.1.2 Short History of 6PPD in Tires

6PPD is the most widely used anti-degradant in tires (Gradient 2024[LHN7K744] Gradient. 2024. "Preliminary (Stage 1) Alternatives Analysis Report: Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N'-Phenyl-p-Phenylenediamine (6PPD)." https://www.ustires.org/sites/default/files/2024-03/USTMA%20Consortium%206PPD%20AA%20Preliminary%20Report_3-25-24.pdf.). It belongs to the chemical class *para*-phenylenediamines (PPDs), which are broadly used as antioxidants or antiozonants in rubber and other products (Gradient 2024[LHN7K744] Gradient. 2024. "Preliminary (Stage 1) Alternatives Analysis Report: Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N'-Phenyl-p-Phenylenediamine (6PPD)." https://www.ustires.org/sites/default/files/2024-03/USTMA%20Consortium%206PPD%20AA%20Preliminary%20Report_3-25-24.pdf.). 6PPD is an efficient anti-degradant, reacting with oxygen and ozone to limit weathering and degradative oxidation of tire rubber (Figure 1-4) (Rossomme et al. 2023[AXGUT6MJ] Rossomme, Elliot, William M. Hart-Cooper, William J. Orts, Colleen M. McMahan, and Martin Head-Gordon. 2023. "Computational Studies of Rubber Ozonation Explain the Effectiveness of 6PPD as an Antidegradant and the Mechanism of Its Quinone Formation." Environmental Science & Technology, March, acs.est.2c08717. https://doi.org/10.1021/acs.est.2c08717.; (Hu et al. 2022[ZYXPMXFA] Hu, Ximin, Haoqi Nina Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2022. "Transformation Product Formation upon Heterogeneous Ozonation of the Tire Rubber Antioxidant 6PPD (N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine)." Environmental Science & Technology Letters, April. https://doi.org/10.1021/acs.estlett.2c00187.); Santoso, Giese, and Schuster 2007[GZL3D5KN] Santoso, M., U. Giese, and R.H. Schuster. 2007. "Investigations on Initial Stage of Aging of Tire Rubbers by Chemiluminescence Spectroscopy" 80:762–76. https://hero.epa.gov/hero/index.cfm/reference/details/reference_id/5714930.). The addition of 6PPD prevents hardening of rubber compounds in the tire, including treads, and thus improves tire wear life and contributes to consistent traction over the lifetime of the tire (Pulford 1983[RFZN73MA] Pulford, C. 1983. "Antioxidant Effects during Blade Abrasion of Natural Rubber" 28:709–13.).

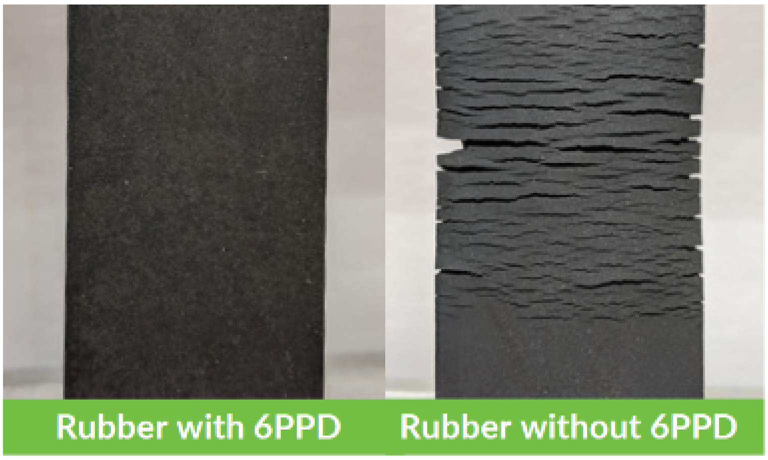


Figure 1-4 Aged rubber with and without 6PPD.
SOURCE: U.S. Tire Manufacturers Association, used with permission.

In addition to providing direct protection to the exterior of the tire against oxygen and ozone, 6PPD also protects internal components of the tire from heat and free radicals that can degrade the tire throughout its life (Kuczkowski 1990[GJD3TURD] Kuczkowski, J.A. 1990. "Effects of Ozone on Tires and the Control of These Effects." In Ozone Risk Communication and Management, Gilbert, C. E., Beck, B. D., Calabrese, E. J. (eds.), 93–104. United Kingdom: Taylor & Francis.Huntink, N.M. and Datta, R.N. 2003[RTIIEIBC] Huntink, N.M., and Datta, R.N. 2003. "A Novel Slow Release Antidegradant for the Rubber Industry—Part 1: Migration Behavior of Newly Developed Anti-Ozonant Compared to Conventional Antidegradants." Kautschuk Gummi Kunststoffe 56 (6): 310–15.Chasar and Layer 2010[HM7KYWSL] Chasar, DW, and R. W. Layer. 2010. "Basic Rubber Compounding." In The Vanderbilt Rubber Handbook, 14th ed., 10–21. M.F. Sheridan (Ed.). R.T. Vanderbilt Company.). Due to this protective effect against rubber degradation, 6PPD is currently critical to tire durability and ultimately to motor vehicle safety (Gradient 2024[LHN7K744] Gradient. 2024. "Preliminary (Stage 1) Alternatives Analysis Report: Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N'-Phenyl-p-Phenylenediamine (6PPD)." https://www.ustires.org/sites/default/files/2024-03/USTMA%20Consortium%206PPD%20AA%20Preliminary%20Report_3-25-24.pdf.). Over time, the amount of 6PPD in the tire decreases as it reacts with ozone and oxygen, triggering aging. The weathered tire eventually starts to crack, harden, and lose strength. 6PPD is consumed as it reacts, and 6PPD-q is one of the transformation products (Figure 1-5).

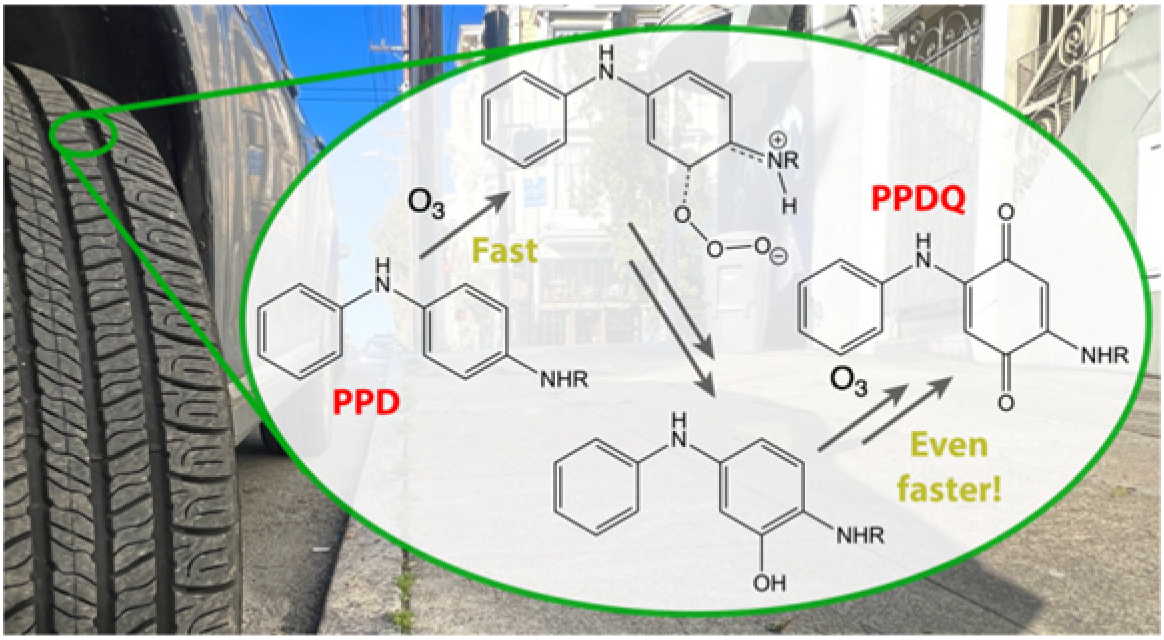


Figure 1-5: 6PPD is consumed when it reacts with ozone. In this figure, 6PPD is represented as PPD and 6PPD-q is represented as PPDQ. PPD reacts with ozone, forming short-lived intermediates (unlabeled), and ultimately yields PPDquinone. Other reactions between ozone and 6PPD also occur (Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. "Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone." Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.).
SOURCE: Rossomme et al. (2023), used with permission CC-BY 4.0.

Prior to the development of the PPD family of antiozonants, there was often "rapid deterioration and loss of physical properties which caused failures in rubber goods" (Kuczkowski 1989[IDS6JDJZ] Kuczkowski, J.A. 1989. "The Inhibition of Oxidative and Ozonic Processes in Elastomers." In Oxidation Inhibition in Organic Materials, J. Pospisil and P.P Klemchuk (eds.). v. 2. Boca Raton, FL: Taylor & Francis. https://books.google.com/books?id=HEOnh9bgu0IC.). The effect of ozone on the degradation of tire-rubber compounds was not fully understood until the 1930s. At that time, a typical tire lasted only 10,000 miles or roughly two years. In the 1930s, waxes were identified as a static ozone protector for rubber compounds, but wax did not work for products that required dynamic applications, where the rubber stretches and flexes when in use, like a tire. Failure of tires and other rubber parts on military vehicles, which were stored from World War II and placed into service for the Korean War, led the U.S. government to sponsor research to study ways to prevent the cracking and degrading of rubber compounds. This research was published in the Rock Island Arsenal Technical Report (Ofner 1967[R8ATIUAM] Ofner, Robert. 1967. "Information Sources on Rubber for Engineers and Designers." U.S. Army Weapons Command. Rock Island Arsenal: Research and Engineering Division. https://apps.dtic.mil/sti/tr/pdf/AD0660315.pdf.), which identified a broad class of chemically modified PPDs as the most effective antiozonants for rubber compounds (Gilbert, Beck, and Calabrese 1990[DL5MC2ZL] Gilbert, C.E., B.D. Beck, and E.J. Calabrese. 1990. Ozone Risk Communication and Management. United Kingdom: Taylor & Francis.).

Following the Rock Island Arsenal Technical Report, the first PPD antiozonants developed were active against ozone but they were not as effective as 6PPD because they protected rubber compounds for only approximately 1.5 years. Phenyl-p-phenylenediamine (IPPD) and diaryl-p-phenylene diamine (DAPD) were among the first PPDs to be developed and were the first to be used in rubber compounds, in the mid-1960s. DAPD reacts minimally with ozone. IPPD reacts too fast with ozone, leading to premature depletion. The speed of the reaction with ozone is a critical consideration when assessing the utility of the antiozonants. The final PPDs to become commercialized were 6PPD, 7PPD, and 8PPD (Kuczkowski 1989[IDS6JDJZ] Kuczkowski, J.A. 1989. "The Inhibition of Oxidative and Ozonic Processes in Elastomers." In Oxidation Inhibition in Organic Materials, J. Pospisil and P.P Klemchuk (eds.). v. 2. Boca Raton, FL: Taylor & Francis.

https://books.google.com/books?id=HEOnh9bgu0IC.).

Some tire manufacturers began using 6PPD in tire manufacturing in the mid-1960s and early 1970s. In 1964, a British patent (Monsanto Company 1965[I3PYYL4M] Monsanto Company. 1965. Preservation of Diene Rubbers (Great Britain Patent No. 1035262A). 1035262A, issued 1965.) was published regarding the manufacturing of the 6PPD molecule, and in 1968 a new factory was built, which increased the supply of 6PPD to the U.S. tire industry. By 1975, 6PPD accounted for 60% of the antiozonants used in tires (USEPA 1975[9GIVZ872] USEPA. 1975. "Environmental Aspects of Chemical Use in Rubber Processing Operations." EPA-560/1-75-002; Akron, OH: Office of Toxic Substances. https://nepis.epa.gov/Exe/ZyPDF.cgi/2000IUPB.PDF?Dockey=2000IUPB.PDF.). To this day, 6PPD is used in all tires and is the primary anti-degradant used, although 6PPD may be blended with other anti-degradants (USTMA 2024[372BNAEP] USTMA. 2024. "USTMA Consortium Preliminary (Stage 1) Alternatives Analysis Report for CA DTSC." https://www.ustires.org/sites/default/files/2024-03/USTMA%20Consortium%206PPD%20AA%20Preliminary%20Report_3-25-24.pdf.).

1.2 Transport Pathways: How Do 6PPD and 6PPD-q Get into the Environment?

1.2.1 Overview

As tires roll over a road surface, friction between the road and the tire generates tiny fragments of rubber, called TRWP. These particles contain both the intentionally added 6PPD and its transformation product, 6PPD-q. 6PPD-q is one of several transformation products formed by the reaction of 6PPD and ozone (Seiwert et al. 2022[QDRRVWMW] Seiwert, Bettina, Maolida Nihemaiti, Mareva Troussier, Steffen Weyrauch, and Thorsten Reemtsma. 2022. "Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater." Water Research 212:118122. https://doi.org/10.1016/j.watres.2022.118122.). TRWP, 6PPD, and 6PPD-q may be present in many places impacted by tire use. More information is available in Section 4: Occurrence, Fate, Transport, and Exposure Pathways of this document. The callout box Tire and Road-Wear Particle Background and Related Terms presents a definition for TRWP and how this term relates to tire-wear particles (TWP) and other types of tire particles.

Tire and Road-Wear Particle Background and Related Terms

Tire and road-wear particles (TRWP) act as vectors for transport of 6PPD and 6PPD-q and, after settled in the environment, TRWP may act as a source of these and other chemicals. Thus, the fate and transport of 6PPD and 6PPD-q are inextricably linked with the fate and transport of TRWP. At times, this document discusses TRWP when information is not available on the fate and transport of 6PPD and 6PPD-q specifically.

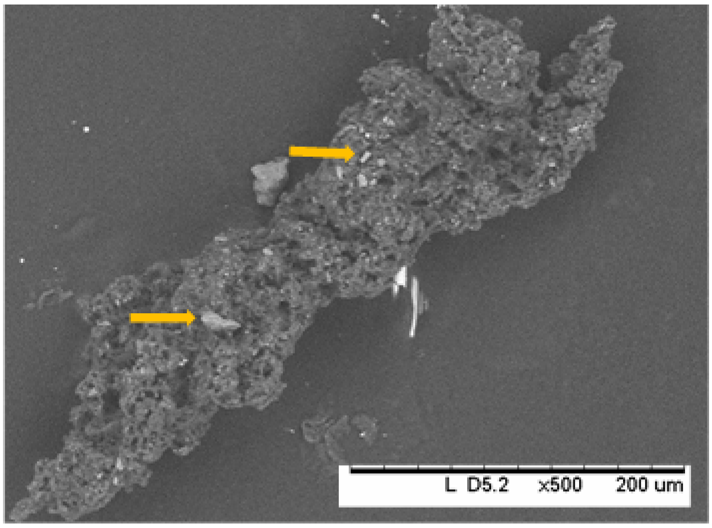


Figure 1-6. Scanning electron micrograph of TRWP collected from a storm drain. Yellow arrows indicate the inclusion of debris, from the road or brakes. The large surface area of the TRWP facilitates leaching of 6PPD and 6PPD-q.

Source: K. Paterson of the San Francisco Estuary Institute (Used with permission)

TRWP form from friction between a tire and the road surface during driving, braking, and turning. As the name TRWP implies, they have two separate components—tire-wear particles (TWP) and the road component (see Figure 1-6). TWP are made of tire rubber, which contains natural and synthetic polymers, chemical additives (such as 6PPD), and chemical transformation products (such as 6PPD-q). The large surface area of TWP facilitates leaching of 6PPD, 6PPD-q, and other chemicals to the environment. TWP are one of the most prevalent types of microplastics found in urban stormwater runoff (Mayer et al. 2024[ZTAVFS9G] Mayer, Paul, Kelly Moran, Ezra Miller, Susanne Brander, Stacey Harper, Manuel Garcia-Jaramillo, Victor Carrasco-Navarro, et al. 2024. "Where the Rubber Meets the Road: Emerging Environmental Impacts of Tire Wear Particles and Their Chemical Cocktails." Science of The Total Environment 927 (June):171153. https://doi.org/10.1016/j.scitotenv.2024.171153.Ziajahromi et al. 2023[YZAD6ZJV] Ziajahromi, Shima, Hsuan-Cheng Lu, Darren Drapper, Andy Hornbuckle, and Frederic D. L. Leusch. 2023. "Microplastics and Tire Wear Particles in Urban Stormwater: Abundance, Characteristics, and Potential Mitigation Strategies." Environmental Science & Technology 57 (34): 12829–37. https://doi.org/10.1021/acs.est.3c03949.). Models predict that more than 1.52 million metric tonnes of TWP (equivalent to approximately 10.3 pounds per person) are emitted annually in the United States (Kole et al. 2017[NZZMY6WC] Kole, Pieter Jan, Ansje J. Löhr, Frank G. A. J. Van Belleghem, and Ad M. J. Ragas. 2017. "Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment." International Journal of Environmental Research and Public Health 14 (10): 1265. https://doi.org/10.3390/ijerph14101265.]).

The road-wear component of TRWP contains road fragments and other car-related contaminants, such as those generated from brake wear (Ha et al. 2023[PYHTRF8Y] Ha, Jin U., Seok H. Bae, Yu J. Choi, Pyoung-Chan Lee, Sun K. Jeoung, Sanghoon Song, Choong Choi, Jae S. Lee, Jaeyun Kim, and In S. Han. 2023. "Control of Tire Wear Particulate Matter through Tire Tread Prescription." Polymers 15 (13): 2795. https://doi.org/10.3390/polym15132795.). These road-wear components impact the physical characteristics (for example, mass, surface area, density) of TRWP, which therefore impacts TRWP fate and transport in the environment (Kreider et al. 2010[QCJY4JI9] Kreider, Marisa L., Julie M. Panko, Britt L. McAtee, Leonard I. Sweet, and Brent L. Finley. 2010. "Physical and Chemical Characterization of Tire-Related Particles: Comparison of Particles Generated Using Different Methodologies." Science of the Total Environment 408 (3): 652–59. https://doi.org/10.1016/j.scitotenv.2009.10.016.Baensch-Baltruschat et al. 2020[SG7DEPVC] Baensch-Baltruschat, Beate, Birgit Kocher, Friederike Stock, and Georg Reifferscheid. 2020. "Tyre and Road Wear Particles (TRWP)—A Review of Generation, Properties, Emissions, Human Health Risk, Ecotoxicity, and Fate in the Environment." Science of the Total Environment 733 (September):137823. https://doi.org/10.1016/j.scitotenv.2020.137823.).

The source materials used in studies of 6PPD, 6PPD-q, and other tire-related chemicals includes both TRWP and lab-generated tire particles. Some lab-generated tire particles are prepared using techniques that do not simulate road conditions, such as sanding or cryo-milling. Other lab-generated tire particles are prepared using techniques that simulate tire and road wear, such as rolling drums covered in asphalt over the tire's tread. For simplicity, this document includes all types of lab-generated tire particles within our definition of TWP because these particles were not generated from friction between a tire and an actual road surface.

A third source of tire particles is the shredding and grinding of scrap tires for other uses, such as crumb rubber infill on artificial turf fields, rubber-modified asphalt, and other products including those listed in Table 1-3. In this document, studies of the fate and transport of these products and/or their components are identified by product type/use and not included in our definition of TWP.

The terminology surrounding tire particles is evolving, which leads to inconsistency in the published literature. To get around this challenge, some researchers have proposed using the umbrella term microrubber to include all microplastics that predominantly contain synthetic and natural rubber polymers (Halle et al. 2020[47UILE7G] Halle, Louise L., Annemette Palmqvist, Kristoffer Kampmann, and Farhan R. Khan. 2020. "Ecotoxicology of Micronized Tire Rubber: Past, Present and Future Considerations." Science of The Total Environment 706 (March):135694. https://doi.org/10.1016/j.scitotenv.2019.135694.Tamis et al. 2021[MPU4FIFJ] Tamis, Jacqueline E., Albert A. Koelmans, Rianne Dröge, Nicolaas H. B. M. Kaag, Marinus C. Keur, Peter C. Tromp, and Ruud H. Jongbloed. 2021. "Environmental Risks of Car Tire Microplastic Particles and Other Road Runoff Pollutants." Microplastics and Nanoplastics 1 (1): 10. https://doi.org/10.1186/s43591-021-00008-w.). To date, the term microrubber has not been universally embraced.

The consensus of this ITRC team was to use TRWP for particles generated from vehicular travel on roads; use TWP for lab-generated tire particles and the tire component of TRWP; and identify non-vehicular sources of tire particles by the intended use.

As shown in Figure 1-7, TRWP containing 6PPD and 6PPD-q migrate to waterways through various transport pathways including atmospheric deposition, direct runoff from roads, and conveyance from stormwater drains. TRWP have also been detected in stormwater and surface waters on multiple continents (McIntyre et al. 2021[MVL2LKBM] McIntyre, Jenifer K., Jasmine Prat, James Cameron, Jillian Wetzel, Emma Mudrock, Katherine T. Peter, Zhenyu Tian, et al. 2021. “Treading Water: Tire Wear Particle Leachate Recreates an Urban Runoff Mortality Syndrome in Coho but Not Chum Salmon.” Environmental Science & Technology 55 (17): 11767–74. https://doi.org/10.1021/acs.est.1c03569.Rauert et al. 2022[LAH96NFL] Rauert, Cassandra, Suzanne Vardy, Benjamin Daniell, Nathan Charlton, and Kevin V. Thomas. 2022. “Tyre Additive Chemicals, Tyre Road Wear Particles and High Production Polymers in Surface Water at 5 Urban Centres in Queensland, Australia.” Science of The Total Environment 852:158468. https://doi.org/10.1016/j.scitotenv.2022.158468.Challis et al. 2021[T8TEWPCL] Challis, J. K., H. Popick, S. Prajapati, P. Harder, J. P. Giesy, K. McPhedran, and M. Brinkmann. 2021. “Occurrences of Tire Rubber–Derived Contaminants in Cold-Climate Urban Runoff.” Environmental Science & Technology Letters 8 (11): 961–67. https://doi.org/10.1021/acs.estlett.1c00682.Maurer et al. 2023[TJQR62IC] Maurer, Loïc, Eric Carmona, Oliver Machate, Tobias Schulze, Martin Krauss, and Werner Brack. 2023. “Contamination Pattern and Risk Assessment of Polar Compounds in Snow Melt: An Integrative Proxy of Road Runoffs.” Environmental Science & Technology 57 (10): 4143–52. https://doi.org/10.1021/acs.est.2c05784.Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. “New Evidence of Rubber-Derived Quinones in Water, Air, and Soil.” Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.Johannessen and Metcalfe 2022[6AEMVTD8] Johannessen, Cassandra, and Chris D. Metcalfe. 2022. “The Occurrence of Tire Wear Compounds and Their Transformation Products in Municipal Wastewater and Drinking Water Treatment Plants.” Environmental Monitoring and Assessment 194 (10): 731. https://doi.org/10.1007/s10661-022-10450-9.). 6PPD and 6PPD-q have been found in the following contexts:

- Airborne particulates (Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. “Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers.” Environmental Pollution 314 (December):120206. https://doi.org/10.1016/j.envpol.2022.120206.Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. “New Evidence of Rubber-Derived Quinones in Water, Air, and Soil.” Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.; Zhang et al. 2022[G77DTKD6] Zhang, Yanhao, Caihong Xu, Wenfen Zhang, Zenghua Qi, Yuanyuan Song, Lin Zhu, Chuan Dong, Jianmin Chen, and Zongwei Cai. 2022. “p-Phenylenediamine Antioxidants in PM2.5: The Underestimated Urban Air Pollutants.” Environmental Science & Technology 56 (11): 6914–21. https://doi.org/https://doi.org/10.1021/acs.est.1c04500.; Ji et al. 2022[QJ23CAKR] Ji, Jiawen, Jinze Huang, Niannian Cao, Xianghong Hao, Yanhua Wu, Yongqiang Ma, Dong An, Sen Pang, and Xuefeng Li. 2022. “Multiview Behavior and Neurotransmitter Analysis of Zebrafish Dyskinesia Induced by 6PPD and Its Metabolites.” Science of The Total Environment 838:156013. https://doi.org/10.1016/j.scitotenv.2022.156013.)
- Sediment (Zhu et al. 2024[3FETIQAB] Zhu, Jianqiang, Ruyue Guo, Fangfang Ren, Shengtao Jiang, and Hangbiao Jin. 2024. “Occurrence and Partitioning of p-Phenylenediamine Antioxidants and Their Quinone Derivatives in Water and Sediment.” Science of the Total Environment 914 (March):170046. https://doi.org/10.1016/j.scitotenv.2024.170046.Zeng et al. 2023[TK5YR8WJ] Zeng, Lixi, Yi Li, Yuxin Sun, Liang-Ying Liu, Mingjie Shen, and Bibai Du. 2023. “Widespread Occurrence and Transport of p-Phenylenediamines and Their Quinones in Sediments across Urban Rivers, Estuaries, Coasts, and Deep-Sea Regions.” Environmental Science & Technology, January, acs.est.2c07652. https://doi.org/10.1021/acs.est.2c07652.)
- Soil (Cao et al. 2023[D5FPK9YB] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Han Qiao, Huankai Li, Gefei Huang, Zhu Yang, and Zongwei Cai. 2023. “Occurrence and Fate of Substituted P-Phenylenediamine-Derived Quinones in Hong Kong Wastewater Treatment Plants.” Environmental Science & Technology, October. https://doi.org/10.1021/acs.est.3c03758.)

- Biosolids (Cao et al. 2023[D5FPK9YB] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Han Qiao, Huankai Li, Gefei Huang, Zhu Yang, and Zongwei Cai. 2023. “Occurrence and Fate of Substituted P-Phenylenediamine-Derived Quinones in Hong Kong Wastewater Treatment Plants.” Environmental Science & Technology, October. https://doi.org/10.1021/acs.est.3c03758.)
- Rubber products other than tires (Sherman et al. 2024[NGSQ8TR4] Sherman, Anya, Thibault Masset, Lukas Wimmer, Lea Ann Dailey, Thorsten Hüffer, Florian Breider, and Thilo Hofmann. 2024. “The Invisible Footprint of Climbing Shoes: High Exposure to Rubber Additives in Indoor Facilities.” https://chemrxiv.org/engage/api-gateway/chemrxiv/assets/orp/resource/item/65b74ca0e9ebbb4db9311694/original/the-invisible-footprint-of-climbing-shoes-high-exposure-to-rubber-additives-in-indoor-facilities.pdf.Zhao et al.

  2023[NMVDB224] Zhao, Haoqi Nina, Ximin Hu, Melissa Gonzalez, Craig A. Rideout, Grant C. Hobby, Matthew F. Fisher, Carter J. McCormick, et al. 2023. “Screening P-Phenylenediamine Antioxidants, Their Transformation Products, and Industrial Chemical Additives in Crumb Rubber and Elastomeric Consumer Products.” Environmental Science & Technology, February. https://doi.org/10.1021/acs.est.2c07014.)
- Indoor dust (Zhang et al. 2024[ZQPREK6H] Zhang, Zhuxia, Xijin Xu, Ziyi Qian, Qi Zhong, Qihua Wang, Machteld N. Hylkema, Harold Snieder, and Xia Huo. 2024. “Association between 6PPD-Quinone Exposure and BMI, Influenza, and Diarrhea in Children.” Environmental Research 247:118201.

  https://doi.org/10.1016/j.envres.2024.118201.Zhu et al. 2024[WEPL88BC] Zhu, Jianqiang, Ruyue Guo, Shengtao Jiang, Pengfei Wu, and Hangbiao Jin. 2024. “Occurrence of p-Phenylenediamine Antioxidants (PPDs) and PPDs-Derived Quinones in Indoor Dust.” Science of the Total Environment 912:169325.

  https://doi.org/10.1016/j.scitotenv.2023.169325.Huang et al. 2021[EZEWIV8E] Huang, Wei, Yumeng Shi, Jialing Huang, Chengliang Deng, Shuqin Tang, Xiaotu Liu, and Da Chen. 2021. “Occurrence of Substituted p-Phenylenediamine Antioxidants in Dusts.” Environmental Science & Technology Letters 8 (5): 381–85. https://doi.org/10.1021/acs.estlett.1c00148.)
- Road dust (Huang et al. 2021[EZEWIV8E] Huang, Wei, Yumeng Shi, Jialing Huang, Chengliang Deng, Shuqin Tang, Xiaotu Liu, and Da Chen. 2021. “Occurrence of Substituted p-Phenylenediamine Antioxidants in Dusts.” Environmental Science & Technology Letters 8 (5): 381–85. https://doi.org/10.1021/acs.estlett.1c00148.Jin et al.

  2023[P9WXQJUR] Jin, Ruihe, Yan Wu, Qun He, Pei Sun, Qiqing Chen, Chunjie Xia, Ye Huang, Jing Yang, and Min Liu. 2023. “Ubiquity of Amino Accelerators and Antioxidants in Road Dust from Multiple Land Types: Targeted and Nontargeted Analysis.” Environmental Science & Technology 57 (28): 10361–72. https://doi.org/10.1021/acs.est.3c01448.)

In humans 6PPD-q has been measured in urine (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. “First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China.” Environmental Science & Technology Letters,

November. https://doi.org/10.1021/acs.estlett.2c00821.), serum (Zhang et al. 2024[BZQEGEXI] Zhang, Jing, Guodong Cao, Wei Wang, Han Qiao, Yi Chen, Xiaoxiao Wang, Fuyue Wang, Wenlan Liu, and Zongwei Cai. 2024. “Stable Isotope-Assisted Mass Spectrometry Reveals in Vivo Distribution, Metabolism, and Excretion of Tire Rubber-Derived 6PPD-Quinone in Mice.” Science of the Total Environment 912 (February):169291. https://doi.org/10.1016/j.scitotenv.2023.169291.), and CSF (Fang et al.

2024[2L4QI2CG] Fang, Jiacheng, Xiaoxiao Wang, Guodong Cao, Fuyue Wang, Yi Ru, Bolun Wang, Yanhao Zhang, et al. 2024. “6PPD-Quinone Exposure Induces Neuronal Mitochondrial Dysfunction to Exacerbate Lewy Neurites Formation Induced by α-Synuclein Preformed Fibrils Seeding.” Journal of Hazardous Materials 465 (March):133312. https://doi.org/10.1016/j.jhazmat.2023.133312.).

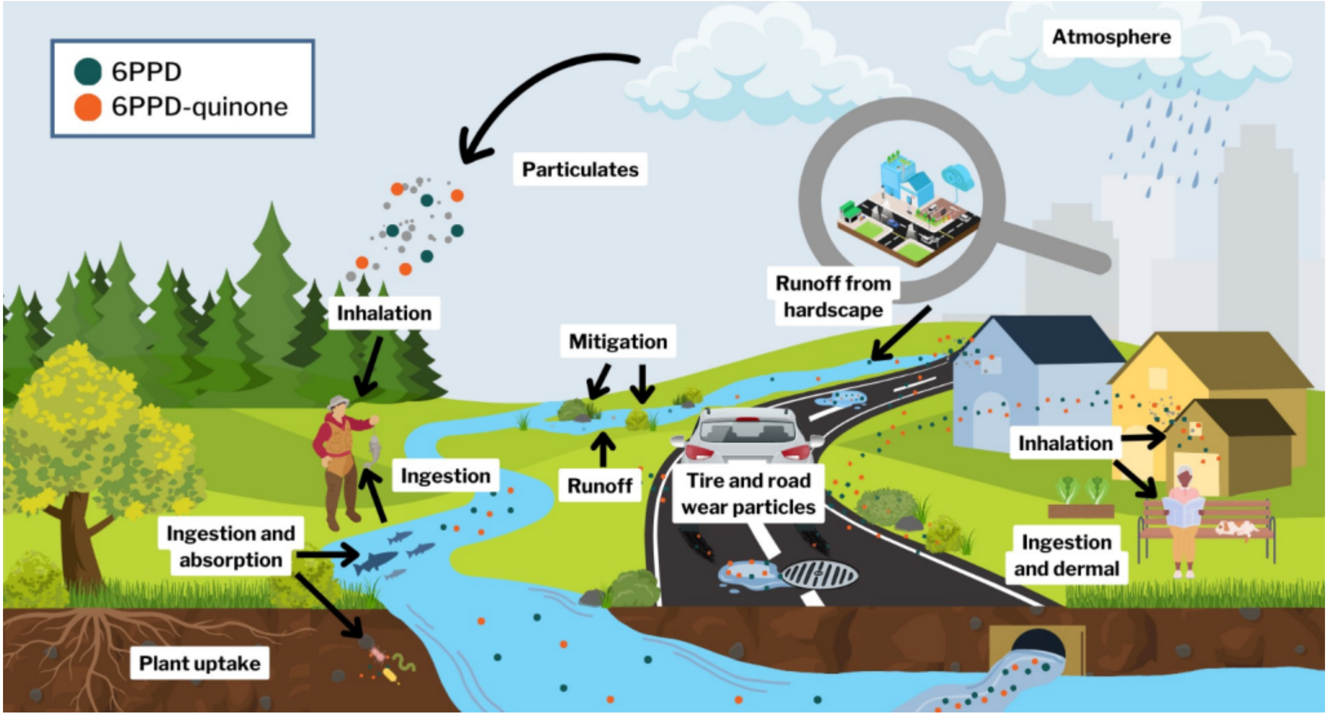


Figure 1-7. Conceptual transport and exposure model. 6PPD in tires is converted to 6PPD-q when exposed to ozone. 6PPD and 6PPD-q are contained in tire- and road-wear particles (TRWP) that can be transported in the air and can stay near the roadway and be transported to surface waters through stormwater drains and runoff. TRWP containing 6PPD and 6PPD-q in surface waters can be ingested and absorbed by fishes and other aquatic species and cause acute mortality. The aquatic exposure pathway is well established. Biomonitoring studies indicate that people are exposed, but the primary pathways of exposure are the subject of ongoing research. Potential exposure routes to humans can include inhalation, dermal exposure, and ingestion via TRWP deposition on surfaces, soils, and plants (including foods) and uptake into plants. Exposed fish can be ingested by humans and other species. 6PPD and 6PPD-q contamination in the environment can potentially be mitigated by green stormwater infrastructure. Research is ongoing to further define 6PPD-q's environmental behaviors, exposures, and the potential development of adverse health outcomes.
Source: Washington State Department of Ecology.

1.2.2 How Does 6PPD-q Reach Waterways?

TRWPs are nearly ubiquitous in the urban environment (Wagner et al. 2018[4UCJI65Q] Wagner, Stephan, Thorsten Hüffer, Philipp Klöckner, Maren Wehrhahn, Thilo Hofmann, and Thorsten Reemtsma. 2018. “Tire Wear Particles in the Aquatic Environment — A Review on Generation, Analysis, Occurrence, Fate and Effects.” Water Research 139 (August):83–100.

https://doi.org/10.1016/j.watres.2018.03.051.Kole et al. 2017[NZZMY6WC] Kole, Pieter Jan, Ansje J. Löhr, Frank G. A. J. Van Belleghem, and Ad M. J. Ragas. 2017. “Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment.” International Journal of Environmental Research and Public Health 14 (10): 1265. https://doi.org/10.3390/ijerph14101265.).

see Figure 1-7). TRWPs may contain 6PPD-q when they are emitted from the tire (Zhao et al. 2023[ENE6F3HC] Zhao, Haoqi Nina, Ximin Hu, Zhenyu Tian, Melissa Gonzalez, Craig A. Rideout, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Transformation Products of Tire Rubber Antioxidant 6PPD in Heterogeneous Gas-Phase Ozonation: Identification and Environmental Occurrence.” Environmental Science & Technology 57 (14): 5621–32.

https://doi.org/10.1021/acs.est.2c08690.Lattimer et al. 1983[3WW4X5AB] Lattimer, R. P., E. R. Hooser, R. W. Layer, and C. K. Rhee. 1983. “Mechanisms of Ozonation of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine.” Rubber Chemistry and Technology 56 (2): 431–39. https://doi.org/10.5254/1.3538136.). After TRWPs are in the environment, the 6PPD they contain may continue to act as a source for the generation of 6PPD-q. TRWPs are shed along roadways and parking areas and transported via air and surface water. Stormwater is a major route of transport from the road to waterbodies where, if

present, aquatic species can be exposed to 6PPD-q (Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. “A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon.” Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.Tian et al.

2022[BICQHLBC] Tian, Zhenyu, Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C.

Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej. 2022. “6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard.” Environmental Science & Technology Letters, January, acs.estlett.1c00910. https://doi.org/10.1021/acs.estlett.1c00910.). Coarse TRWP are likely to be deposited onto surfaces near roadways, while finer TRWP can be transported and dispersed in air (Baensch-Baltruschat et al. 2020[SG7DEPVC] Baensch-Baltruschat, Beate, Birgit Kocher, Friederike Stock, and Georg Reifferscheid. 2020. “Tyre and Road Wear Particles (TRWP)—A Review of Generation, Properties, Emissions, Human Health Risk, Ecotoxicity, and Fate in the Environment.” Science of the Total Environment 733 (September):137823. https://doi.org/10.1016/j.scitotenv.2020.137823.). TRWP transport may result in direct 6PPD-q deposition into surface waters or onto streambanks and impervious surfaces where it can be mobilized by stormwater runoff (Johannessen et al. 2022[YXQSYBCM] Johannessen, Cassandra, John Liggio, Xianming Zhang, Amandeep Saini, and Tom Harner. 2022. “Composition and Transformation Chemistry of Tire-Wear Derived Organic Chemicals and Implications for Air Pollution.” Atmospheric Pollution Research 13 (9): 101533. https://doi.org/10.1016/j.apr.2022.101533.Johannessen et al. 2022[E9K7U5U3] Johannessen, Cassandra, Paul Helm, Brent Lashuk, Viviane Yargeau, and Chris D. Metcalfe. 2022. “The Tire Wear Compounds 6PPD-Quinone and 1,3-Diphenylguanidine in an Urban Watershed.” Archives of Environmental Contamination and Toxicology 82 (2): 171–79. https://doi.org/10.1007/s00244-021-00878-4.).

Many urban stormwater systems are designed to control flooding, not capture and treat contaminants that are transported to and contained in the stormwater. In separate storm sewer systems, rainwater is transported to natural receiving waters through a network of ditches and pipes, usually without natural or engineered green spaces to remove deposited airborne particulates or water pollutants. Additionally, some areas with installed stormwater best management practices (BMPs) fail to contain stormwater discharge due to increased urbanization and storm events that are larger than the infrastructure was designed for (Levin, Howe, and Robertson 2020[28SGXBLF] Levin, Phillip S., Emily R. Howe, and James C. Robertson. 2020. “Impacts of Stormwater on Coastal Ecosystems: The Need to Match the Scales of Management Objectives and Solutions.” Philosophical Transactions of the Royal Society B: Biological Sciences 375 (1814): 20190460. https://doi.org/10.1098/rstb.2019.0460.), leading to direct conveyance of 6PPD and 6PPD-q to vulnerable aquatic ecosystems. In general, combined sewer systems limit the discharge of 6PPD-q into surface water by sending stormwater to wastewater treatment plants (WWTP) (Seiwert et al. 2022[QDRRVWMW] Seiwert, Bettina, Maolida Nihemaiti, Mareva Troussier, Steffen Weyrauch, and Thorsten Reemtsma. 2022. “Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater.” Water Research 212:118122. https://doi.org/10.1016/j.watres.2022.118122.Maurer et al. 2023[TJQR62IC] Maurer, Loïc, Eric Carmona, Oliver Machate, Tobias Schulze, Martin Krauss, and Werner Brack. 2023. “Contamination Pattern and Risk Assessment of Polar Compounds in Snow Melt: An Integrative Proxy of Road Runoffs.” Environmental Science & Technology 57 (10): 4143–52. https://doi.org/10.1021/acs.est.2c05784.Zhang et al. 2023[JWRBWTKN] Zhang, Hai-Yan, Zheng Huang, Yue-Hong Liu, Li-Xin Hu, Liang-Ying He, You-Sheng Liu, Jian-Liang Zhao, and Guang-Guo Ying. 2023. “Occurrence and Risks of 23 Tire Additives and Their Transformation Products in an Urban Water System.” Environment International 171 (January):107715. https://doi.org/10.1016/j.envint.2022.107715.). A Canadian study found two WWTP that use the same type of reactors to degrade waste had net discharge of 6PPD-q into surface waters (Johannessen and Metcalfe 2022[6AEMVTD8] Johannessen, Cassandra, and Chris D. Metcalfe. 2022. “The Occurrence of Tire Wear Compounds and Their Transformation Products in Municipal Wastewater and Drinking Water Treatment Plants.” Environmental Monitoring and Assessment 194 (10): 731. https://doi.org/10.1007/s10661-022-10450-9.). More research is needed to understand the dynamics of 6PPD and 6PPD-q in different WWTP.

Additional investigation is needed to determine the environmental concentrations of both 6PPD and 6PPD-q in urban streams to understand potential impacts on sensitive species in regions throughout the United States (see Figure 1-3). The fate of 6PPD and 6PPD-q in the environment requires more research, including, for example, factors that influence the formation of 6PPD-q in tires and TRWPs. Additional uncertainties include the transport and deposition of 6PPD and 6PPD-q from TRWPs, leaching rates from TRWPs, and the persistence and bioaccumulation potential of both 6PPD and 6PPD-q.

Many states have programs to divert scrap tires from landfills. Scrap tires are repurposed and recycled into crumb rubber used on sports fields, rubber-modified asphalt, and tire-derived aggregate used in civil engineering projects. Research is ongoing to determine whether and to what extent these potential sources result in human or ecological exposures. Table 1-3 provides a summary of dispositions for waste tires, including beneficial uses and applications in which tires are used as ingredients or components and methods of discard, including disposal and burning.

Table 1-3. Examples of used tire disposition

Disposition	Description or Examples
Building Construction	Accessibility ramps, flooring, sealant, roofing, waterproof membranes, and other construction materials can be produced from used tires.
Synthetic Fields, Tracks, and Playgrounds	Athletic fields using synthetic turf may use crumb rubber as a cushioning infill. Track and field facilities may use crumb rubber recycled from old tires in or under new synthetic surfaces.
Road and Traffic Maintenance	Erosion control, weed abatement, seismic transition coverings, traffic control cones, wheel stops, and curb ramps are all practical applications for used tires.
Rubberized Asphalt Concrete / Rubber-Modified Asphalt (RAC/RMA)	RAC/RMA produces a durable surface by blending ground-up recycled tires with asphalt prior to mixing in conventional materials.
Tire-Derived Aggregate	Chipped tires are often repurposed in civil engineering for fill, drainage, and vibration mitigation in construction projects.
Retread	Worn commercial tires receive new treads.
Material Feedstock	Ground tires are used to feed industrial processes as rubber or fuel.
Miscellaneous Repurposing	Aquatic bumpers, art projects, Earthship homes, swings, shoe soles, etc.
Disposal and Open Dumping	Whole tires may be disposed of in landfills or, in some instances, dumped.
Other	Burning, export, etc.

Notes: RAC=rubberized asphalt concrete; RMA=rubber-modified asphalt

Section 4: Occurrence, Fate, Transport, and Exposure Pathways discusses other potential routes of exposure.

1.3 What and Who Are Affected?

1.3.1 Impacts on Fishes

Of the species studied to date, coho salmon have the highest sensitivity to 6PPD-q (Tian et al. 2022[BICQHLBC] Tian, Zhenyu, Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C. Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej. 2022. "6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard." Environmental Science & Technology Letters, January, acs.estlett.1c00910. https://doi.org/10.1021/acs.estlett.1c00910.). In observations of URMS, mortality ranged from 20%–90% (Scholz et al. 2011[S8ASEIXU] Scholz, Nathaniel L., Mark S. Myers, Sarah G. McCarthy, Jana S. Labenia, Jenifer K. McIntyre, Gina M. Ylitalo, Linda D. Rhodes, et al. 2011. "Recurrent Die-Offs of Adult Coho Salmon Returning to Spawn in Puget Sound Lowland Urban Streams." PLOS ONE 6 (12): e28013. https://doi.org/10.1371/journal.pone.0028013.Spromberg and Scholz 2011[CT5HUEEI] Spromberg, Julann A, and Nathaniel L Scholz. 2011. "Estimating the Future Decline of Wild Coho Salmon Populations Resulting from Early Spawner Die-Offs in Urbanizing Watersheds of the Pacific Northwest, USA." Integrated Environmental Assessment and Management 7 (4): 648–56. https://doi.org/10.1002/ieam.219.). Modeling indicates that this level of mortality could result in localized extinction of coho within 8 to 115 years, depending on whether the URMS occurs at the low end (20%) or the high end (90%) of the observed range (Spromberg and Scholz 2011[CT5HUEEI] Spromberg, Julann A, and Nathaniel L Scholz. 2011. "Estimating the Future Decline of Wild Coho Salmon Populations Resulting from Early Spawner Die-Offs in Urbanizing Watersheds of the Pacific Northwest, USA." Integrated Environmental Assessment and Management 7 (4): 648–56. https://doi.org/10.1002/ieam.219.). Some populations of coho salmon are already listed under the Endangered Species Act (ESA), such as the lower Columbia River (threatened) and California Central Coast (endangered). The degree to which URMS has played a role in their decline is unknown (DTSC 2022[2M3Z8Z4F] DTSC. 2022. "Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the California Department of Toxic Substances Control (DTSC)." https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf .).

Regarding other species of salmonids, we did not identify any current information about observations of URMS in populations of brook trout or rainbow trout/steelhead.[2] Brook trout populations have been reported to be in decline in many locations within their range (Smith and Sklarew 2013[EGWKDGVU] Smith, Albert K., and Dann Sklarew. 2013. “A Mid Atlantic Brook Trout (Salvelinus fontinalis) Stream Sustainability Statistic for Rating Non-Tidal Streams.” Sustainability of Water Quality and Ecology 1–2 (December):68–81. https://doi.org/10.1016/j.swaqe.2013.08.001.Eastern Brook Trout Venture 2024[6I74E3G5] Eastern Brook Trout Venture. 2024. “Eastern Brook Trout Health Map (Trout Unlimited).” accessed 2024. https://easternbrooktrout.org/science-data/ebtjv-maps/copy_of_EBTJV%20Map%206_09_11.jpg/image_view_fullscreen.).

Smith and Sklarew (Smith and Sklarew 2013[EGWKDGVU] Smith, Albert K., and Dann Sklarew. 2013. “A Mid Atlantic Brook Trout (Salvelinus fontinalis) Stream Sustainability Statistic for Rating Non-Tidal Streams.” Sustainability of Water Quality and Ecology 1–2 (December):68–81. https://doi.org/10.1016/j.swaqe.2013.08.001.) found several factors related to stream quality that correlate with the absence or reduction in brook trout numbers; one of those factors was the distance between a creek and nearby roads. This correlation may not be directly related to 6PPD-q. Instead, as can be the case with many aquatic ecosystems, such declines could be a result of multiple stressors, including other water quality issues associated with impervious surfaces. Additional research would be needed to determine whether 6PPD-q poses a direct risk to brook trout populations. Rainbow trout are present or have been introduced throughout the United States. Native West Coast populations of rainbow trout and steelhead, the oceangoing form of rainbow trout, are in decline and include threatened and endangered populations (NOAA Fisheries 2023[97J7UAAD] NOAA Fisheries. 2023. “Steelhead Trout | NOAA Fisheries.” NOAA. February 9, 2023. https://www.fisheries.noaa.gov/species/steelhead-trout.). Current species assessments, many of which were developed before the identification of 6PPD-q, point to myriad impacts driving the decline, including habitat loss and degradation, dams, urbanization, stormwater, water diversion, temperature increases, agriculture, and timber harvesting. For example, the California Department of Fish and Wildlife developed an assessment for rainbow trout / steelhead. (California Department of Fish and Wildlife, n.d.[UQBR2QNX] California Department of Fish and Wildlife. n.d. Biogeographic Information and Observation System (BIOS) (version v5.99.22). Accessed April 9, 2019. https://apps.wildlife.ca.gov/bios/.).

1.3.2 Potential Ecological System Impacts

As keystone species, salmon contribute to wider ecosystem integrity (Hyatt, K.D. and Godbout, L. 2000[5GZ6MNL3] Hyatt, K.D., and Godbout, L. 2000. “A Review of Salmon as Keystone Species and Their Utility as Critical Indicators of Regional Biodiversity and Ecosystem Integrity.” In L. M. Darling, Editor. Proceedings of a Conference on the Biology and Management of Species and Habitats at Risk, Kamloops, B.C., 15–19 Feb., 1999, Two:520. Victoria, B.C.: B.C. Ministry of Environment, Lands and Parks. https://www.env.gov.bc.ca/wld/documents/fr02hyatt2.pdf.). Coho salmon and oceangoing steelhead support ecosystem health (including riverine and marine) by providing a food source for other species and contributing to nutrient cycling (Field and Reynolds 2012[MSBZH2UY] Field, R.D., and J.D. Reynolds. 2012. “Ecological Links between Salmon, Large Carnivore Predation, and Scavenging Birds.” Journal of Avian Biology 44:9–16.Holtgrieve and Schindler 2011[52CBYUQ3] Holtgrieve, G.W., and D.E. Schindler. 2011. “Marine-Derived Nutrients, Bioturbation, and Ecosystem Metabolism: Reconsidering the Role of Salmon in Streams.” Ecological Society of America 92:375–85.). Their migration from the ocean to their natal streams, where they spawn and ultimately die, provides marine nutrients to terrestrial environments (Naiman et al. 2002[7UB96QLR] Naiman, Bilby, Schindler, and Helfield. 2002. “Pacific Salmon, Nutrients, and the Dynamics of Freshwater and Riparian Ecosystems.” Ecosystems 5:399–417.). Additionally, Washington State’s Puget Sound Southern Resident orca whales—federally listed as an endangered species—rely on salmon as a primary food source (NOAA Fisheries 2022[P3KT2TMB] NOAA Fisheries. 2022. “In the Spotlight: Southern Resident Killer Whale.” January 4, 2022. https://www.fisheries.noaa.gov/species/killer-whale/spotlight.). Additional research is needed to assess how acute mortality in coho salmon and potential sublethal and/or chronic effects of 6PPD-q may impact population and ecosystem-level outcomes (see Section 8: Information Gaps and Research Needs).

1.3.3 Tribal Nations

Indigenous communities have serious concerns about the loss of coho salmon and potentially other aquatic species due to exposure to 6PPD-q from stormwater runoff into fish-bearing watersheds. Testimony from Natural Resources Director of the Nisqually Tribe David Troutt to the U.S. House of Representatives Committee on Natural Resources on 6PPD-q introduces some of the deep concerns raised by some tribal nations:

The tribes of the Salish Sea consider the salmon to be their brothers—family members to be honored, protected, treasured, and a gift from the creator. Salmon have been the primary source of protein for the tribes for 10,000 years. The location and movement of their villages were directly connected to the returns of salmon and steelhead. Their mythology and traditions are inextricably linked to salmon. Salmon is the central figure in Nisqually culture and traditions.

Salmon and fishing for salmon on the Nisqually River is the life blood of the Nisqually people. (Troutt 2021[Q4K9HZHT] Troutt, David. 2021. Testimony of David Troutt. https://democrats-naturalresources.house.gov/imo/media/doc/2021_07_15_Written%20Testimony_David%20Troutt.pdf.)

In the Pacific Northwest in particular, salmon play a significant role in the cultural practices, food sovereignty, community health, traditional knowledge, way of life, and identity as Salmon People for various tribal nations (Columbia River Inter-Tribal Fish Commission, 2021). These tribal nations' right to fish is an inherent right, and for tribal nations along the West Coast (NOAA Fisheries 2023[2SAX845N] NOAA Fisheries. 2023. "Sovereign Relations on the West Coast | NOAA Fisheries." NOAA. October 24, 2023. https://www.fisheries.noaa.gov/west-coast/partners/sovereign-relations-west-coast.) the right has been affirmed through treaty rights and reaffirmed through court case decisions. For example, the Boldt Decision (also known as United States v. Washington, 1974) established that the tribes are entitled to 50% of the fishing catch in their usual and accustomed fishing grounds within Washington State. Additionally, the decision requires that the tribes and Washington State comanage fisheries (University of Washington Gallagher Law Library, 2023). Because of this comanagement status, the tribes are important decision-makers in Washington State. More than 50 additional court filings under U.S. v. Washington between 1974 and 2021 have expanded on the Boldt Decision and have continued to reaffirm tribal treaty rights. The Boldt Decision created a precedent that has impacted Indigenous and Aboriginal rights to fish and use natural resources nationally and internationally. The decision has been cited in court cases involving the Chippewa Tribe in Minnesota (Tribal Treaties Database, 2024), tribes in Michigan and Wisconsin, the Māori people in New Zealand (New Zealand Ministry for Culture and Heritage, 2023), First Nations in Canada (Harris 2008[5X7TJCHU] Harris, Douglas C. 2008. "The Boldt Decision in Canada: Aboriginal Treaty Rights to Fish on the Pacific, in Alexandra Harmon, Ed." In The Power of Promises: Rethinking Indian Treaties In the Pacific Northwest, 128–53. Seattle, Washington: University of Washington Press. https://commons.allard.ubc.ca/cgi/viewcontent.cgi?referer=&httpsredir=1&article=1179&context=fac_pubs.), and other Indigenous peoples (Ziontz, n.d.[ZW5F8CK3] Ziontz, Jacob. n.d. "Far-Reaching Rights: An Era of Innovation in Treaty Law in Washington State That Impacted the Rights of Aboriginal Peoples Worldwide." Accessed July 15, 2024. https://www.historylink.org/File/10085.).

Although many tribes share a common interest in protecting salmon populations, each tribal nation has its own interests. The impact of 6PPD-q on salmon mortality is a compounding factor that complicates tribally led salmon recovery efforts like reintroduction, hatchery management, and habitat restoration. Additionally, a variety of factors negatively impact the resilience of salmon populations and poses challenges to tribal fisheries management. The following information captures some, but not all, of these interests and concerns as identified by tribal nations. Human-made blockages of waterways (for example, dams and culverts) create physical barriers for salmon passage, impeding their ability to spawn and complete their life cycle in natal streams. Habitat degradation and climate change reduce the availability of habitats that can support living salmon. Climate change increases water temperatures, reduces the availability of cold-water refuges and estuary habitats, and lowers the water level of many streams by reducing precipitation and snow melt (NOAA Fisheries 2023[BVP2RCVL] NOAA Fisheries. 2023. "Ecosystem Interactions and Pacific Salmon | NOAA Fisheries." NOAA. August 31, 2023. https://www.fisheries.noaa.gov/west-coast/sustainable-fisheries/ecosystem-interactions-and-pacific-salmon.); alternatively, climate change can lead to increased streamflow from extreme weather events like heavy rain events, which can change salmon habitat (Mantua, Tohver, and Hamlet 2010[ZHLUKQ2D] Mantua, Nathan, Ingrid Tohver, and Alan Hamlet. 2010. "Climate Change Impacts on Streamflow Extremes and Summertime Stream Temperature and Their Possible Consequences for Freshwater Salmon Habitat in Washington State." Climatic Change 102 (1–2): 187–223. https://doi.org/10.1007/s10584-010-9845-2.; Snover et al. 2019[UN9SA5AK] Snover, A.K., C.L. Raymond, H.A. Roop, and H. Morgan. 2019. "No Time to Waste. The Intergovernmental Panel on Climate Change's Special Report on Global Warming of 1.5°C and Implications for Washington State." Briefing Paper Prepared by the Climate Impacts Group, University of Washington, Seattle. https://cig.uw.edu/wp-content/uploads/sites/2/2019/02/NoTimeToWaste_CIG_Feb2019.pdf.). Tribal resource managers face many challenges; therefore, to have a tangible impact on salmon populations they often address salmon recovery from a holistic point of view.

As David Troutt's testimony indicated, coho salmon and other sensitive trout species are an important element of the cultural practice and diet of many tribal nations in the Pacific Northwest. Thus, for the tribal nations of this region, the decline of the coho salmon population from 6PPD-q may diminish the availability of a healthy protein source and a culturally appropriate food and negatively affect the cultural traditions associated with harvesting and preparing the food (DTSC 2022[2M3Z8Z4F] DTSC. 2022. “Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the California Department of Toxic Substances Control (DTSC).” https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf .). Another concern expressed by some tribal members (DTSC 2021[TIUY9CXL] DTSC. 2021. “DTSC Tribal Consultations and Meetings: Summary of Input on Motor Vehicle Tires Containing 6PPD.” https://dtsc.ca.gov/wp-content/uploads/sites/31/2021/12/Summary-of-Tribal-Input-SCP-6PPD.pdf.) is the concern that 6PPD-q may pass through the food web (DTSC 2022[2M3Z8Z4F] DTSC. 2022. “Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the California Department of Toxic Substances Control (DTSC).” https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf ., DTSC 2021[TIUY9CXL] DTSC. 2021. “DTSC Tribal Consultations and Meetings: Summary of Input on Motor Vehicle Tires Containing 6PPD.” https://dtsc.ca.gov/wp-content/uploads/sites/31/2021/12/Summary-of-Tribal-Input-SCP-6PPD.pdf.). Many tribal nations harvest salmon as the fish come back to freshwater to spawn. That migration can be triggered by storms; the flow of water helps the salmon surmount physical stream barriers, such as sand bars, but stormwater may contain 6PPD and 6PPD-q (Challis et al. 2021[T8TEWPCL] Challis, J. K., H. Popick, S. Prajapati, P. Harder, J. P. Giesy, K. McPhedran, and M. Brinkmann. 2021. “Occurrences of Tire Rubber–Derived Contaminants in Cold-Climate Urban Runoff.” Environmental Science & Technology Letters 8 (11): 961–67. https://doi.org/10.1021/acs.estlett.1c00682.Johannessen, Helm, and Metcalfe 2021[U9BWIDJ5] Johannessen, Cassandra, Paul Helm, and Chris D. Metcalfe. 2021. “Detection of Selected Tire Wear Compounds in Urban Receiving Waters.” Environmental Pollution 287 (October):117659. https://doi.org/10.1016/j.envpol.2021.117659.Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. “A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon.” Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.Tian et al. 2022[BICQHLBC] Tian, Zhenyu, Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C. Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej. 2022. “6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard.” Environmental Science & Technology Letters, January, acs.estlett.1c00910. https://doi.org/10.1021/acs.estlett.1c00910.). Thus, in addition to the potential toxicity to the fish themselves, the people who harvest and eat the salmon may be exposed to these chemicals. The human health impacts of exposure to 6PPD-q are still unstudied. That same concern about 6PPD-q passing though the food web exists for the animals that hunt or scavenge salmon or the carcasses. The toxicokinetics of 6PPD-q in exposed fish and their carcasses has yet to be characterized, so whether this represents a route of exposure remains a data gap, and the toxicological impacts on these species are largely unstudied.

Some tribal members have also cited concerns about plant uptake of 6PPD-q, which could impact the safety of traditionally harvested plants. There is also a larger concern stemming from the fact that salmon are a keystone species; reductions in their populations have implications not just for population health, but for ecosystem resilience.

Given these many concerns, Earthjustice submitted a petition on behalf of the Yurok Tribe, the Port Gamble S’Klallam Tribe, and the Puyallup Tribe of Indians to the USEPA in 2023 to establish regulations prohibiting the manufacturing, processing, use, and distribution of 6PPD under Section 21 of the Toxic Substances Control Act (TSCA) (Earthjustice 2023[PB6HUXGY] Earthjustice. 2023. “U.S. Fishing Groups Sue Tire Manufacturers Over 6PPD Impacts on Salmon, Steelhead.” Earthjustice. 2023. https://earthjustice.org/press/2023/u-s-fishing-groups-sue-tire-manufacturers-over-6ppd-impacts-on-salmon-steelhead.). This petition was supported by the Affiliated Tribes of Northwest Indians and the states of Connecticut, Oregon, Rhode Island, Vermont, and Washington (EPA-HQ-OPPT 2023).

Many tribal nations have called for the federal and state governments to evaluate this dilemma through a holistic lens, which may include assessing the structures and institutions that caused the problem in the first place. This includes, but is not limited to, transportation infrastructure and pursuing solutions that address these underlying challenges.

1.3.4 Potential Economic and Community Health Concerns

If exposure to 6PPD-q is shown to cause population declines in sensitive species (DTSC 2022[2M3Z8Z4F] DTSC. 2022. “Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the

California Department of Toxic Substances Control (DTSC)." https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf .Feist et al. 2017[4PSDP2BG] Feist, Blake E., Eric R. Buhle, David H. Baldwin, Julann A. Spromberg, Steven E. Damm, Jay W. Davis, and Nathaniel L. Scholz. 2017. "Roads to Ruin: Conservation Threats to a Sentinel Species across an Urban Gradient." Ecological Applications 27 (8): 2382–96. https://doi.org/https://doi.org/10.1002/eap.1615.), those declines can have an impact on the economic well-being of communities that rely on the species for subsistence, commercial, recreational, and tourism-based fish-related activities. The known sensitive species, coho salmon, brook trout, lake trout, and rainbow trout, provide significant economic value because of their importance for commercial fishers and recreational anglers (USGS 2023[BHT5YTKH] USGS. 2023. "Brook Trout (Salvelinus fontinalis) — Species Profile. United States Geological Survey (USGS)." USGS Nonindigenous Aquatic Species Database. 2023. https://nas.er.usgs.gov/queries/factsheet.aspx?SpeciesID=939.USFWS 2000[W2Z72ERF] USFWS. 2000. "Rainbow Trout (Oncorhynchus mykiss) | U.S. Fish & Wildlife Service." July 10, 2000. https://www.fws.gov/species/rainbow-trout-oncorhynchus-mykiss.). Impacts to the populations of these species from 6PPD-q exposures may raise concerns for state fish and wildlife agencies throughout the country.

Impacts to human health from environmental exposures to 6PPD and/or 6PPD-q have yet to be documented. If 6PPD-q or low levels of 6PPD are discovered to have adverse human health impacts, there may be environmental justice concerns for communities near roadways (Health Effects Institute Panel on the Health Effects of Long-Term Exposure to Traffic-Related Air Pollution. 2022[P6LUHI38] Health Effects Institute Panel on the Health Effects of Long-Term Exposure to Traffic-Related Air Pollution. 2022. "Systematic Review and Meta-Analysis of Selected Health Effects of Long-Term Exposure to Traffic-Related Air Pollution." Special Report 23. Boston, MA: Health Effects Institute. https://www.healtheffects.org/system/files/hei-special-report-23_6.pdf.). 6PPD-q has been found in roadway dust and airborne particulate (Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. "Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers." Environmental Pollution 314 (December):120206. https://doi.org/10.1016/j.envpol.2022.120206.Cao et al. 2023[D5FPK9YB] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Han Qiao, Huankai Li, Gefei Huang, Zhu Yang, and Zongwei Cai. 2023. "Occurrence and Fate of Substituted P-Phenylenediamine-Derived Quinones in Hong Kong Wastewater Treatment Plants." Environmental Science & Technology, October. https://doi.org/10.1021/acs.est.3c03758.), and communities living near roadways are predominantly persons of color and lower income (Rowangould 2013[9KKD6N4U] Rowangould, G.M. 2013. "A Census of the US Near-Roadway Population: Public Health and Environmental Justice Considerations." Transportation Research, Part D: Transport and Environment 2013 (25): 59–67. https://doi.org/10.1016/j.trd.2013.08.003.; Boogaard et al. 2022[JTM8JHCV] Boogaard, H., A.P. Patton, R.W. Atkinson, J.R. Brook, H.H. Chang, D.L. Crouse, J.C. Fussell, et al. 2022. "Long-Term Exposure to Traffic-Related Air Pollution and Selected Health Outcomes: A Systematic Review and Meta-Analysis." Environment International 164:107262. https://doi.org/10.1016/j.envint.2022.107262.). Differential exposures to 6PPD-q may occur in vulnerable populations and overburdened communities. For more information see Section 2: Effects Characterization and Toxicity, Section 4: Occurrence, Fate, Transport, and Exposure Pathways, and Section 8: Information Gaps and Research Needs of this document.

1.4 How Do We Identify and Measure 6PPD-q?

Some private labs developed methods to detect and quantitate 6PPD-q in aqueous matrices (see for example Hunt, Hindle, and Anumol 2021[FI465BMH] Hunt, Kathy, Ralph Hindle, and Tarun Anumol. 2021. "Quantitation of Toxic Tire Degradant 6PPD-Quinone in Surface Water." Application Note: Environmental. Agilent Technologies, Inc.; Neilson 2021[HWAFMKHN] Neilson, Leighanne. 2021. "SGS AXYS Measures the Major Antiozonant Degradation Product 6-PPD Quinone and 6-PPD." SGS AXYS. December 14, 2021. https://www.sgsaxys.com/2021/12/14/new-sgs-axys-is-pleased-to-measure-the-major-antiozonant-degradation-product-6-ppd-quinone-and-its-parent-compound-6-ppd-at-sub-ng-l-reporting-limits/.), and some commercial labs provide 6PPD-q testing. USEPA released a draft analytical method for detection of 6PPD-q in aqueous matrices, predominantly stormwater and surface water (USEPA 2023[7AAJEWWG] USEPA. 2023. "Draft Method 1634: Determination of 6PPD-Quinone in Aqueous Matrices Using Liquid Chromatography with Tandem Mass Spectrometry (LC/MS/MS)." EPA 821-D-24-001. Office of Water (4303T), Office of Science and Technology. https://www.epa.gov/system/files/documents/2024-01/draft-method-1634-for-web-posting-1-23-24_508.pdf.), using liquid chromatography (LC) with tandem mass spectrometry (LC-MS/MS). Washington State Department of Ecology (Washington State Department of Ecology 2023[HJQ3HEWU] Washington State Department of Ecology. 2023. “Standard Operating Procedure (SOP): Extraction and Analysis of 6PPD-Quinone (Mel730136, Version 1.2).”) also has a procedure for measuring 6PPD-q (“Standard Operating Procedure (SOP): Extraction and Analysis of 6PPD-quinone”). These methods are especially important because they allow us to quantitatively characterize the nature and extent of 6PPD-q contamination in the environment and are fundamental to establishing long-term monitoring programs as well. Vetted water sampling protocols are equally important because 6PPD-q levels tend to peak during and shortly after storms, making monitoring a challenge. Section 5: Measuring, Mapping, and Modeling 6PPD and 6PPD-q discusses best practices.

Another approach to finding 6PPD-q is field research—specifically salmonid biological monitoring for URMS or pre-spawn morality—which has been used to identify salmon-bearing streams where stormwater pollution might be a driver for water quality and aquatic life impacts (Halama et al. 2024[5UMEQW95] Halama, Jonathan, Robert B. McKane, Bradley L. Barnhart, Paul P. Pettus, Allen F. Brookes, Angela K. Adams, Catherine K. Gockel, et al. 2024. “Watershed Analysis of Urban Stormwater Contaminant 6PPD-Quinone Hotspots and Stream Concentrations Using a Process-Based Ecohydrological Model.” Frontiers in Environmental Science 12 (March). https://doi.org/10.3389/fenvs.2024.1364673.). One example of this type of research has been Longfellow Creek in Seattle, which has been studied by agencies and community scientists since at least 2002. Watershed analyses of storm sewer systems, hydrology, and salmon habitat can help identify 6PPD-q hotspots and set the stage for spatial analysis of solution prioritization (Washington State Department of Ecology 2022[K2CG7KTE] Washington State Department of Ecology. 2022. “6PPD in Road Runoff Assessment and Mitigation Strategies.” 22-03–020. Olympia, Washington: Environmental Assessment and Water Quality Programs. https://apps.ecology.wa.gov/publications/documents/2203020.pdf.).

1.5 After We Find It, How Can We Mitigate It? What Else Can We Do?

Implementation and expansion of stormwater control measures (SCM) may reduce exposure to 6PPD-q and other pollutants in aquatic habitats. Research efforts are seeking to enhance and improve upon these SCMs, such as optimizing for the removal of 6PPD-q and other contaminants from stormwater runoff before it enters receiving water bodies. Mitigation and stormwater management will be key to reducing the potential impacts in the near term. Bioretention filtration has been shown to be effective at preventing coho mortality (McIntyre et al. 2023[F7NAIVJ4] McIntyre, Jenifer, Julann Spromberg, James Cameron, John P. Incardona, Jay W. Davis, and Nathaniel L. Scholz. 2023. “Bioretention Filtration Prevents Acute Mortality and Reduces Chronic Toxicity for Early Life Stage Coho Salmon (Oncorhynchus kisutch) Episodically Exposed to Urban Stormwater Runoff.” Science of the Total Environment 902 (December):165759. https://doi.org/10.1016/j.scitotenv.2023.165759.Spromberg et al. 2016[GI97QYN4] Spromberg, Julann A., David H. Baldwin, Steven E. Damm, Jenifer K. McIntyre, Michael Huff, Catherine A. Sloan, Bernadita F. Anulacion, Jay W. Davis, and Nathaniel L. Scholz. 2016. “Coho Salmon Spawner Mortality in Western US Urban Watersheds: Bioinfiltration Prevents Lethal Storm Water Impacts.” Journal of Applied Ecology 53 (2): 398–407. https://doi.org/https://doi.org/10.1111/1365-2664.12534.). Reductions in other stormwater pollutants, such as metals, are also seen when this SCM is applied (McIntyre et al. 2021[MVL2LKBM] McIntyre, Jenifer K., Jasmine Prat, James Cameron, Jillian Wetzel, Emma Mudrock, Katherine T. Peter, Zhenyu Tian, et al. 2021. “Treading Water: Tire Wear Particle Leachate Recreates an Urban Runoff Mortality Syndrome in Coho but Not Chum Salmon.” Environmental Science & Technology 55 (17): 11767–74. https://doi.org/10.1021/acs.est.1c03569.). SCM can be expensive to implement and maintain; thus, there is a need to ensure that implementation is focused on the areas of highest risk, to the extent possible. Mitigation strategies should also consider the potential for airborne transport and exposures when designing BMPs for 6PPD-q. Solutions to 6PPD-q will likely include a mixture of approaches such as source control, alternatives to 6PPD in tires, and SCMs. Consideration of alternatives to 6PPD are already underway (Gradient 2024[LHN7K744] Gradient. 2024. “Preliminary (Stage 1) Alternatives Analysis Report: Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N’-Phenyl-p-Phenylenediamine (6PPD).” https://www.ustires.org/sites/default/files/2024-03/USTMA%20Consortium%206PPD%20AA%20Preliminary%20Report_3-25-24.pdf.; DTSC 2022[2M3Z8Z4F] DTSC. 2022. “Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the California Department of Toxic Substances Control (DTSC).” https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf.Washington State Department of Ecology 2023[M64YC38F] Washington State Department of Ecology. 2023. “6PPD Alternatives Assessment Hazard Criteria.” 23-04–036. https://apps.ecology.wa.gov/publications/documents/2304036.pdf.Washington

State Department of Ecology 2021[2UEJGNJ2] Washington State Department of Ecology. 2021. “Technical Memo: Assessment of Potential Hazards of 6PPD and Alternatives.” https://www.ezview.wa.gov/Portals/_1962/Documents/6ppd/6PPD%20Alternatives%20Technical%20Memo.pdf.). See Section 6: Mitigation Measures and Solutions for more information.

1.6 What We Don’t Know: Knowledge and Research Gaps

6PPD and 6PPD-q are contaminants of emerging concern (CEC), and many data gaps and questions about them remain. These questions, while important, do not obviate the need for action based on available information to date regarding the impact of 6PPD and 6PPD-q. For a detailed list with explanation, see Section 8: Information Gaps and Research Needs.

1.7 Governance

Ongoing research is investigating the full scope of rubber products containing 6PPD, the ubiquitousness of tires, and TRWPs that may contain 6PPD and 6PPD-q. Meanwhile, the issue is already being considered on the legal and governance fronts. We include some examples here for greater awareness and note how different statutes are being and may be used to address the 6PPD/6PPD-q challenge.

Stormwater laws and permits (authorized through the Clean Water Act [CWA], including the National Pollutant Discharge Elimination System [NPDES]) permits,) may be tools to mitigate 6PPD and 6PPDq pollution. How stormwater permits are changed, used, or developed to address 6PPDq is generally yet to be determined; two draft permits developed within Washington State include permit changes that are intended to address 6PPDq: the Washington State municipal separate storm sewer systems (MS4) stormwater general permits (Washington State Department of Ecology 2023[TX3IER4R] Washington State Department of Ecology. 2023. “Municipal Stormwater Permit Reissuance—Washington State Department of Ecology.” Accessed 2023. https://ecology.wa.gov/regulations-permits/permits-certifications/stormwater-general-permits/municipal-stormwater-general-permits/municipal-stormwater-permit-reissuance.) and the USEPA’s stormwater individual permit for Joint Base Lewis-McChord (USEPA 2017[W3Z5GUCI] USEPA, Region 10. 2017. “NPDES Stormwater Permit for Joint Base Lewis-McChord MS4 in Washington.” Reports and Assessments. September 29, 2017. https://www.epa.gov/npdes-permits/npdes-stormwater-permit-joint-base-lewis-mcchord-ms4-washington.). In August 2024, Washington State adopted a quantitative freshwater acute water quality standard for 6PPD-q under the authority of the CWA (see Section 7.8.2: Other Relevant CWA Programs).

Beyond stormwater management, several other statutes may play a role in controlling, mitigating, or eliminating 6PPD and 6PPD-q, depending on the fate and transport and/or exposure pathway. Relevant statutes may include the following:

- Toxic Substances Control Act (TSCA, see Section 7.2)
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund (see Section 7.3)
- Resource Conversation and Recovery Act (RCRA, see Section 7.4)
- Endangered Species Act (ESA, see Section 7.5)
- Magnuson-Stevens Fishery Conservation and Management Act (MSA, see Section 7.6)
- Safe Drinking Water Act (SDWA, see Section 7.7)

For example, the USEPA granted a citizens petition under the TSCA and “plans to take action to address the risk to the environment presented by 6PPD, and the degradant 6PPD-q through an advance notice of proposed rulemaking under TSCA section 6,” (USEPA 2023[EUYBKVIF] USEPA. 2023. “EPA Grants Tribal Petition to Protect Salmon from Lethal Chemical.” News Release. November 2, 2023. https://www.epa.gov/newsreleases/epa-grants-tribal-petition-protect-salmon-lethal-chemical.). USEPA’s 6PPD-q website includes information on available resources and agency actions to address 6PPD-q. In addition, the states of California and Washington have already initiated some regulatory actions on alternatives and more. For more information see Section 6.2.1 and Section 7: Policies, Regulations, and Laws.

In November 2023, two fishing groups, the Institute for Fisheries Resources and the Pacific Coast Federation of Fishermen’s Associations, filed a lawsuit against 13 U.S.-based tire manufacturers under Section 9 of the ESA (Earthjustice 2023[PB6HUXGY] Earthjustice. 2023. “U.S. Fishing Groups Sue Tire Manufacturers Over 6PPD Impacts on Salmon, Steelhead.” Earthjustice.

2023. https://earthjustice.org/press/2023/u-s-fishing-groups-sue-tire-manufacturers-over-6ppd-impacts-on-salmon-steelhead.). In June 2022, notice letters of intent to sue under the CWA were sent to five municipalities in the Puget Sound (Seattle, Mukilteo, Normandy Park, Burien, and SeaTac) by the organization Puget Soundkeeper, though no complaints have been filed in court at this time (Puget Soundkeeper 2022[4FJMQ2WI] Puget Soundkeeper. 2022. “Puget Sound Municipalities Fail to Address 6PPD-Quinone, Putting Salmon at Risk.” Puget Soundkeeper Alliance. June 16, 2022. https://pugetsoundkeeper.org/2022/06/16/6ppd-mukilteo-burien-seatac-normandy-park-seattle/.).

Environmental regulations may often regulate a specific media (stormwater, groundwater, solid waste, air, etc.), but they are not mutually exclusive—hence the challenge in regulating something like TRWP containing 6PPD and 6PPD-q. For multiple routes of exposure, including for example via aerial deposition, a multi-regulatory approach may need to be taken to significantly impact the issue. For more information see Section 7: Policies, Regulations, and Laws.

1.8 Steps for Addressing 6PPD-q

Table 1-4 provides the basic steps for an environmental decision-maker to follow when assessing 6PPD and 6PPD-q. It also explains how they can use this guidance document in their decision-making.

Table 1-4: Checklist for decision-makers and environmental managers—Do you have this problem, and what are the first steps?

Problem	Resources
Do I have sources of 6PPD?	See this Introduction, Section 4: Occurrence, Fate, Transport and Exposure Pathways, and Section 5: Measuring, Mapping, and Modeling
Do I have potential ecological or human receptors? Do I have concentrations of 6PPD-q in my aquatic environment that can impact sensitive species?	See Section 2: Effects Characterization and Toxicity and Section 5: Measuring, Mapping, and Modeling
Do I have ways (exposure pathways) for 6PPD/6PPD-q to reach potentially sensitive species at concentrations that may cause adverse effects? Examples: stormwater inventory, discharges, confluence of sources (for example, roadways) to aquatic habitats, tire-derived assets (for example, artificial turf fields), etc.	See Section 4: Occurrence, Fate, Transport, and Exposure Pathways
Do I have tools to interrupt exposure pathways and manage sources?	See Section 6: Mitigation Measures and Solutions and Section 7: Policies, Regulations, and Laws
What are the information gaps for 6PPD and 6PPD-q?	See Section 8: Information Gaps and Research Needs

6PPD and 6PPD-q pose many challenges that are often associated with CEC, including addressing critical effects observed in the environment when many knowledge gaps exist. For more information on a framework for addressing CEC in general, see the ITRC document on CEC.

Section 2 Tables

The following tables summarize the range of known effect levels observed in various ecological species for acute and chronic toxicity, and toxicology data relevant to the assessment of human health. The information in these tables was compiled from peer-reviewed studies that this ITRC team was aware of as of March 2024.

Table Number and Title	**Link to PDF**	**Link to Executable File (Word Processor Format)**
2-1 Summary of acute aquatic toxicity data for 6PPD and 6PPD-q		
2-2 Summary of chronic aquatic toxicity data for 6PPD and 6PPD-q		
2-3 Summary of toxicity studies reviewed for the evaluation of human health effects		

PDF versions of each table are provided for the reader to view information in a visual format that is consistent across browsers and platforms. Executable files are provided to allow readers to sort information by the column of their choice, but may appear different visually depending on the software used to view this file. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

2 Effects Characterization and Toxicity

ITRC has prepared an overview of the current understanding of 6PPD-q sources, exposure, fate, transport, toxicity, mitigation strategies, on-going research, and data needs. This section describes the following:

- the toxicity of 6PPD-q and its parent compound 6PPD
- the ecological and human health effects associated with exposure to these contaminants
- potential populations of concern that may come into contact with 6PPD-q and 6PPD
- current knowledge gaps regarding potential ecological and human health hazards

Section 1 (Introduction) and Section 4 (Occurrence, Fate, Transport, and Exposure Pathways) provide detailed discussions of sources, fate, and transport mechanisms and levels of 6PPD-q and 6PPD in environmental compartments and potential exposure pathways that are relevant to the effects discussed within this section.

2.1 Introduction

Human or ecological receptors may be exposed to 6PPD-q and its parent compound 6PPD via several different exposure pathways (see Figure 1-7).

Potential aquatic ecological receptors, which include freshwater and marine organisms (vertebrates, invertebrates, and plants), may be exposed to 6PPD-q and 6PPD through direct uptake of water through respiratory surfaces, ingestion, and absorption. The route of exposure may vary among species or life stages. Exposure in terrestrial organisms (vertebrates, invertebrates, and plants) is poorly characterized, but it is possible that terrestrial receptors may be exposed via ingestion, inhalation, or absorption.

Potential routes of exposures for humans include ingestion of soil, sediment, dust and water, dust inhalation, and dermal contact. Research supports the biological uptake of both 6PPD and 6PPD-q, which may potentially expose humans via food sources (see Section 4.5 and Table 4-10). At present, however, quantitative measurement of 6PPD-q, 6PPD, and their metabolic products in humans is limited. U.S.-based biomonitoring studies of 6PPD-q or 6PPD exposure are not currently available.

The effects of 6PPD-q and 6PPD on ecological and human health, as with most other chemicals, depends on the magnitude, frequency, and duration of exposure. Research on 6PPD-q toxicity is rapidly expanding and, while some data are presented herein for 6PPD-q, data gaps have been identified in our understanding of health effects. The knowledge base on human and ecological effects of both 6PPD and 6PPD-q is still evolving. 6PPD is the only known source of 6PPD-q in the environment, but the relationship between the toxicity of 6PPD and the toxicity of 6PPD-q is currently unknown. At this time, data gaps remain regarding the effects on human and ecological receptors of exposure to both 6PPD and 6PPD-q. Data on the effects of 6PPD are presented in case a read-across using 6PPD is deemed appropriate in future work as a method for predicting the effects of 6PPD-q. Currently, data are insufficient to conduct a read-across from 6PPD to 6PPD-q. In addition, regulatory authorities may need to address the impacts of 6PPD-q through regulation of the use of 6PPD in products. In doing so, regulatory agencies may have a need to evaluate potential effects of 6PPD relative to a proposed alternative.

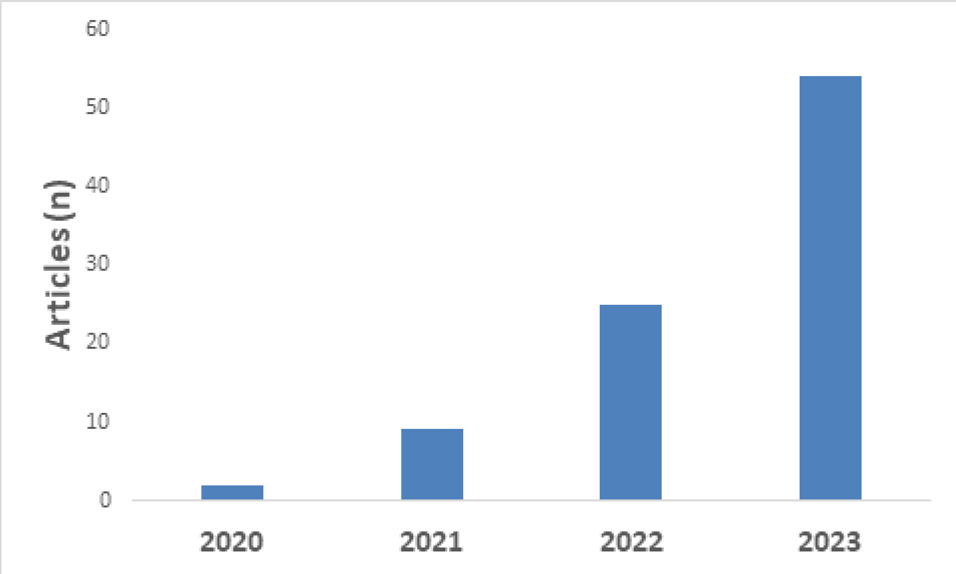


Figure 2-1. Number of articles mentioning 6PPD or 6PPD-q from 2020–2023.

Since the publication of work by Z. Tian et al. (Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. “A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon.” Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.), interest in 6PPD-q has grown substantially. A search of the PubMed database[3] shows that the number of articles has risen exponentially year-over-year (Figure 2-1). This section is not intended to represent a comprehensive review of 6PPD-q and 6PPD toxicity studies, and a formal study reliability evaluation was not performed for the studies discussed in this section. Given the active research on this topic, additional studies have been published since the completion of this document. While the intent of this section is to present the most salient and recently available information on the toxicological effects of 6PPD-q and 6PPD, interested readers are encouraged to search the scientific literature for newly available information.

2.2 Environmental Toxicology

This section reports the currently available toxicity information and knowledge gaps concerning the effects of 6PPD-q and 6PPD on freshwater, marine, and terrestrial organisms (vertebrates, invertebrates, and plants). Although 6PPD-q and 6PPD are similar in chemical structure, the toxicological relationship between the two chemicals is nuanced and depends highly on the species and endpoints under consideration as described in the subsections below. Given these considerations, each chemical will be discussed in its own subsection, and toxicity will be described on the basis of ecological taxa. The absence of a taxon in the following subsections represents a data gap at the time this document was published. Additional information is available from other previously published reports (DTSC 2022[2M3Z8Z4F] DTSC. 2022. “Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the California Department of Toxic Substances Control (DTSC).” https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf .OECD 2004[FCJPCPVW] OECD. 2004. “SIDS Initial Assessment Report for N-(1,3-Dimethylbutyl)-N´-Phenyl-1,4-Phenylenediamine (6PPD), Organisation for Economic Co-Operation and Development (OECD).” https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e.Washington State Department of Ecology 2024[A9RGZ5XI] Washington State Department of Ecology. 2024. “Safer Products for Washington 2024 Report.” Seattle, Washington. https://ecology.wa.gov/waste-toxics/reducing-toxic-chemicals/washingtons-toxics-in-products-laws/safer-products.ToxServices, LLC 2021[IDJRCJR2] ToxServices, LLC. 2021. “N-(1,3-Dimethylbutyl)-N’-Phenyl-p-Phenylenediamine (6PPD) (CAS #793-24-8) Greenscreen® for Safer Chemicals (Greenscreen®) Assessment.” GS-1204. Washington, D.C.: ToxServices Toxicology Risk Assessment Consulting. https://www.ezview.wa.gov/Portals/_1962/Documents/6ppd/GreenScreenExecutiveSummaryFor6PPD.pdf.OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. “Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update).” Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.ECHA 2021[Y79Z3ZWV] ECHA. 2021.

“Substance Infocard: N-1,3-Dimethylbutyl-N’-Phenyl-p-Phenylenediamine. European Chemicals Agency (ECHA).” April 7, 2021. https://echa.europa.eu/substance-information/-/substanceinfo/100.011.222.).

2.2.1 Environmental Toxicity of 6PPD-q

As noted in Section 1: Introduction, 6PPD-q, a transformation product of the antiozonant 6PPD, was identified in stormwater samples in late 2020 as a causal toxicant in URMS among adult and juvenile coho salmon (*Oncorhynchus kisutch*) (Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. “A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon.” Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.). While a considerable amount of work has focused on characterizing aquatic toxicity in various fish species, there are still relatively few studies on invertebrates and algae and no data on aquatic-dependent amphibians. Research to date regarding the aquatic toxicity of 6PPD-q is discussed in the subsections below, and Tables 2-1 and Table 2-2 summarize the range of known effect levels observed in various species for acute and chronic toxicity, respectively. Compared to those of aquatic studies, data for terrestrial wildlife is generally limited. Currently, no data are available on the toxicity of 6PPD-q in birds, reptiles, and terrestrial amphibians, while information for other terrestrial receptors is scarce. The following subsections summarize key information on the toxicological effects of 6PPD-q for taxa with available data.

2.2.1.1 6PPD-q Toxicity in Fishes

6PPD-q’s Toxicity in Salmonids

- 6PPD-q is highly toxic to coho salmon.
- Of the fish species studied thus far, coho salmon are the most sensitive
- The effects of exposure to 6PPD-q in other aquatic species are varied, even in closely related species.
- Other sensitive fish species include rainbow trout (and likely steelhead), brook trout, lake trout, and coastal cutthroat trout.

In coho salmon, URMS begins with a common progression of behavioral symptoms, which include increased surface swimming, loss of equilibrium and buoyancy, gasping at the surface, and ultimately mortality (Chow et al. 2019[7RMZ3UNQ] Chow, Michelle I., Jessica I. Lundin, Chelsea J. Mitchell, Jay W. Davis, Graham Young, Nathaniel L. Scholz, and Jenifer K. McIntyre. 2019. “An Urban Stormwater Runoff Mortality Syndrome in Juvenile Coho Salmon.” Aquatic Toxicology 214 (September):105231. https://doi.org/10.1016/j.aquatox.2019.105231.Scholz et al. 2011[S8ASEIXU] Scholz, Nathaniel L., Mark S. Myers, Sarah G. McCarthy, Jana S. Labenia, Jenifer K. McIntyre, Gina M. Ylitalo, Linda D. Rhodes, et al. 2011. “Recurrent Die-Offs of Adult Coho Salmon Returning to Spawn in Puget Sound Lowland Urban Streams.” PLOS ONE 6 (12): e28013. https://doi.org/10.1371/journal.pone.0028013.Tian et al. 2022[BICQHLBC] Tian, Zhenyu, Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C. Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej. 2022. “6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard.” Environmental Science & Technology Letters, January, acs.estlett.1c00910. https://doi.org/10.1021/acs.estlett.1c00910.). The behavioral characteristics of URMS are described in Section 2.2.1.1.2. After identification of this chemical in stormwater and surface water, follow-up laboratory toxicity tests using 6PPD-q confirmed that 6PPD-q is acutely toxic to coho salmon, with 24-hour median lethal concentration (LC_{50}) ranging from 0.041 µg/L in coho hatchlings (3 weeks post-swim up) to 0.095 µg/L in juveniles (1+ year old) (Lo et al. 2023[LA4CEWYX] Lo, Bonnie P., Vicki L. Marlatt, Xiangjun Liao, Sofya Reger, Carys Gallilee, Andrew R.S. Ross, and Tanya M. Brown. 2023. “Acute Toxicity of 6PPD-Quinone to Early Life Stage Juvenile Chinook (Oncorhynchus tshawytscha) and Coho (Oncorhynchus kisutch) Salmon.” Environmental Toxicology and Chemistry 42 (4): 815–22. https://doi.org/10.1002/etc.5568.Greer et al. 2023[P6RF5UFR] Greer, Justin B., Ellie M. Dalsky, Rachael F. Lane, and John D. Hansen. 2023. “Establishing an In Vitro Model to Assess the Toxicity of 6PPD-Quinone and Other Tire Wear Transformation Products.” Environmental Science & Technology Letters, May. https://doi.org/10.1021/acs.estlett.3c00196.Tian et al. 2022[BICQHLBC] Tian, Zhenyu, Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C. Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej. 2022. “6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard.” Environmental Science & Technology Letters, January, acs.estlett.1c00910. https://doi.org/10.1021/acs.estlett.1c00910.). For comparison, Johannessen, Helm, et al. (Johannessen et al. 2022[E9K7U5U3] Johannessen, Cassandra, Paul Helm, Brent Lashuk, Viviane Yargeau, and Chris D. Metcalfe. 2022. “The Tire Wear Compounds 6PPD-Quinone and 1,3-Diphenylguanidine in an Urban Watershed.” Archives of Environmental Contamination and Toxicology 82 (2): 171–79. https://doi.org/10.1007/s00244-021-00878-4.) measured 6PPD-q at 2.85 µg/L in the Don River in Toronto, Canada; this is the highest level we found in the literature for surface water.

Since the publication of Z. Tian et al. (Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. “A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon.” Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.), acute mortality has been evaluated in more than a dozen species of fish (see Tables 2-1 and Table 2-2). Of the fish species studied thus far, coho salmon are the most sensitive. Lethal concentrations vary widely among fish (24-hour LC_{50} of 0.041 µg/L in coho salmon to a 96-hour LC_{50} greater than 500 µg/L in the Chinese rare minnow (*Gobiocypris rarus*), highlighting the likelihood of a unique species-specific physiological mechanism for URMS (Lo et al. 2023[LA4CEWYX] Lo, Bonnie P., Vicki L. Marlatt, Xiangjun Liao, Sofya Reger, Carys Gallilee, Andrew R.S. Ross, and Tanya M. Brown. 2023. “Acute Toxicity of 6PPD-Quinone to Early Life Stage Juvenile Chinook (Oncorhynchus tshawytscha) and Coho (Oncorhynchus kisutch) Salmon.” Environmental Toxicology and Chemistry 42 (4): 815–22. https://doi.org/10.1002/etc.5568.Di et al. 2022[BLEFEP7S] Di, Shanshan, Zhenzhen Liu, Huiyu Zhao, Ying Li, Peipei Qi, Zhiwei Wang, Hao Xu, Yuanxiang Jin, and Xinquan Wang. 2022. “Chiral Perspective Evaluations: Enantioselective Hydrolysis of 6PPD and 6PPD-Quinone in Water and Enantioselective Toxicity to Gobiocypris Rarus and Oncorhynchus Mykiss.” Environment International 166 (August):107374. https://doi.org/10.1016/j.envint.2022.107374.). To date, no known adverse outcome pathway can explain the difference in sensitivities among species; however, hypothesized mechanisms of action are discussed in Section 2.2.1.1.2.

Toxicological responses to 6PPD-q vary among species and within species. 6PPD-q appears to exhibit age-dependent toxicity in coho salmon, with Lo et al. (Lo et al. 2023[LA4CEWYX] Lo, Bonnie P., Vicki L. Marlatt, Xiangjun Liao, Sofya Reger, Carys Gallilee, Andrew R.S. Ross, and Tanya M. Brown. 2023. “Acute Toxicity of 6PPD-Quinone to Early Life Stage Juvenile Chinook (Oncorhynchus tshawytscha) and Coho (Oncorhynchus kisutch) Salmon.” Environmental Toxicology and Chemistry 42 (4): 815–22. https://doi.org/10.1002/etc.5568.) reporting a 24-hour LC_{50} of 0.041 µg/L in newly feeding (approximately 3 weeks post-swim up) fish, Greer et al. (Greer et al. 2023[P6RF5UFR] Greer, Justin B., Ellie M. Dalsky, Rachael F. Lane, and John D. Hansen. 2023. “Establishing an In Vitro Model to Assess the Toxicity of 6PPD-Quinone and Other Tire Wear Transformation Products.” Environmental Science & Technology Letters, May. https://doi.org/10.1021/acs.estlett.3c00196.) reporting a 12-hour LC_{50} of 0.080 µg/L in fish with a mean age of 189 days, and Z. Tian et al. (Tian et al. 2022[BICQHLBC] Tian, Zhenyu, Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C. Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej. 2022. “6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard.” Environmental Science & Technology Letters, January, acs.estlett.1c00910. https://doi.org/10.1021/acs.estlett.1c00910.) reporting a 24-hour LC_{50} of 0.095 µg/L in fish greater than 1 year old. Greer et al. (Greer et al. 2023[PSLHUQ22] Greer, Justin B., Ellie M. Dalsky, Rachael F. Lane, and John D. Hansen. 2023. “Tire-Derived Transformation Product 6PPD-Quinone Induces Mortality and Transcriptionally Disrupts Vascular Permeability Pathways in Developing Coho Salmon.” Environmental Science & Technology, July. https://doi.org/10.1021/acs.est.3c01040.) exposed unhatched coho embryos (starting at the stage when their eyes became apparent) to a 24-hour pulse of 6PPD-q (0.10, 0.90, or 7.22 µg/L) twice weekly, which simulated intermittent rain events under laboratory conditions. Exposures occurred until most of the embryos had hatched during the final (fourth) exposure pulse. No significant embryo mortality occurred in the 0.10 µg/L treatment, even though this exposure is about the same as the 24-hour LC_{50} for juveniles. Significant mortality occurred in the 7.22 µg/L treatment by the second exposure pulse with only 21% of embryos surviving to hatching and egg yolk absorption. These data suggest that the chorion, a protective membrane enveloping embryos, potentially mitigates uptake of some waterborne toxicants like 6PPD-q to the embryo (see Table 2-2).

Sensitivity to 6PPD-q does not seem to be correlated with genetic relationships. Although effect concentrations of 6PPD-q have been reported for several salmon species, none are as sensitive as the coho. Figure 2-2 shows several LC_{50} values for species that have been tested in laboratory studies and highlights that toxicity to 6PPD-q does not follow a phylogenetic relationship among fish. Additional data regarding the toxicity of 6PPD-q for other species is described in Tables 2-1 and Table 2-2.

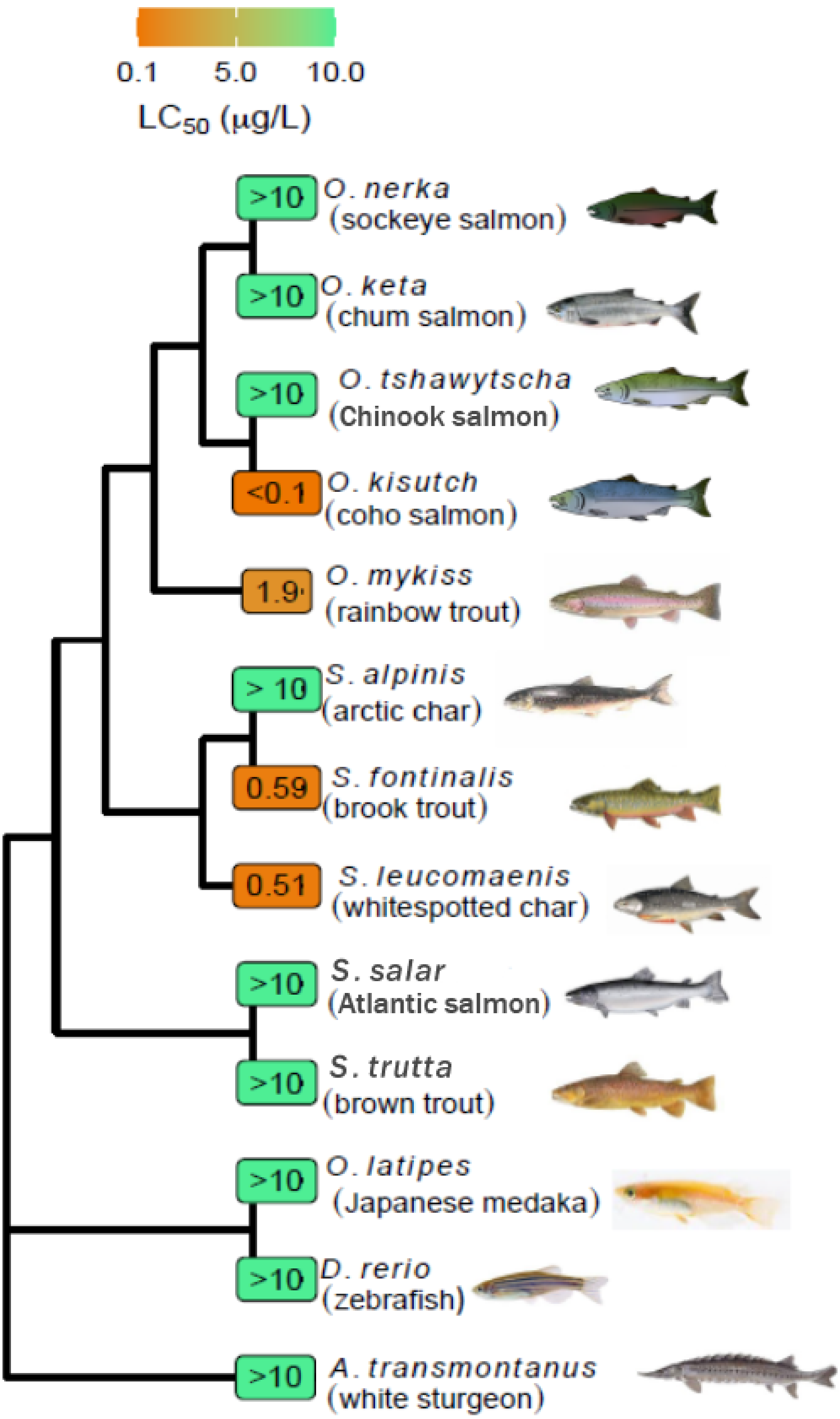


Figure 2-2. Toxicity of 6PPD-q does not follow a phylogenetic relationship. The diagram shows the phylogeny of fish that have been tested for acute toxicity to 6PPD-q as of mid-2023. For each fish, the associated LC_{50} in µg/L (based on an individual study) is represented by the color-gradient scale and numeric value. Genus abbreviations: *A.* (*Acipenser*), *D.* (*Danio*), *O.* (*Oncorhynchus*), *S.* (*Salmo* or *Salvelinus*). Several species are not included in the figure because the results were released late in the production of this document. Pink salmon

(*O. gorbuscha*) have an LC_{50} greater than 10 (Foldvik et al. 2024[NFMULGUG] Foldvik, Anders, Fedor Kryuchkov, Eva Ulvan, Roar Sandodden, and Elii Kvingedal. 2024. "Acute Toxicity Testing of Pink Salmon (Oncorhynchus gorbuscha) with the Tire Rubber–Derived Chemical 6PPD-Quinone." Environmental Toxicology and Chemistry. https://doi.org/https://doi.org/10.1002/etc.5875.). Lake trout (*Salvelinus namaycush*), 24-hour LC_{50} is 0.51 µg/L (Roberts et al. 2024[FMG8VP7Y] Roberts, Catherine, Junyi Lin, Evan Kohlman, Niteesh Jain, Mawuli Amekor, Alper James Alcaraz, Natacha Hogan, Markus Hecker, and Markus Brinkmann. 2024. "Acute and Sub-Chronic Toxicity of 6PPD-Quinone to Early-Life Stage Lake Trout (Salvelinus namaycush)." bioRxiv. https://doi.org/10.1101/2024.03.26.586843.). These results were publicly released prior to peer review. The analysis of the LC_{50} of coastal cutthroat trout (*Oncorhynchus clarkii clarkii*) has not been released (Shankar et al. 2024[FBNQNIWI] Shankar, Prarthana, Ellie M. Dalsky, Joanne E Salzer, Justin B Greer, Rachael F. Lane, William N Batts, Jacob Gregg, Gael Kurath, Paul K Hershberger, and John D Hansen. 2024. "Evaluation of Lethal and Sublethal Effects of 6PPD-Q on Coastal Cutthroat Trout (Oncorhynchus Clarkii Clarkii)." Csv,xml. U.S. Geological Survey. https://doi.org/10.5066/P16SMKIJ.). The highest-known levels 6PPD-q in surface water, 2.85 µg/L, were measured by Johannessen, Helm, et al. (Johannessen et al. 2022[E9K7U5U3] Johannessen, Cassandra, Paul Helm, Brent Lashuk, Viviane Yargeau, and Chris D. Metcalfe. 2022. "The Tire Wear Compounds 6PPD-Quinone and 1,3-Diphenylguanidine in an Urban Watershed." Archives of Environmental Contamination and Toxicology 82 (2): 171–79. https://doi.org/10.1007/s00244-021-00878-4.) in the Don River in Toronto, Canada.

Source: Justin Greer (reproduced with permission of the U.S. Geological Survey).

2.2.1.1.1 Sublethal or Chronic Toxicity in Salmonids

Greer et al. (Greer et al. 2023[PSLHUQ22] Greer, Justin B., Ellie M. Dalsky, Rachael F. Lane, and John D. Hansen. 2023. "Tire-Derived Transformation Product 6PPD-Quinone Induces Mortality and Transcriptionally Disrupts Vascular Permeability Pathways in Developing Coho Salmon." Environmental Science & Technology, July. https://doi.org/10.1021/acs.est.3c01040.) identified sublethal impacts to coho embryos and alevin (hatchlings) but at doses equal to or higher than the LC_{50} of later life stages. See the description of the study in Section 2.2.1.1. In a preprint publication (not yet peer-reviewed), Roberts et al. (Roberts et al. 2024[FMG8VP7Y] Roberts, Catherine, Junyi Lin, Evan Kohlman, Niteesh Jain, Mawuli Amekor, Alper James Alcaraz, Natacha Hogan, Markus Hecker, and Markus Brinkmann. 2024. "Acute and Sub-Chronic Toxicity of 6PPD-Quinone to Early-Life Stage Lake Trout (Salvelinus namaycush)." bioRxiv. https://doi.org/10.1101/2024.03.26.586843.) observed developmental abnormalities, including pooling blood, yolk sac edema, and spinal curvature, in chronic toxicity experiments on lake trout (*Salvelinus namaycush*) alevin at environmentally relevant concentrations. These abnormalities became evident after 72 hours and continued to manifest until day 28 of exposure; exposure lasted for 45 days. Philibert et al. (Philibert et al. 2024[2M74ZR52] Philibert, Danielle, Ryan S. Stanton, Christine Tang, Naomi L. Stock, Tillmann Benfey, Michael Pirrung, and Benjamin de Jourdan. 2024. "The Lethal and Sublethal Impacts of Two Tire Rubber–Derived Chemicals on Brook Trout (Salvelinus fontinalis) Fry and Fingerlings." Chemosphere, May. https://doi.org/10.1016/j.chemosphere.2024.142319.) demonstrated that blood chemistry parameters and gill morphology were altered in brook trout fingerlings that survived a 24-hour exposure to 0.5 µg/L 6PPD-q. Further research is needed to characterize how long these alterations persist and how they might impact long-term fitness.

2.2.1.1.2 Unknown 6PPD-q Mechanism of Action in Fish

The specific mechanism, or mechanisms, that underlie the acute mortality associated with 6PPD-q are not fully understood. While observable effects may provide some insight into potential mechanisms of toxicity, tracing them back to a discrete molecular initiating event remains a work in progress.

The Toxicological Mechanism of 6PPD-q Remains Unknown

- Behavioral symptoms of URMS were categorized into six successive stages:

1. Asymptomatic with discrete surfacing events (less than 0.25 seconds)
2. Short episodes of surfacing (0.25–2 seconds)
3. Sustained episodes of surface swimming
4. Spiraling and loss of equilibrium
5. Loss of buoyancy

6. Moribund and unresponsive to touch

- Physiological and transcriptional profiling have implicated dysfunction of the vasculature, including the blood-brain barrier.
- Studies have implicated mitochondrial uncoupling and biotransformation in the toxicity of 6PPD-q.

Prior to the discovery of 6PPD-q, URMS was investigated in laboratory studies by exposing coho salmon to urban runoff. Chow et al. (Chow et al. 2019[7RMZ3UNQ] Chow, Michelle I., Jessica I. Lundin, Chelsea J. Mitchell, Jay W. Davis, Graham Young, Nathaniel L. Scholz, and Jenifer K. McIntyre. 2019. "An Urban Stormwater Runoff Mortality Syndrome in Juvenile Coho Salmon." Aquatic Toxicology 214 (September):105231. https://doi.org/10.1016/j.aquatox.2019.105231.) found that the symptomology of URMS in juvenile coho salmon was consistent even within and between storm runoff events. Because of this, the authors were able to divide the behavioral characteristics of URMS into six stages. In Stage 1, fish were generally asymptomatic but had discrete surfacing events shorter than 0.25 seconds. These events included swimming within 1 cm of the exposure tank's surface. Stage 2 was characterized by short surface-swimming episodes between 0.25 and 2 seconds. In Stage 3, fish exhibited sustained (more than 2 seconds) surface swimming, which included both linear and circular swimming paths. By Stage 4, fish appeared to lose equilibrium and exhibited swimming patterns characterized by side swimming and spiraling. In Stage 5, fish lost their buoyancy and settled at the bottom of the exposure tank. Finally, fish in Stage 6 were considered moribund and exhibited changes in ventilation rate, gaping, spasms, and no response to touch.

Greater than 96% of fish were in Stage 6 of URMS within 7 hours of exposure to runoff. Chow et al. (Chow et al. 2019[7RMZ3UNQ] Chow, Michelle I., Jessica I. Lundin, Chelsea J. Mitchell, Jay W. Davis, Graham Young, Nathaniel L. Scholz, and Jenifer K. McIntyre. 2019. "An Urban Stormwater Runoff Mortality Syndrome in Juvenile Coho Salmon." Aquatic Toxicology 214 (September):105231. https://doi.org/10.1016/j.aquatox.2019.105231.) additionally showed that symptomatic coho salmon were moribund and did not recover if transferred to a clean (runoff-free) exposure medium.

Studies evaluating the blood chemistry of runoff-exposed coho salmon noted decreased blood ion content and increased blood glucose, lactate, and hematocrit, along with progressively increased blood acidosis (McIntyre et al. 2018[G7QW7PSD] McIntyre, Jenifer, Jessica Lundin, James Cameron, Michelle Chow, Jay Davis, John Incardona, and Nathaniel Scholz. 2018. "Interspecies Variation in the Susceptibility of Adult Pacific Salmon to Toxic Urban Stormwater Runoff." Environmental Pollution 238:196–203. https://doi.org/https://doi.org/10.1016/j.envpol.2018.03.012.Chow et al. 2019[7RMZ3UNQ] Chow, Michelle I., Jessica I. Lundin, Chelsea J. Mitchell, Jay W. Davis, Graham Young, Nathaniel L. Scholz, and Jenifer K. McIntyre. 2019. "An Urban Stormwater Runoff Mortality Syndrome in Juvenile Coho Salmon." Aquatic Toxicology 214 (September):105231. https://doi.org/10.1016/j.aquatox.2019.105231.). These physiological changes, which were indicative of hypoxia and acute stress, were consistent with the behaviors observed in URMS. A subsequent study showed that these changes in blood chemistry may have been attributable to the loss of blood plasma due to vascular dysfunction. Blair et al. (Blair, Barlow, and McIntyre 2021[B647MUXL] Blair, Stephanie I., Clyde H. Barlow, and Jenifer K. McIntyre. 2021. "Acute Cerebrovascular Effects in Juvenile Coho Salmon Exposed to Roadway Runoff." Canadian Journal of Fisheries and Aquatic Sciences, February. https://doi.org/10.1139/cjfas-2020-0240.) used dye tracing to demonstrate that plasma accumulated in the brain and olfactory rosettes of coho salmon following runoff exposure. Additionally, when a high concentration of dye was used, blood plasma visibly leaked through the gills of exposed fish. The authors suggested that disruption of blood vasculature, particularly the blood–brain barrier and possibly the blood vessels of the gills, underlies the physiological and behavioral effects of URMS.

By the time the report by Blair et al. (Blair, Barlow, and McIntyre 2021[B647MUXL] Blair, Stephanie I., Clyde H. Barlow, and Jenifer K. McIntyre. 2021. "Acute Cerebrovascular Effects in Juvenile Coho Salmon Exposed to Roadway Runoff." Canadian Journal of Fisheries and Aquatic Sciences, February. https://doi.org/10.1139/cjfas-2020-0240.) was published, 6PPD-q was discovered as the causal agent of URMS and could be studied more directly. To characterize the molecular effects of 6PPD-q exposure, Greer et al. (Greer et al. 2023[PSLHUQ22] Greer, Justin B., Ellie M. Dalsky, Rachael F. Lane, and John D. Hansen. 2023. "Tire-Derived Transformation Product 6PPD-Quinone Induces Mortality and Transcriptionally Disrupts Vascular Permeability Pathways in Developing Coho Salmon." Environmental Science & Technology, July. https://doi.org/10.1021/acs.est.3c01040.) profiled gene expression changes in coho salmon hatchlings exposed to a chemical standard of 6PPD-q. Using whole-transcriptome ribonucleic acid (RNA) sequencing, the authors observed dose-dependent effects on the expression of genes that regulate endothelial permeability and cell–cell contacts. They also noted that some of the behavioral and physiological characteristics of URMS parallel a disease state known in humans as capillary leak syndrome, a condition in which blood plasma diffuses into surrounding tissue and can cause swelling around the brain. This further implicated blood vasculature, including the blood–brain barrier, as a target tissue of 6PPD-q toxicity.

It is still unclear why some species are susceptible to 6PPD-q while others are tolerant. Current evidence suggests that the ability to biotransform 6PPD-q into less-toxic metabolites may play a role.

Mahoney et al. (Mahoney et al. 2022[V5HSELRG] Mahoney, Hannah, Francisco C. da Silva Junior, Catherine Roberts, Matthew Schultz, Xiaowen Ji, Alper James Alcaraz, David Montgomery, et al. 2022. “Exposure to the Tire Rubber-Derived Contaminant 6PPD-Quinone Causes Mitochondrial Dysfunction In Vitro.” Environmental Science & Technology Letters 9 (9): 765–71. https://doi.org/10.1021/acs.estlett.2c00431.) reported that rainbow trout liver cells were not sensitive to 6PPD-q, although cell viability was decreased and oxygen consumption rate was increased by a proposed uncoupling of the mitochondrial electron transport chain in gill cells. Monohydroxy metabolites of 6PPD-q were detected in the liver but not gill tissues, suggesting that the chemical was more effectively metabolized in the liver (Mahoney et al. 2022[V5HSELRG] Mahoney, Hannah, Francisco C. da Silva Junior, Catherine Roberts, Matthew Schultz, Xiaowen Ji, Alper James Alcaraz, David Montgomery, et al. 2022. “Exposure to the Tire Rubber-Derived Contaminant 6PPD-Quinone Causes Mitochondrial Dysfunction In Vitro.” Environmental Science & Technology Letters 9 (9): 765–71. https://doi.org/10.1021/acs.estlett.2c00431.). In another recent study, biliary O-glucuronide metabolites of 6PPD-q were found to be present at higher levels in tolerant species than in sensitive species, such as coho salmon. The authors suggest that species-specific differences in expression of biotransformation enzymes may be a key factor in the variable toxicity of 6PPD-q (Montgomery et al. 2023[X3FANIWH] Montgomery, David, Xiaowen Ji, Jenna Cantin, Danielle Philibert, Garrett Foster, Summer Selinger, Niteesh Jain, et al. 2023. “Not Yet Peer Reviewed: Toxicokinetic Characterization of the Inter-Species Differences in 6PPD-Quinone Toxicity Across Seven Fish Species: Metabolite Identification and Semi-Quantification.” bioRxiv. https://doi.org/10.1101/2023.08.18.553920.). In a study of zebrafish embryos exposed to 6PPD-q, Grasse et al. (zotpress items=”{4911552:WJHX578U}” style=”chicago-author-date”) used mass spectrometry (MS) to semi-quantify transformation products based on measured peak area. Within 96 hours of exposure, more than 95% of 6PPD-q was biotransformed with “6PPD-q + O + glucuronide” accounting for more than 80% of the total peak area. These results suggested that zebrafish embryos can tolerate 6PPD-q exposure by rapidly detoxifying it through metabolism. In a separate study (preprint, not yet peer-reviewed), Nair et al. (Nair et al. 2023[9V5ES4MI] Nair, Pranav, Jianxian Sun, Linna Xie, Lisa Kennedy, Derek Kozakiewicz, Sonya Kleywegt, Chunyan Hao, et al. 2023. “In Process: Synthesis and Toxicity Evaluation of Tire Rubber–Derived Quinones.” Preprint. Chemistry. https://doi.org/10.26434/chemrxiv-2023-pmxvc.) exposed juvenile rainbow trout to 6PPD and seven different PPD-quinones (including 6PPD-q) for 96 hours and subsequently analyzed whole-body homogenates for nontargeted identification of metabolites. The LC_{50} for 6PPD-q was 0.64 micrograms per liter (µg/L); however, no toxicity occurred for any of the other PPD-quinones up to 50 µg/L. Tissue concentrations of 6PPD-q were an order of magnitude higher than the six other PPD-quinones. Fish that survived 6PPD-q exposure also exhibited lower concentrations of 6PPD-q, again suggesting that survival may depend on an organism’s ability to biotransform PPD-quinones to less-toxic hydroxy-metabolites. It is not fully understood why 6PPD-q was uniquely toxic among the tested PPD-quinones. Nair et al. (Nair et al. 2023[9V5ES4MI] Nair, Pranav, Jianxian Sun, Linna Xie, Lisa Kennedy, Derek Kozakiewicz, Sonya Kleywegt, Chunyan Hao, et al. 2023. “In Process: Synthesis and Toxicity Evaluation of Tire Rubber–Derived Quinones.” Preprint. Chemistry. https://doi.org/10.26434/chemrxiv-2023-pmxvc.) reported that two hydroxylated 6PPD-q isomers were detected in fish exposed to 6PPD-q. One isomer exhibited hydroxylation on the alkyl side chain, and one exhibited it on the aromatic ring. In contrast, the other six less-toxic PPD-quinones only appeared to undergo aromatic ring hydroxylation. It is unknown whether this alkyl side chain isomer may elicit toxicity through interaction with an unknown protein target (Nair et al. 2023[9V5ES4MI] Nair, Pranav, Jianxian Sun, Linna Xie, Lisa Kennedy, Derek Kozakiewicz, Sonya Kleywegt, Chunyan Hao, et al. 2023. “In Process: Synthesis and Toxicity Evaluation of Tire Rubber–Derived Quinones.” Preprint. Chemistry. https://doi.org/10.26434/chemrxiv-2023-pmxvc.).

Some data indicate potential enantioselective toxicity of 6PPD-q. In a study by Di et al. (Di et al. 2022[BLEFEP7S] Di, Shanshan, Zhenzhen Liu, Huiyu Zhao, Ying Li, Peipei Qi, Zhiwei Wang, Hao Xu, Yuanxiang Jin, and Xinquan Wang. 2022. “Chiral Perspective Evaluations: Enantioselective Hydrolysis of 6PPD and 6PPD-Quinone in Water and Enantioselective Toxicity to Gobiocypris Rarus and Oncorhynchus Mykiss.” Environment International 166 (August):107374. https://doi.org/10.1016/j.envint.2022.107374.), rainbow trout and the rare minnow (*G. rarus*) were exposed to *R*-enantiomer, *S*-enantiomer, or a racemate of both 6PPD and 6PPD-q (Figure 2-3) for 96 hours. In *G. rarus*, LC_{50} values were identical for both *R*-6PPD and *S*-6PPD (201 µg/L), while the 6PPD racemate was slightly lower (162 µg/L). No mortality occurred up to 500 µg/L *R*-6PPD-q, *S*-6PPD-q, or 6PPD-q racemate. In contrast, rainbow trout were not sensitive to 6PPD, and no mortality occurred at concentrations up to 400 µg/L. Rainbow trout responded differently to *R*-6PPD-q, *S*-6PPD-q, or 6PPD-q racemate, with LC_{50} values of 4.31, 1.66, and 2.26 µg/L, respectively. As rainbow trout are known to be sensitive to 6PPD-q, it is feasible, as the authors propose, that 6PPD-q enantiomers may bind a presently unknown molecular target with varying affinity.

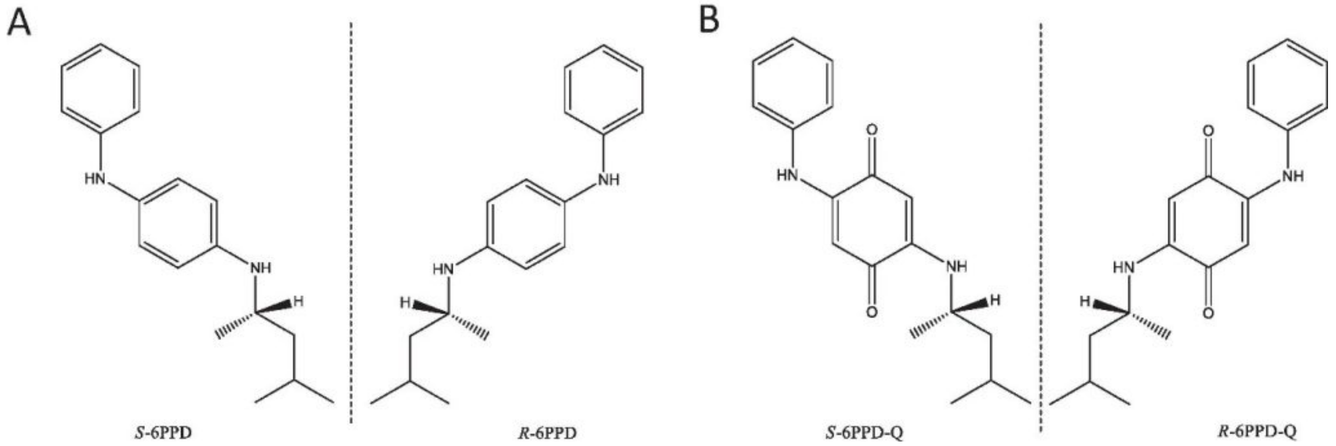


Figure 2-3. Molecular structures of (A) 6PPD and (B) 6PPD-q enantiomers.

Source: Reproduced from Di et al. (Di et al. 2022[BLEFEP7S] Di, Shanshan, Zhenzhen Liu, Huiyu Zhao, Ying Li, Peipei Qi, Zhiwei Wang, Hao Xu, Yuanxiang Jin, and Xinquan Wang. 2022. "Chiral Perspective Evaluations: Enantioselective Hydrolysis of 6PPD and 6PPD-Quinone in Water and Enantioselective Toxicity to Gobiocypris Rarus and Oncorhynchus Mykiss." Environment International 166 (August):107374. https://doi.org/10.1016/j.envint.2022.107374.) under the Creative Commons Public License (https://creativecommons.org/licenses/by-nc-nd/4.0/).

2.2.1.2 6PPD-q Toxicity in Aquatic and Benthic Invertebrates

Acute toxicity tests using invertebrate species thus far have shown that, among the species tested, aquatic and benthic invertebrates are not acutely sensitive to 6PPD-q. No significant mortality was observed in the following freshwater species: amphipods (*Hyalella azteca*), water flea (*Daphnia magna*), rotifer (*Brachionus calyciflorus*), file ramshorn snail (*Planorbella pilsbryi*), washboard mussel (*Megalonaias nervosa*), or mayfly (*Hexagenia* spp.) (see Table 2-1) (Klauschies and Isanta-Navarro 2022[B9C96GRR] Klauschies, Toni, and Jana Isanta-Navarro. 2022. "The Joint Effects of Salt and 6PPD Contamination on a Freshwater Herbivore." Science of the Total Environment 829:154675. https://doi.org/10.1016/j.scitotenv.2022.154675.Hiki et al. 2021[WZF69GXC] Hiki, Kyoshiro, Kenta Asahina, Kota Kato, Takahiro Yamagishi, Ryo Omagari, Yuichi Iwasaki, Haruna Watanabe, and Hiroshi Yamamoto. 2021. "Acute Toxicity of a Tire Rubber–Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species." Environmental Science & Technology Letters 8 (9): 779–84. https://doi.org/10.1021/acs.estlett.1c00453.Prosser, Salole, and Hang 2023[X2FC6LV6] Prosser, R. S., J. Salole, and S. Hang. 2023. "Toxicity of 6PPD-Quinone to Four Freshwater Invertebrate Species." Environmental Pollution, September, 122512. https://doi.org/10.1016/j.envpol.2023.122512.). Klauschies and Isanta-Navarro (Klauschies and Isanta-Navarro 2022[B9C96GRR] Klauschies, Toni, and Jana Isanta-Navarro. 2022. "The Joint Effects of Salt and 6PPD Contamination on a Freshwater Herbivore." Science of the Total Environment 829:154675. https://doi.org/10.1016/j.scitotenv.2022.154675.) also reported no mortality in *B. calyciflorus* after 12 days of exposure to 6PPD-q. Sublethal endpoints such as fecundity and oxidative stress were also not affected in *B. calyciflorus* at concentrations up to 1,000 µg/L 6PPD-q. Additionally, the only two studies currently available that assessed acute toxicity of 6PPD-q to marine invertebrates also found no significant mortality in the amphipod *Parhyale hawaiensis* and the rotifer *Brachionus koreanus*, although 6PPD-q was found to be mutagenic to *P. hawaiensis* (Maji et al. 2023[D8QNSW4K] Maji, Usha Jyoti, Kyuhyeong Kim, In-Cheol Yeo, Kyu-Young Shim, and Chang-Bum Jeong. 2023. "Toxicological Effects of Tire Rubber–Derived 6PPD-Quinone, a Species-Specific Toxicant, and Dithiobisbenzanilide (DTBBA) in the Marine Rotifer Brachionus koreanus." Marine Pollution Bulletin 192 (July):115002. https://doi.org/10.1016/j.marpolbul.2023.115002.Botelho et al. 2023[WZC7F928] Botelho, Marina Tenório, Gabriely Groto Militão, Markus Brinkmann, and Gisela de Aragão Umbuzeiro. 2023. "Toxicity and Mutagenicity Studies of 6PPD-Quinone in a Marine Invertebrate Species and Bacteria." Environmental and Molecular Mutagenesis 64 (6): 335–41. https://doi.org/10.1002/em.22560.) . Therefore, it appears that aquatic and benthic invertebrates are not acutely sensitive to 6PPD-q, while sublethal and chronic effects represent a data gap.

2.2.1.3 6PPD-q Toxicity in Algae and Aquatic Plants

To date, one study has specifically evaluated the toxicity to 6PPD-q in algae (Wu et al. 2023[PYQQU7AG] Wu, Jiabin, Guodong Cao, Feng Zhang, and Zongwei Cai. 2023. "A New Toxicity Mechanism of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine Quinone: Formation of DNA Adducts in Mammalian Cells and Aqueous Organisms." Science of the Total Environment 866:161373. https://doi.org/10.1016/j.scitotenv.2022.161373.). Cultures of the single-celled green alga *Chlamydomonas reinhardtii* were exposed to 6PPD-q for 72 hours at concentrations of 250 and 1,000 µg/L, and cell viability was evaluated by calculating absorbance ratios between exposed and unexposed groups. The study observed a significant treatment effect with an increase in algal cell death between the exposed and unexposed groups, but there was no major difference in viability between the 250 and 1,000 µg/L treatments (Wu et al. 2023[PYQQU7AG] Wu, Jiabin, Guodong Cao, Feng Zhang, and Zongwei Cai. 2023. "A New Toxicity Mechanism of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine Quinone: Formation of DNA Adducts in Mammalian Cells and Aqueous Organisms." Science of the Total Environment 866:161373. https://doi.org/10.1016/j.scitotenv.2022.161373.). Although the exposure concentrations exceeded environmental relevance, the study provided evidence of a possible genotoxicity mechanism (Wu et al. 2023[PYQQU7AG] Wu, Jiabin, Guodong Cao, Feng Zhang, and Zongwei Cai. 2023. "A New Toxicity Mechanism of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine Quinone: Formation of DNA Adducts in Mammalian Cells and Aqueous Organisms." Science of the Total Environment 866:161373. https://doi.org/10.1016/j.scitotenv.2022.161373.).

2.2.1.4 6PPD-q Toxicity in Mammals

Some data are available that may be used to evaluate the sublethal effects of 6PPD-q on mammalian wildlife (Table 2-3). One study found that oral exposure of laboratory mice to 10 and 100 milligrams per kilograms (mg/kg) 6PPD-q in corn oil for 6 weeks resulted in fatty liver syndrome, an outcome that was shared with the parent compound 6PPD; however, the authors noted that these relatively high concentrations were selected for hazard assessment and were not intended to represent environmentally relevant exposure concentrations (Fang et al. 2023[B66X64SI] Fang, Liya, Chanlin Fang, Shanshan Di, Yundong Yu, Caihong Wang, Xinquan Wang, and Yuanxiang Jin. 2023. "Oral Exposure to Tire Rubber–Derived Contaminant 6PPD and 6PPD-Quinone Induce Hepatotoxicity in Mice." Science of the Total Environment 869 (April):161836. https://doi.org/10.1016/j.scitotenv.2023.161836.). The authors determined that 6PPD tended to affect gene expression related to fatty acid metabolism; in comparison, 6PPD-q affected inflammatory pathways. Mice were not monitored for apical outcomes. Although steatosis is an adverse outcome and indicator of liver damage in human health evaluations, no studies in wild mammals are available that would define steatosis as an adverse apical outcome in nonhuman organisms. Another study (He, Gu, and Wang 2023[6MPWVZGE] He, Wenmiao, Aihua Gu, and Dayong Wang. 2023. "Four-Week Repeated Exposure to Tire-Derived 6-PPD Quinone Causes Multiple Organ Injury in Male BALB/c Mice." Science of the Total Environment 894 (October):164842. https://doi.org/10.1016/j.scitotenv.2023.164842.) evaluated toxicity to multiple organs in rodents and found that 28 days of 6PPD-q injection (intraperitoneal) exposure damaged the liver and other organs. Concentrations in the livers in this study were approximately 20 nanograms per gram (ng/g), which was similar to what was found in their oral exposure study. Additionally, H. N. Zhao, Thomas, et al. (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. "Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways." Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.) found that oral gavage exposure to 4 mg/kg 6PPD-q in pregnant mice resulted in chemical transfer to pups, resulting in concentrations in livers (mean 200 ng/g) that were greater than in the studies cited above. Although the route of exposure is not environmentally relevant, these results may be of use for ecological risk assessment based on tissue residue values if an apical outcome was associated with organ damage as shown in the study.

2.2.1.5 6PPD-q Toxicity in Soil Invertebrates

A limited number of studies examine the effects of 6PPD-q on terrestrial invertebrates and can be directly used for ecological risk assessments (see Table 2-2). The most relevant study was conducted in springtails (*Folsomia candida*), a commonly tested soil-dwelling organism with a global distribution (Xu et al. 2023[WDVQCW7M] Xu, Qiao, Wei Wu, Zufei Xiao, Xin Sun, Jun Ma, Jing Ding, Zhe Zhu, and Gang Li. 2023. "Responses of Soil and Collembolan (Folsomia candida) Gut Microbiomes to 6PPD-Q Pollution." Science of the Total Environment 900 (November):165810. https://doi.org/10.1016/j.scitotenv.2023.165810.). The authors estimated a nominal 28-day LC_{50} of 16.31 micrograms of 6PPD per kilogram (µg/kg) of soil for adult springtails. Reproduction was not significantly affected by 6PPD-q exposure at nominal soil concentrations up to 5,000 µg/kg. Notably, genomic analysis showed a difference in effect on microbes from soil compared to those from the guts of springtails.

Exposure to 5,000 µg/kg was associated with an increase in nitrogen cycling genes in soil microbes and a decrease in springtail gut microbes. Changes to microbial community structure and function in response to 6PPD-q exposure may be an important endpoint to examine with respect to the provisioning of terrestrial ecosystem services.

Further work with invertebrate taxa has been conducted in *C. elegans* and may provide information about effects in soil invertebrates (Hua et al. 2023[RJ86H9T3] Hua, Xin, Xiao Feng, Geyu Liang, Jie Chao, and Dayong Wang. 2023. "Long-Term Exposure to 6-PPD Quinone Reduces Reproductive Capacity by Enhancing Germline Apoptosis Associated with Activation of Both DNA Damage and Cell Corpse Engulfment in Caenorhabditis elegans." Journal of Hazardous Materials 454 (July):131495. https://doi.org/10.1016/j.jhazmat.2023.131495.Wang, Hua, and Wang 2023[PMPW53J5] Wang, Yuxing, Xin Hua, and Dayong Wang. 2023. "Exposure to 6-PPD Quinone Enhances Lipid Accumulation through Activating Metabolic Sensors of SBP-1 and MDT-15 in Caenorhabditis elegans." Environmental Pollution 333 (September):121937. https://doi.org/10.1016/j.envpol.2023.121937.Hua et al. 2023[LJTX7EWE] Hua, Xin, Xiao Feng, Geyu Liang, Jie Chao, and Dayong Wang. 2023. "Exposure to 6-PPD Quinone at Environmentally Relevant Concentrations Causes Abnormal Locomotion Behaviors and Neurodegeneration in Caenorhabditis elegans." Environmental Science & Technology, March. https://doi.org/10.1021/acs.est.2c08644.) (see Table 2-2). Because this work involved aqueous exposures (0.1, 1, and 10 µg/L 6PPD-q), extrapolation to exposure concentrations in the terrestrial environment is uncertain. Nevertheless, it is worth summarizing effects because *C. elegans* is a soil-dwelling organism. Hua et al. (Hua et al. 2023[RJ86H9T3] Hua, Xin, Xiao Feng, Geyu Liang, Jie Chao, and Dayong Wang. 2023. "Long-Term Exposure to 6-PPD Quinone Reduces Reproductive Capacity by Enhancing Germline Apoptosis Associated with Activation of Both DNA Damage and Cell Corpse Engulfment in Caenorhabditis elegans." Journal of Hazardous Materials 454 (July):131495. https://doi.org/10.1016/j.jhazmat.2023.131495.) found that reproductive capacity declined with increasing aqueous 6PPD-q concentration, potentially as related to gonadal development. 6PPD-q exposure at concentrations as low as 1 µg/L reduced locomotion in *C. elegans*. It also led to the development of neurodegeneration, with the former occurring at lower concentrations than the latter (Hua et al. 2023[LJTX7EWE] Hua, Xin, Xiao Feng, Geyu Liang, Jie Chao, and Dayong Wang. 2023. "Exposure to 6-PPD Quinone at Environmentally Relevant Concentrations Causes Abnormal Locomotion Behaviors and Neurodegeneration in Caenorhabditis elegans." Environmental Science & Technology, March. https://doi.org/10.1021/acs.est.2c08644.), indicating a potential for neurobehavioral and thus apical effects in this species. The same exposure conditions also led to an accumulation of lipids in vivo, suggesting that 6PPD-q has the potential to alter lipid metabolism in invertebrates such as *C. elegans* (Zhang et al. 2024[BZQEGEXI] Zhang, Jing, Guodong Cao, Wei Wang, Han Qiao, Yi Chen, Xiaoxiao Wang, Fuyue Wang, Wenlan Liu, and Zongwei Cai. 2024. "Stable Isotope-Assisted Mass Spectrometry Reveals in Vivo Distribution, Metabolism, and Excretion of Tire Rubber-Derived 6PPD-Quinone in Mice." Science of the Total Environment 912 (February):169291. https://doi.org/10.1016/j.scitotenv.2023.169291.).

2.2.1.6 6PPD-q Toxicity in Terrestrial Plants

Although it has been shown that 6PPD-q can be taken up in plant tissues (Castan et al. 2023[3RBDETGD] Castan, Stephanie, Anya Sherman, Ruoting Peng, Michael T. Zumstein, Wolfgang Wanek, Thorsten Hüffer, and Thilo Hofmann. 2023. "Uptake, Metabolism, and Accumulation of Tire Wear Particle–Derived Compounds in Lettuce." Environmental Science & Technology 57 (1): 168–78. https://doi.org/10.1021/acs.est.2c05660.), no published plant toxicity tests could be found as of the writing of this summary.

2.2.1.7 6PPD-q Toxicity in Terrestrial Microorganisms

There are limited ecologically relevant studies examining the effect of 6PPD-q on terrestrial microorganisms. One study, as described above, assessed the impact of 6PPD-q in soil exposure on microbial diversity and taxonomic abundance, with potential ramifications for nitrogen cycling (Xu et al. 2023[WDVQCW7M] Xu, Qiao, Wei Wu, Zufei Xiao, Xin Sun, Jun Ma, Jing Ding, Zhe Zhu, and Gang Li. 2023. "Responses of Soil and Collembolan (Folsomia candida) Gut Microbiomes to 6PPD-Q Pollution." Science of the Total Environment 900 (November):165810. https://doi.org/10.1016/j.scitotenv.2023.165810.). Although these findings suggest the potential for 6PPD-q to impact ecosystem services through its effects on terrestrial microorganisms, additional research is needed in this area.

2.2.2 Environmental Toxicity of 6PPD

2.2.2.1 6PPD Toxicity in Fishes

Coho salmon (*O. kisutch)* are less sensitive to 6PPD compared to 6PPD-q, with a reported nominal 24-hour LC_{50} of 251 µg/L for 6PPD (Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. “A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon.” Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.) (see Table 2-1). This study notes a lack of confidence in the measured concentrations of 6PPD in water due to its poor solubility, high instability, and formation of transformation products during exposure. As such, only nominal values were used to estimate the LC_{50} value. In another study using the common laboratory test species, zebrafish (*Danio rerio),* the 96-hour LC_{50} for 6PPD was 442.62 µg/L (Varshney et al. 2022[APRMZJBS] Varshney, Shubham, Adnan H. Gora, Prabhugouda Siriyappagouder, Viswanath Kiron, and Pål A. Olsvik. 2022. “Toxicological Effects of 6PPD and 6PPD Quinone in Zebrafish Larvae.” Journal of Hazardous Materials 424 (February):127623. https://doi.org/10.1016/j.jhazmat.2021.127623.). Similarly, this study noted that the LC_{50} values for 6PPD should be used with caution due to the chemical’s low water solubility and stability, high Kow, and formation of transformation products. Another study, conducted under good laboratory practice, reported a 96-hour LC_{50} for 6PPD equal to 28 µg/L (measured) for Japanese medaka (*O. latipes)* (ECHA 2021[Y79Z3ZWV] ECHA. 2021. “Substance Infocard: N-1,3-Dimethylbutyl-N’-Phenyl-p-Phenylenediamine. European Chemicals Agency (ECHA).” April 7, 2021. https://echa.europa.eu/substance-information/-/substanceinfo/100.011.222.). A similar study using Japanese medaka corroborated these results and reported 80% mortality in medaka after a 96-hour exposure to a time-weighted average concentration of 107 µg/L 6PPD (Hiki et al. 2021[WZF69GXC] Hiki, Kyoshiro, Kenta Asahina, Kota Kato, Takahiro Yamagishi, Ryo Omagari, Yuichi Iwasaki, Haruna Watanabe, and Hiroshi Yamamoto. 2021. “Acute Toxicity of a Tire Rubber–Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species.” Environmental Science & Technology Letters 8 (9): 779–84. https://doi.org/10.1021/acs.estlett.1c00453.), indicating that the LC_{50} was lower than 107 µg/L. Two long-term studies tested the toxicity of 6PPD in fathead minnow (*P. promelas*), and the LC_{50} values ranged from 35 µg/L (21-day exposure) to 150 µg/L (28-day exposure) (Prosser et al. 2017[G5HZ4XYX] Prosser, Ryan S., Joanne L. Parrott, Melissa Galicia, Kallie Shires, Cheryl Sullivan, John Toito, Adrienne J. Bartlett, Danielle Milani, Patty L. Gillis, and Vimal K. Balakrishnan. 2017. “Toxicity of Sediment-Associated Substituted Phenylamine Antioxidants on the Early Life Stages of Pimephales promelas and a Characterization of Effects on Freshwater Organisms.” Environmental Toxicology and Chemistry 36 (10): 2730–38. https://doi.org/10.1002/etc.3828.Monsanto Company 1979[QBCWTBKB] Monsanto Company. 1979. “Dynamic Toxicity of Santoflex 13 to Fatheads Minnows (Pimephales promelas). Curated Toxicity Data Were Retrieved from the ECOTOXicology Knowledgebase, U.S. Environmental Protection Agency. Http:/Www.Epa.Gov/Ecotox/ (November 10, 2023).” 21850-A/AB-780121B. St. Louis, Missouri.). 6PPD was not acutely toxic to rainbow trout (*O. mykiss)* exposed to a concentration of 50 µg/L for 96 hours (Nair et al. 2023[9V5ES4MI] Nair, Pranav, Jianxian Sun, Linna Xie, Lisa Kennedy, Derek Kozakiewicz, Sonya Kleywegt, Chunyan Hao, et al. 2023. “In Process: Synthesis and Toxicity Evaluation of Tire Rubber–Derived Quinones.” Preprint. Chemistry. https://doi.org/10.26434/chemrxiv-2023-pmxvc.). Overall, the reported LC_{50} values for 6PPD acute toxicity in fish species are much higher than the maximum measured concentrations of 6PPD in river water (0.00129 µg/L) and road runoff (0.00752 µg/L) (Zhang et al. 2023[JWRBWTKN] Zhang, Hai-Yan, Zheng Huang, Yue-Hong Liu, Li-Xin Hu, Liang-Ying He, You-Sheng Liu, Jian-Liang Zhao, and Guang-Guo Ying. 2023. “Occurrence and Risks of 23 Tire Additives and Their Transformation Products in an Urban Water System.” Environment International 171 (January):107715. https://doi.org/10.1016/j.envint.2022.107715.).

Several studies using zebrafish (*D. rerio*) reported sublethal effects after exposure to 6PPD. For example, endpoints such as development, locomotor behavior, respiration and heart rate, or oxidative damage were affected after exposure to 6PPD at various concentrations tested in the literature (see Table 2-2) (Ji et al. 2022[QJ23CAKR] Ji, Jiawen, Jinze Huang, Niannian Cao, Xianghong Hao, Yanhua Wu, Yongqiang Ma, Dong An, Sen Pang, and Xuefeng Li. 2022. “Multiview Behavior and Neurotransmitter Analysis of Zebrafish Dyskinesia Induced by 6PPD and Its Metabolites.” Science of The Total Environment 838:156013. https://doi.org/10.1016/j.scitotenv.2022.156013.Fang et al. 2023[FFFKR3MY] Fang, Chanlin, Liya Fang, Shanshan Di, Yundong Yu, Xinquan Wang, Caihong Wang, and Yuanxiang Jin. 2023. “Characterization of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD)-Induced Cardiotoxicity in Larval Zebrafish (Danio Rerio).” Science of the Total Environment 882 (July):163595. https://doi.org/10.1016/j.scitotenv.2023.163595.Hiki et al. 2021[WZF69GXC] Hiki, Kyoshiro, Kenta Asahina, Kota Kato, Takahiro Yamagishi, Ryo Omagari, Yuichi Iwasaki, Haruna Watanabe, and Hiroshi Yamamoto. 2021. “Acute Toxicity of a Tire Rubber–Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species.” Environmental Science & Technology Letters 8 (9): 779–84. https://doi.org/10.1021/acs.estlett.1c00453.Varshney et al. 2022[APRMZJBS] Varshney, Shubham, Adnan H. Gora, Prabhugouda Siriyappagouder, Viswanath Kiron, and Pål A. Olsvik. 2022. “Toxicological Effects of 6PPD and 6PPD Quinone in Zebrafish Larvae.” Journal of Hazardous Materials 424 (February):127623.

https://doi.org/10.1016/j.jhazmat.2021.127623.Zhang et al. 2023[3FCHDXBN] Zhang, Shu-Yun, Xiufeng Gan, Baoguo Shen, Jian Jiang, Huimin Shen, Yuhang Lei, Qiuju Liang, et al. 2023. “6PPD and Its Metabolite 6PPDQ Induce Different Developmental Toxicities and Phenotypes in Embryonic Zebrafish.” Journal of Hazardous Materials 455 (August):131601. https://doi.org/10.1016/j.jhazmat.2023.131601.).

2.2.2.2 6PPD Toxicity in Aquatic and Benthic Invertebrates

Data are limited on the acute toxicity of 6PPD to aquatic and benthic invertebrates (see Table 2-1). In water flea (*D. magna),* a 48-hour LC_{50} value equal to 230 µg/L was reported from a good laboratory practice study based on measured concentrations (ECHA 2021[Y79Z3ZWV] ECHA. 2021. “Substance Infocard: N-1,3-Dimethylbutyl-N’-Phenyl-p-Phenylenediamine. European Chemicals Agency (ECHA).” April 7, 2021. https://echa.europa.eu/substance-information/-/substanceinfo/100.011.222.). A more recent study observed 100% mortality of *D. magna* after 48-hour exposure to 6PPD at a time-weighted average concentration of 138 µg/L, indicating that the 48-hour LC_{50} is less than 138 µg/L (Hiki et al. 2021[WZF69GXC] Hiki, Kyoshiro, Kenta Asahina, Kota Kato, Takahiro Yamagishi, Ryo Omagari, Yuichi Iwasaki, Haruna Watanabe, and Hiroshi Yamamoto. 2021. “Acute Toxicity of a Tire Rubber–Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species.” Environmental Science & Technology Letters 8 (9): 779–84. https://doi.org/10.1021/acs.estlett.1c00453.). It is unclear why there are inconsistencies between the studies that tested *D. magna*. Physicochemical properties of 6PPD such as low water solubility and stability, high Kow, and formation of transformation products may have resulted in uncertainties regarding the derived LC_{50} values.

In the epibenthic amphipod *H. azteca*, the 96-hour LC_{50} based on measured concentrations was 250 µg/L (Prosser et al. 2017[N22D9LHY] Prosser, R. S., A. J. Bartlett, D. Milani, E. A. M. Holman, H. Ikert, D. Schissler, J. Toito, J. L. Parrott, P. L. Gillis, and V. K. Balakrishnan. 2017. “Variation in the Toxicity of Sediment-Associated Substituted Phenylamine Antioxidants to an Epibenthic (Hyalella azteca) and Endobenthic (Tubifex tubifex) Invertebrate.” Chemosphere 181 (August):250–58. https://doi.org/10.1016/j.chemosphere.2017.04.066.). Chronic toxicity (28-day exposure) tests were also performed as part of this study in both water and sediment, and the 28-day LC_{50} was equal to 13 µg/L for water exposures and 135 µg per gram (µg/g) sediment dry weight for sediment exposures (see Table 2-2). The results from the chronic water and sediment toxicity tests indicated that 6PPD is more bioavailable in water versus sediment, and the authors suggested this may be due to sorption of 6PPD to organic matter in sediment. Additionally, the concentration of 6PPD in sediment and water declined over the study duration, and the authors noted that bioavailability of 6PPD to aquatic and sediment-dwelling organisms in freshwater ecosystems should be specifically investigated due to the chemical’s apparent degradation. Prosser, Bartlett, et al. (Prosser et al. 2017[N22D9LHY] Prosser, R. S., A. J. Bartlett, D. Milani, E. A. M. Holman, H. Ikert, D. Schissler, J. Toito, J. L. Parrott, P. L. Gillis, and V. K. Balakrishnan. 2017. “Variation in the Toxicity of Sediment-Associated Substituted Phenylamine Antioxidants to an Epibenthic (Hyalella azteca) and Endobenthic (Tubifex tubifex) Invertebrate.” Chemosphere 181 (August):250–58. https://doi.org/10.1016/j.chemosphere.2017.04.066.) also exposed aquatic worms (*Tubifex* sp.) in a chronic (28-day exposure) sediment toxicity test. Their results indicated that mortality was the least sensitive endpoint (28-day LC_{50} of 67 µg/g dry weight), while reproduction was a more sensitive endpoint. Exposed worms produced fewer total juveniles and fewer large juveniles (those greater than 500 micrometers (µm) in length). The EC_{10} for both these outcomes was 3 µg/g, and the concentration at which an effect was observed in 50 percent of test subjects (EC_{50}) was 4 µg/g for dry weight sediment (EC_{10}, the concentration at which an effect was observed in 10 percent of test subjects). Compared to *H. azteca* in sediment, their results suggested that *Tubifex* may be more exposed to 6PPD due to species-specific differences in behavior (for example, *Tubifex* remains buried in sediment to feed on organic matter and is likely exposed to sediment-bound 6PPD and 6PPD in pore water consumed by the worms).

In a study that investigated the effects of 6PPD on different life stages of freshwater mussels, the viability of glochidia (larvae) of two mussel species (the fatmucket mussel, *Lampsilis siliquoidea,* and the wavy-rayed lampmussel *Lampsilis fasciola*) was assessed after a 48-hour exposure to 6PPD in water (Prosser et al. 2017[L96F85XM] Prosser, R. S., P.L. Gillis, E.A.M. Holman, D. Schissler, H. Ikert, J. Toito, E. Gilroy, et al. 2017. “Effect of Substituted Phenylamine Antioxidants on Three Life Stages of the Freshwater Mussel Lampsilis siliquoidea.” Environmental Pollution 229:281–89. https://doi.org/10.1016/j.envpol.2017.05.086.). The 48-hour median effect concentration (EC_{50}) values for larval viability were 439 µg/L 6PPD for *L. siliquoidea* and 137 µg/L for *L. fasciola* (see Table 2-1). For the juvenile stage of fatmucket mussels (*L. siliquoidea),* the same study exposed test organisms to 6PPD for 28 days in sediment and water. The reported 28-day LC_{50} measurements were 62 µg/g dry weight sediment and 17 µg/L water. Adult mussels exposed for 28 days did not exhibit significant sublethal impacts, including a lack of oxidative stress in any tissue examined (gill, gonad, and digestive), no adverse effect on viability of hemocytes, and no deoxyribonucleic acid (DNA) damage in hemocytes. The authors concluded that genotoxicity was not observed in mussel hemocytes at concentrations up to 115.9 µg/g dry weight sediment (Prosser et al. 2017[L96F85XM] Prosser, R. S., P.L. Gillis, E.A.M. Holman, D. Schissler, H. Ikert, J. Toito, E. Gilroy, et al. 2017. "Effect of Substituted Phenylamine Antioxidants on Three Life Stages of the Freshwater Mussel Lampsilis siliquoidea." Environmental Pollution 229:281–89. https://doi.org/10.1016/j.envpol.2017.05.086.).

2.2.2.3 6PPD Toxicity in Algae and Aquatic Plants

There are few studies on the toxicity of 6PPD to algae and aquatic plants. An algal study presented in the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) dossier for 6PPD reported a 96-hour EC_{50} equal to 600 µg/L and a 96-hour no-observed-effect concentration for growth rate equal to 200 µg/L in the green algae species *Pseudokirchneriella subcapitata* (previously *Selenastrum capricornutum*) (ECHA 2021[Y79Z3ZWV] ECHA. 2021. "Substance Infocard: N-1,3-Dimethylbutyl-N'-Phenyl-p-Phenylenediamine. European Chemicals Agency (ECHA)." April 7, 2021. https://echa.europa.eu/substance-information/-/substanceinfo/100.011.222.). This study was categorized as not reliable (Klimisch score of 3) in the REACH dossier due to "significant methodological deficiencies" including the lack of exponential growth of the test organism during the incubation period, which is required in most standardized algal toxicity tests. Therefore, the reported effect levels cannot reliably be interpreted as a result of exposure to 6PPD.

2.2.2.4 6PPD Toxicity in Mammals

Some studies on the toxicity of 6PPD to mammals were conducted in parallel with 6PPD-q; therefore, the available information is similar to that provided in Section 2.2.1.4 and Table 2-3.

One study found that oral exposure at 10 and 100 mg/kg 6PPD to mice for 6 weeks resulted in fatty liver syndrome (Fang et al. 2023[B66X64SI] Fang, Liya, Chanlin Fang, Shanshan Di, Yundong Yu, Caihong Wang, Xinquan Wang, and Yuanxiang Jin. 2023. "Oral Exposure to Tire Rubber–Derived Contaminant 6PPD and 6PPD-Quinone Induce Hepatotoxicity in Mice." Science of the Total Environment 869 (April):161836. https://doi.org/10.1016/j.scitotenv.2023.161836.), similar to 6PPD-q. Unlike 6PPD-q, which affected inflammatory pathways, the authors determined that 6PPD tended to affect gene expression related to fatty acid metabolism. The mice were not monitored for apical outcomes. Although steatosis is an adverse outcome and indicator of liver damage in human health evaluations, no studies in wild mammals are available that would define steatosis as an adverse apical outcome in nonhuman organisms. H. N. Zhao, Thomas, et al. (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. "Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways." Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.) found that oral gavage exposure to 4 mg/kg 6PPD in pregnant mice resulted in chemical transfer to pups, resulting in concentrations in livers (mean 200 ng/g) that were greater than in the studies cited above. These results may be of use for ecological risk assessment based on tissue residue values if an apical outcome was associated with organ damage as shown in the study.

2.3 Potential for Bioaccumulation and Adduct Formation

Additional data are required to thoroughly evaluate the bioaccumulation potential of 6PPD-q and 6PPD in aquatic organisms and potential toxic effects, such as adduct formation, that result from uptake of the chemicals. See Section 3.5: Biological Uptake for further discussion of biological uptake and bioaccumulation. In addition, Table 4-10 summarizes concentrations of 6PPD-q measured in studies of aquatic organisms.

2.4 Human Health and Toxicology

This section highlights 6PPD-q toxicity studies relevant to the evaluation of human health effects. Data summarizing the human health effects of 6PPD are presented below and have been included in case a read-across is conducted in the future when data on 6PPD might be used to infer toxicologic endpoints where data are currently lacking for 6PPD-q. At this point in time, data are currently insufficient to conduct such a read-across.

6PPD-quinone Toxicity Relevant to Humans

- Mouse studies indicate that 6PPD-q accumulates primarily in the liver and lung, as well as adipose tissue, kidneys, the brain, and other organs.

- 6PPD-q can cross both the placenta and blood–brain barrier.
- Oral doses of 6PPD-q, at levels much higher than found in the environment, caused liver toxicity in mice.
- 6PPD-q can be excreted in urine and fecal matter.
- Some early studies have identified neurotoxicity, reproductive toxicity, and genotoxicity in various assays. More studies are needed to replicate these findings.

A summary of toxicology data relevant to the assessment of human health for 6PPD-q and its parent 6PPD is provided in Table 2-3.

2.4.1 Toxicity of 6PPD-q

2.4.1.1 Toxicokinetics of 6PPD-q

Toxicokinetic studies provide insights into how substances are absorbed, distributed, metabolized, and excreted in living organisms. These studies can provide insights into potential toxic effects.

Repeat dose intraperitoneal administration, which allows for rapid and efficient absorption and increased bioavailability of 6PPD-q (Al Shoyaib, Archie, and Karamyan 2019[E4MBH586] Al Shoyaib, Abdullah, Sabrina Rahman Archie, and Vardan T. Karamyan. 2019. “Intraperitoneal Route of Drug Administration: Should It Be Used in Experimental Animal Studies?” Pharmaceutical Research 37 (1): 12. https://doi.org/10.1007/s11095-019-2745-x.), indicated accumulation in the liver and lung of mice (He, Gu, and Wang 2023[6MPWVZGE] He, Wenmiao, Aihua Gu, and Dayong Wang. 2023. “Four-Week Repeated Exposure to Tire-Derived 6-PPD Quinone Causes Multiple Organ Injury in Male BALB/c Mice.” Science of the Total Environment 894 (October):164842. https://doi.org/10.1016/j.scitotenv.2023.164842.). In mice fed a single dose of deuterated 6PPD-q_5, 6PPD-q was primarily distributed in the adipose tissue followed by the kidney, lung, testis, liver, spleen, heart, and muscle (Zhang et al. 2024[BZQEGEXI] Zhang, Jing, Guodong Cao, Wei Wang, Han Qiao, Yi Chen, Xiaoxiao Wang, Fuyue Wang, Wenlan Liu, and Zongwei Cai. 2024. “Stable Isotope-Assisted Mass Spectrometry Reveals in Vivo Distribution, Metabolism, and Excretion of Tire Rubber-Derived 6PPD-Quinone in Mice.” Science of the Total Environment 912 (February):169291. https://doi.org/10.1016/j.scitotenv.2023.169291.). Following oral gavage of pregnant mice, 6PPD-q was distributed to the brain and liver of dams and fetal body and fetal brain (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. “Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways.” Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.). Lower concentrations of 6PPD-q were measured in the fetal brain as compared with the dam brain, which indicates the partial protection effect of the placenta (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. “Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways.” Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.). (The 6PPD results from H. N. Zhao, Thomas, et al. (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. “Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways.” Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.) are discussed in Section 2.4.2.1). A study conducted by J. Zhang et al. (Zhang et al. 2024[BZQEGEXI] Zhang, Jing, Guodong Cao, Wei Wang, Han Qiao, Yi Chen, Xiaoxiao Wang, Fuyue Wang, Wenlan Liu, and Zongwei Cai. 2024. “Stable Isotope-Assisted Mass Spectrometry Reveals in Vivo Distribution, Metabolism, and Excretion of Tire Rubber-Derived 6PPD-Quinone in Mice.” Science of the Total Environment 912 (February):169291. https://doi.org/10.1016/j.scitotenv.2023.169291.) demonstrated that 6PPD-q penetrates the blood–brain barrier of mice.

Urine concentrations measured in male and female mice dosed with 6PPD-q or 6PPD indicated lower excretion of 6PPD-q than 6PPD (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. “Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways.” Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.). J. Zhang et al. (Zhang et al. 2024[BZQEGEXI] Zhang, Jing, Guodong Cao, Wei Wang, Han Qiao, Yi Chen, Xiaoxiao Wang, Fuyue Wang, Wenlan Liu, and Zongwei Cai. 2024. “Stable Isotope-Assisted Mass Spectrometry Reveals in Vivo Distribution, Metabolism, and Excretion of Tire Rubber-Derived 6PPD-Quinone in Mice.” Science of the Total Environment 912 (February):169291. https://doi.org/10.1016/j.scitotenv.2023.169291.) identified fecal excretion rather than urine excretion as the main excretory pathway for 6PPD-q and two newly identified novel hydroxylated metabolites of 6PPD-q (D5-6PPD-q-OH and D5-6PPD-q-2OH).

Human biomonitoring conducted in China (see Section 2.5) has measured 6PPD-q and 6PPD in urine with 6PPD-q concentrations significantly higher than 6PPD and higher concentrations of both chemicals observed in pregnant woman than in in adults or children. Daily excretion rates of 6PPD-q in urine of adults, children, and pregnant women were 11.3 ng per kg of body weight (ng/kg-bw)/day, 2.18 ng/kg-bw/day, and 90.9 ng/kg-bw/day, respectively (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. “First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China.” Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.).

6PPD-q was detected in CSF from a small sample of Parkinson’s disease (PD) patients and a control group (Fang et al. 2024[2L4QI2CG] Fang, Jiacheng, Xiaoxiao Wang, Guodong Cao, Fuyue Wang, Yi Ru, Bolun Wang, Yanhao Zhang, et al. 2024. “6PPD-Quinone Exposure Induces Neuronal Mitochondrial Dysfunction to Exacerbate Lewy Neurites Formation Induced by α-Synuclein Preformed Fibrils Seeding.” Journal of Hazardous Materials 465 (March):133312. https://doi.org/10.1016/j.jhazmat.2023.133312.).

2.4.1.2 Acute Toxicity of 6PPD-q

No acute toxicity data are available for 6PPD-q.

2.4.1.3 Irritation/Sensitization of 6PPD-q

No irritation or sensitization data are available for 6PPD-q.

2.4.1.4 Chronic Toxicity and Systemic Effects of 6PPD-q

In a subchronic toxicity study by L. Fang et al. (Fang et al. 2023[B66X64SI] Fang, Liya, Chanlin Fang, Shanshan Di, Yundong Yu, Caihong Wang, Xinquan Wang, and Yuanxiang Jin. 2023. “Oral Exposure to Tire Rubber–Derived Contaminant 6PPD and 6PPD-Quinone Induce Hepatotoxicity in Mice.” Science of the Total Environment 869 (April):161836. https://doi.org/10.1016/j.scitotenv.2023.161836.), 6PPD-q increased lipid accumulation in the livers of mice that were given oral doses of 10 mg/kg-bw/day for 6 weeks. In addition, 6PPD-q increased liver triglycerides at all doses tested (10, 30, and 100 mg/kg-bw/day), and an altered expression of liver enzymes and inflammatory markers in the liver were also reported (Fang et al. 2023[B66X64SI] Fang, Liya, Chanlin Fang, Shanshan Di, Yundong Yu, Caihong Wang, Xinquan Wang, and Yuanxiang Jin. 2023. “Oral Exposure to Tire Rubber–Derived Contaminant 6PPD and 6PPD-Quinone Induce Hepatotoxicity in Mice.” Science of the Total Environment 869 (April):161836. https://doi.org/10.1016/j.scitotenv.2023.161836.).

In a subchronic toxicity study by He, Gu, and Wang (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. “Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways.” Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.), “…significant pathological changes were formed in liver, kidney, lung, spleen, testis, and brain…” in mice repeatedly administered 0.4 and 4 mg/kg 6PPD-q via IP administration. According to He, Gu, and Wang (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. “Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways.” Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.), “…[b]iochemical parameters of liver [metabolism] (alanine aminotransferase (ALT), aspartate aminotransferase (AST), and alkaline phosphatase (ALP)) and kidney [function] (urea and creatinine) were all significantly upregulated by repeated injection with 0.4 and 4 mg/kg 6PPD-q…”, indicating potential injury to the liver and kidney. But IP studies have significant caveats because it is not a relevant exposure pathway.

2.4.1.5 Carcinogenicity and Genotoxicity of 6PPD-q

6PPD-q was mutagenic to *Parhyale hawaiensis*, a marine invertebrate, and weakly mutagenic to bacteria (Botelho et al. 2023[WZC7F928] Botelho, Marina Tenório, Gabriely Groto Militão, Markus Brinkmann, and Gisela de Aragão Umbuzeiro. 2023. “Toxicity and Mutagenicity Studies of 6PPD-Quinone in a Marine Invertebrate Species and Bacteria.” Environmental and Molecular Mutagenesis 64 (6): 335–41. https://doi.org/10.1002/em.22560.). *Caenorhabditis elegans*, a round worm frequently used in the lab, exposed to 1 µg/L and 10 µg/L 6PPD-q experienced increased DNA damage and increased expression of DNA damage-related genes (Hua et al. 2023[RJ86H9T3] Hua, Xin, Xiao Feng, Geyu Liang, Jie Chao, and Dayong Wang. 2023. “Long-Term Exposure to 6-PPD Quinone Reduces Reproductive Capacity by Enhancing Germline Apoptosis Associated with Activation of Both DNA Damage and Cell Corpse Engulfment in Caenorhabditis elegans.” Journal of Hazardous Materials 454 (July):131495. https://doi.org/10.1016/j.jhazmat.2023.131495.). DNA adducts were detected in 6PPD-q-treated mammalian cells; removal of 6PPD-q led to decreased levels of the adduct, which suggested potential repair pathways (Wu et al. 2023[PYQQU7AG] Wu, Jiabin, Guodong Cao, Feng Zhang, and Zongwei Cai. 2023. “A New Toxicity Mechanism of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine Quinone: Formation of DNA Adducts in Mammalian Cells and Aqueous Organisms.” Science of the Total Environment 866:161373. https://doi.org/10.1016/j.scitotenv.2022.161373.). No carcinogenicity data are available.

2.4.1.6 Reproductive/Developmental Toxicity of 6PPD-q

In a reproductive toxicity study by Hua et al. (Hua et al. 2023[RJ86H9T3] Hua, Xin, Xiao Feng, Geyu Liang, Jie Chao, and Dayong Wang. 2023. “Long-Term Exposure to 6-PPD Quinone Reduces Reproductive Capacity by Enhancing Germline Apoptosis Associated with Activation of Both DNA Damage and Cell Corpse Engulfment in Caenorhabditis elegans.” Journal of Hazardous Materials 454 (July):131495. https://doi.org/10.1016/j.jhazmat.2023.131495.), exposure to 1 µg/L and 10 µg/L 6PPD-q reduced reproductive capacity and negatively affected gonad development in *C. elegans*. The relevance to human health of an effect in *C. elegans* worms is not clear.

In a prenatal developmental toxicity study, pregnant female mice were treated with 4 mg/kg 6PPD-q or 6PPD from embryonic day 11.5 to 15.5. 6PPD-q was found to cross the placenta and was detected in fetal whole-body tissue and fetal brain samples at higher concentrations than 6PPD (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. “Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways.” Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.) . This study did not measure fetotoxicity, just distribution to the fetus. In addition, the authors found that 6PPD-q can activate both the human retinoic acid receptor α (RARα) and retinoid X receptor α (RXRα) in human embryonic kidney cells and indicates the potential for developmental effects (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. “Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways.” Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.).

2.4.1.7 Neurotoxicity of 6PPD-q

6PPD Toxicity Relevant to Humans

- 6PPD is a dermal sensitizer.
- Chronic toxicity studies in mice indicate the liver and blood are the target organs
- ECHA classifies 6PPD as a category 1B reproductive toxicant.
- 6PPD can cross both the placenta and blood–brain barrier.
- 6PPD can be excreted in urine; in vitro studies indicate that 6PPD-q is not a predominant metabolite of 6PPD.

PD may cause leakage in the blood–brain barrier, creating the possibility that chemicals, such as 6PPD-q, can enter CSF and the brain. In this study, 6PPD-q was detected in the CSF of all the PD patients but only 64% of controls, and the levels were twice as high (11.18 nanograms per milliliter [ng/mL]) in PD patients compared to controls (5.07 ng/mL) (Fang et al. 2024[2L4QI2CG] Fang, Jiacheng, Xiaoxiao Wang, Guodong Cao, Fuyue Wang, Yi Ru, Bolun Wang, Yanhao Zhang, et al. 2024. “6PPD-Quinone Exposure Induces Neuronal Mitochondrial Dysfunction to Exacerbate Lewy Neurites Formation Induced by α-Synuclein Preformed Fibrils Seeding.” Journal of Hazardous Materials 465 (March):133312. https://doi.org/10.1016/j.jhazmat.2023.133312.). The sample sizes of both groups were small, so establishing the population-level significance of the results requires additional investigation. Further, J. Fang et al. (Fang et al. 2024[2L4QI2CG] Fang, Jiacheng, Xiaoxiao Wang, Guodong Cao, Fuyue Wang, Yi Ru, Bolun Wang, Yanhao Zhang, et al. 2024. “6PPD-Quinone Exposure Induces Neuronal Mitochondrial Dysfunction to Exacerbate Lewy Neurites Formation Induced by α-Synuclein Preformed Fibrils Seeding.” Journal of Hazardous Materials 465 (March):133312. https://doi.org/10.1016/j.jhazmat.2023.133312.) investigated the potential for 6PPD-q to impact the pathophysiology of PD by studying 6PPD-q’s effects on mouse primary dopaminergic neurons, a cell type impacted by PD. The researchers found some additive effects with 6PPD-q in mitochondria and in outgrowths (neurites) when the neurons were pre-seeded with insoluble protein alpha-synuclein preformed fibrils (α-syn PFF), that can cause Parkinsonian deposits. The results were not compared to other molecules that may also induce oxidative stress. More research is needed to determine whether 6PPD-q can act as a human neurotoxin and whether it can cause mitochondrial dysfunction.

2.4.2 Toxicity of 6PPD

2.4.2.1 Toxicokinetics of 6PPD

No in vivo absorption studies of 6PPD are available. Nonetheless, toxicity studies at acute and repeated doses allow for the derivation of certain conclusions. The primary bioavailability of 6PPD through oral and dermal exposure is demonstrated by the emergence of systemic toxicity following exposure (OECD 2004[FCJPCPVW] OECD. 2004. "SIDS Initial Assessment Report for N-(1,3-Dimethylbutyl)-N´-Phenyl-1,4-Phenylenediamine (6PPD), Organisation for Economic Co-Operation and Development (OECD)." https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e.ECHA 2022[Z9UAAF4F] ECHA. 2022. "6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA)." https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.). Following oral gavage of pregnant mice, 6PPD was shown to distribute to the brain and liver of dams and body and brain of fetuses (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. "Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways." Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.). Lower concentrations of 6PPD were measured in the fetal brain as compared with the dam brain, indicating a partial protective effect of the placenta (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. "Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways." Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.). (Note: The 6PPD-q results from H. N. Zhao, Thomas, et al. (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. "Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways." Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.) are discussed in Section 2.4.1.1).

In an in vitro metabolism study, in the presence of simulated gastric juice, 6PPD had a half-life of 36.9 hours. The major observed hydrolysis product was aniline with trace amounts of benzoquinone imine-N-phenyl; N-1,3 dimethyl-butylamine p-phenol; quinone; and 2-amino-4-methylpentane (ToxServices, LLC 2021[IDJRCJR2] ToxServices, LLC. 2021. "N-(1,3-Dimethylbutyl)-N'-Phenyl-p-Phenylenediamine (6PPD) (CAS #793-24-8) Greenscreen® for Safer Chemicals (Greenscreen®) Assessment." GS-1204. Washington, D.C.: ToxServices Toxicology Risk Assessment Consulting. https://www.ezview.wa.gov/Portals/_1962/Documents/6ppd/GreenScreenExecutiveSummaryFor6PPD.pdf.).

In another study (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. "First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China." Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.), 6PPD was metabolized via human liver microsomes. After 3 hours of incubation with liver microsomes under in vitro conditions, 65% of 6PPD was depleted. Only 2% of the 6PPD was metabolized into 6PPD-q; its production rates were measured at corresponding time intervals, indicating 6PPD may predominantly metabolize into other metabolites.

In mice, 6PPD has been shown to rapidly excrete in urine (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. "Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways." Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.). Human biomonitoring studies have detected 6PPD in urine (Mao et al. 2024[MJI3WKBH] Mao, Weili, Hangbiao Jin, Ruyue Guo, Ping Chen, Songyang Zhong, and Xilin Wu. 2024. "Occurrence of p-Phenylenediamine Antioxidants in Human Urine." Science of the Total Environment 914 (March):170045. https://doi.org/10.1016/j.scitotenv.2024.170045.Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. "First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China." Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.ECHA 2022[Z9UAAF4F] ECHA. 2022. "6PPD:

1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA)." https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.). Du et al. (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. "First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China." Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.) reported that pregnant women had higher daily excretion rates of 6PPD (median value of 2.13 ng/kg-bw/day) compared with adults (0.51 ng/kg-bw/day) and children (0.43 ng/kg-bw/day). Daily excretion rates of 6PPD measured by Mao et al. (Mao et al. 2024[MJI3WKBH] Mao, Weili, Hangbiao Jin, Ruyue Guo, Ping Chen, Songyang Zhong, and Xilin Wu. 2024. "Occurrence of p-Phenylenediamine Antioxidants in Human Urine." Science of the Total Environment 914 (March):170045. https://doi.org/10.1016/j.scitotenv.2024.170045.) in adults were 34 ng/kg-bw/day (mean) and 30 ng/kg-bw/day (median). The differences in the results indicate that more studies are necessary.

2.4.2.2 Acute Toxicity of 6PPD

Acute toxicity of 6PPD is moderate via the oral route of exposure and low via the dermal route of exposure, based on GHS thresholds. Oral median lethal dose (LD_{50}) values measured in rats range between 893 mg/kg and 5,000 mg/kg (ECHA 2022[Z9UAAF4F] ECHA. 2022. "6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA)." https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.). Substance preparation (dosing vehicle) influences the bioavailability after oral application, which may explain the broad range of oral LD_{50} observed (OECD 2004[FCJPCPVW] OECD. 2004. "SIDS Initial Assessment Report for N-(1,3-Dimethylbutyl)-N´-Phenyl-1,4-Phenylenediamine (6PPD), Organisation for Economic Co-Operation and Development (OECD)." https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e.).

Currently, dermal exposure studies of acute toxicity following guidelines from the Organisation for Economic Co-Operation and Development (OECD) guideline have not been completed. However, two older studies (ECHA 2022[Z9UAAF4F] ECHA. 2022. "6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA)." https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.) are available to evaluate dermal acute toxicity. In one study, a dermal LD_{50} value greater than 7,940 mg/kg-bw, the highest dose tested, was measured in rabbits. In a second study, a lethal dose in the range between 3,160 and 5,010 mg/kg-bw was established. According to OECD (2004), symptoms of toxicity included reduced food consumption, hypoactivity, and lethargy. Reliable data were not available to evaluate acute toxicity of 6PPD through an inhalation route of exposure (ECHA 2022[Z9UAAF4F] ECHA. 2022. "6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA)." https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.).

2.4.2.3 Irritation/Sensitization of 6PPD

6PPD is considered to be a skin sensitizer based on multiple animal studies (ECHA 2022[Z9UAAF4F] ECHA. 2022. "6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA)." https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.). Patch tests in human populations resulted in similar observations. Those who had previously been sensitized to rubber samples showed a higher rate of sensitization to 6PPD, whereas healthy volunteers who had not previously been exposed to test rubber formulations showed no or very little sensitization (OECD 2004[FCJPCPVW] OECD. 2004. "SIDS Initial Assessment Report for N-(1,3-Dimethylbutyl)-N´-Phenyl-1,4-Phenylenediamine (6PPD), Organisation for Economic Co-Operation and Development (OECD)." https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e.ECHA 2022[Z9UAAF4F] ECHA. 2022. "6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA)." https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.). Based on these animal and human test results (see Table 2-3), The European Chemicals Agency (ECHA) (2022) classifies 6PPD as a category 1 skin sensitizer without subcategorization.

Studies of rabbits determined that 6PPD was not irritating to skin but slightly irritated eyes (ECHA 2022[Z9UAAF4F] ECHA. 2022. "6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA)." https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.).

2.4.2.4 Chronic Toxicity and Systemic Effects of 6PPD

In a subchronic toxicity study by L. Fang et al. (Fang et al. 2023[B66X64SI] Fang, Liya, Chanlin Fang, Shanshan Di, Yundong Yu, Caihong Wang, Xinquan Wang, and Yuanxiang Jin. 2023. “Oral Exposure to Tire Rubber–Derived Contaminant 6PPD and 6PPD-Quinone Induce Hepatotoxicity in Mice.” Science of the Total Environment 869 (April):161836. https://doi.org/10.1016/j.scitotenv.2023.161836.), 6PPD increased lipid accumulation in the livers of mice that were given oral doses of 10 mg/kg-bw/day for 6 weeks. Similarly, ECHA (ECHA 2022[Z9UAAF4F] ECHA. 2022. “6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA).” https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.) identified the liver and blood cells as targets of toxicity in a 28-day oral exposure rat study. In the rat study, effects on the liver for both sexes were reversible at 20 mg/kg-bw/day (the established no adverse effect level or NOAEL), and both sexes showed fat deposition in the liver and anemia at 100 mg/kg-bw/day (the established lowest observed adverse effect level) (ECHA 2022[Z9UAAF4F] ECHA. 2022. “6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA).” https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.). A sex-specific sensitivity was also observed in the study data where a no-observed-effect level (NOEL) of 4 mg/kg-bw/day was established for female rats only. Mild effects (reversible periportal fatty change of the liver without an increase of liver weight; increased total serum protein) were observed in female rats at the lowest observed effects level (LOEL) of 20 mg/kg-bw/day, which formed the basis of the NOAEL (OECD 2004[FCJPCPVW] OECD. 2004. “SIDS Initial Assessment Report for N-(1,3-Dimethylbutyl)-N´-Phenyl-1,4-Phenylenediamine (6PPD), Organisation for Economic Co-Operation and Development (OECD).” https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e.).

2.4.2.5 Carcinogenicity and Genotoxicity of 6PPD

6PPD is not likely to be mutagenic or genotoxic based on negative mutagenicity data in vitro in bacterial or mammalian cells and negative clastogenicity data in vivo (OECD 2004[FCJPCPVW] OECD. 2004. “SIDS Initial Assessment Report for N-(1,3-Dimethylbutyl)-N´-Phenyl-1,4-Phenylenediamine (6PPD), Organisation for Economic Co-Operation and Development (OECD).” https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e.ECHA 2022[Z9UAAF4F] ECHA. 2022. “6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA).” https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.). 6PPD has low potential for carcinogenicity as indicated in data collected from two-year chronic feeding studies in rats and negative results in an in vitro cell transformation assay with BALB/3T3 cells (ECHA 2022[Z9UAAF4F] ECHA. 2022. “6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA).” https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.).

2.4.2.6 Reproductive/Developmental Toxicity of 6PPD

6PPD is listed as a category 1B reproductive toxicant by ECHA (ECHA 2022[Z9UAAF4F] ECHA. 2022. “6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA).” https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.). Dose-dependent dystocia (difficult birth) was found in multiple treatment groups in rats. A NOAEL of 7 mg/kg-bw/day was established for female reproductive toxicity (ECHA 2022[Z9UAAF4F] ECHA. 2022. “6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA).” https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.). Other studies did not identify reproductive effects in either rats or rabbits (OECD 2004[FCJPCPVW] OECD. 2004. “SIDS Initial Assessment Report for N-(1,3-Dimethylbutyl)-N´-Phenyl-1,4-Phenylenediamine (6PPD), Organisation for Economic Co-Operation and Development (OECD).” https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e.OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. “Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update).” Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.).

Developmental toxicity tests on 6PPD have not been conclusive. No indications for teratogenic or developmental effects were observed in rats up to oral doses of 250 mg/kg-bw/day (the highest dose tested) (OECD 2004[FCJPCPVW] OECD. 2004. “SIDS Initial Assessment Report for N-(1,3-Dimethylbutyl)-N´-Phenyl-1,4-Phenylenediamine (6PPD), Organisation for Economic Co-Operation and Development (OECD).” https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e.ECHA 2022[Z9UAAF4F] ECHA. 2022.

“6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA).” https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.). In a prenatal developmental toxicity study, no conclusion could be drawn regarding whether the developmental effects (lower mean fetal body weights) observed in rabbits were due to decreased maternal feeding or specific effects of 6PPD on the fetus. A dosage level of 25 mg/kg-bw/day was established as the NOAEL for embryo/fetal development (ECHA 2022[Z9UAAF4F] ECHA. 2022. “6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA).” https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.). This NOAEL is supported by other studies where “…[e]xposure during the gestation period demonstrated the absence of a fetotoxic or teratogenic potential and of maternal toxicity in rabbits with doses up to 30 mg/kg-bw/day (highest dose tested)” (OECD 2004[FCJPCPVW] OECD. 2004. “SIDS Initial Assessment Report for N-(1,3-Dimethylbutyl)-N´-Phenyl-1,4-Phenylenediamine (6PPD), Organisation for Economic Co-Operation and Development (OECD).” https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e.).

In a prenatal developmental toxicity study, pregnant female mice were treated with 4 mg/kg 6PPD from embryonic day 11.5 to 15.5. 6PPD was found to cross the placenta and was detected in fetal whole-body tissue and fetal brain samples (Zhao et al. 2023[GZZX9DMJ] Zhao, Haoqi Nina, Sydney P. Thomas, Mark J. Zylka, Pieter C. Dorrestein, and Wenxin Hu. 2023. “Urine Excretion, Organ Distribution, and Placental Transfer of 6PPD and 6PPD-Quinone in Mice and Potential Developmental Toxicity through Nuclear Receptor Pathways.” Environmental Science & Technology 57 (36): 13429–38. https://doi.org/10.1021/acs.est.3c05026.). Zhao et al. also found that 6PPD acted as an agonist on RXRα in human embryonic kidney cells. Collectively, these results suggest the potential for developmental effects. More research is needed to understand whether these results translate into observable outcomes in the embryos (apical endpoints).

2.5 Biomonitoring for 6PPD and 6PPD-q

At the time this document was prepared, there was limited information about biological measures of exposure to 6PPD and 6PPD-q in people. The kinds of samples used to characterize human exposure may vary with the chemical contaminant of concern but can include blood, hair, and urine, among other biological materials. Detection of 6PPD and 6PPD-q in urine, serum, and CSF is summarized below.

6PPD and 6PPD-q were detected in the urine of adults, children, and pregnant individuals living in South China (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. “First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China.” Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.). 6PPD had an overall detection frequency of 68%, and 6PPD-q had a 97% detection frequency. Pregnant women’s urine had the highest levels of 6PPD and 6PPD-q out of all the demographic groups in the study, with 6PPD-q concentrations greater than 6PPD concentrations by two orders of magnitude. Higher levels of 6PPD and 6PPD-q were detected in the urine of adult women than that of adult men, but this difference was not present in children. Additionally, 6PPD-q urine concentrations increased with age in children, with levels higher in children aged 7–13 years and 4–6 years compared to 1–3 years. Du et al. (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. “First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China.” Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.) hypothesized this age difference is due to a difference in toxicokinetics between younger and older children, as well as the change in diet from breast milk/formula to solid foods. Du et al. (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. “First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China.” Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.) only analyzed for 6PPD and 6PPD-q, but there may be other metabolic transformation products of 6PPD and 6PPD-q in urine that are not yet accounted for. For example, J. Zhang et al. (Zhang et al. 2024[BZQEGEXI] Zhang, Jing, Guodong Cao, Wei Wang, Han Qiao, Yi Chen, Xiaoxiao Wang, Fuyue Wang, Wenlan Liu, and Zongwei Cai. 2024. “Stable Isotope-Assisted Mass Spectrometry Reveals in Vivo Distribution, Metabolism, and Excretion of Tire Rubber-Derived 6PPD-Quinone in Mice.” Science of the Total Environment 912 (February):169291. https://doi.org/10.1016/j.scitotenv.2023.169291.) identified two novel hydroxylated metabolites of 6PPD-q (D5-6PPD-q-OH and D5-6PPD-q-2OH) that were not included in the pioneering human urine biomonitoring study by Du et al. (Du et al.

2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. "First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China." Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.).

Mao et al. (Mao et al. 2024[MJI3WKBH] Mao, Weili, Hangbiao Jin, Ruyue Guo, Ping Chen, Songyang Zhong, and Xilin Wu. 2024. "Occurrence of p-Phenylenediamine Antioxidants in Human Urine." Science of the Total Environment 914 (March):170045. https://doi.org/10.1016/j.scitotenv.2024.170045.) analyzed urine sampled from 151 adults for 6PPD but not 6PPD-q in China. 6PPD had an 82% detection frequency. Higher levels of 6PPD were detected in the urine from adult women than from adult men, which supports the findings of Du et al. (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. "First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China." Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.). A general trend of decreasing 6PPD concentration with increasing age was also noted, with significance achieved for the less than 20 years versus 50+ years comparison.

J. Zhang et al. (Zhang et al. 2024[BZQEGEXI] Zhang, Jing, Guodong Cao, Wei Wang, Han Qiao, Yi Chen, Xiaoxiao Wang, Fuyue Wang, Wenlan Liu, and Zongwei Cai. 2024. "Stable Isotope-Assisted Mass Spectrometry Reveals in Vivo Distribution, Metabolism, and Excretion of Tire Rubber-Derived 6PPD-Quinone in Mice." Science of the Total Environment 912 (February):169291. https://doi.org/10.1016/j.scitotenv.2023.169291.) collected serum from 30 volunteers and analyzed for 6PPD-q to identify environmentally relevant exposure concentrations for a laboratory study in mice. The detection frequency of 6PPD-q in these serum samples was 100%, and the median concentration was 0.24 ng/mL. The quality of the data is not confirmed because the paper provides limited methodological information for the serum analysis. Further studies designed to characterize exposure and toxicokinetic properties of 6PPD and 6PPD-q in people are needed.

6PPD-q was detected in CSF from PD patients (n=13; 100% detection frequency) and a control group (n=11; 64% detection frequency) (Fang et al. 2024[2L4QI2CG] Fang, Jiacheng, Xiaoxiao Wang, Guodong Cao, Fuyue Wang, Yi Ru, Bolun Wang, Yanhao Zhang, et al. 2024. "6PPD-Quinone Exposure Induces Neuronal Mitochondrial Dysfunction to Exacerbate Lewy Neurites Formation Induced by α-Synuclein Preformed Fibrils Seeding." Journal of Hazardous Materials 465 (March):133312. https://doi.org/10.1016/j.jhazmat.2023.133312.). Differences were noted between the populations, but could be caused by different exposure or different distribution to CSF in the disease state.

A single study on human breastmilk analyzed 120 samples from healthy lactating women in South China for several antioxidant chemicals. 6PPD was detected in 52% of samples with a median concentration of 4.1 picograms per milliliter (pg/mL). 6PPD-q was below the method quantitation limit in all samples (Liang et al. 2024[BL32NURZ] Liang, Bowen, Jiali Ge, Qing Deng, Yi Li, Bibai Du, Ying Guo, and Lixi Zeng. 2024. "Occurrence of Multiple Classes of Emerging Synthetic Antioxidants, Including p -Phenylenediamines, Diphenylamines, Naphthylamines, Macromolecular Hindered Phenols, and Organophosphites, in Human Milk: Implications for Infant Exposure." Environmental Science & Technology Letters 11 (3): 259–65. https://doi.org/10.1021/acs.estlett.4c00010.).

Older studies of occupational exposure to 6PPD detected levels in the urine of rubber industry workers. 6PPD-q was not recognized at the time and was not measured. In all, 15% of urine samples of 21 Italian rubber industry workers who were exposed by both inhalation and dermal contact contained 6PPD (the maximum was 1.3 µg/L 6PPD in urine). 6PPD was detected in air samples taken in the work area at a concentration range of 0.01–1 micrograms per cubic meter (µg/m^3) (Carlucci et al. 1984[4TK2MX2U] Carlucci, Giovanni, Luisa Airoldi, Roberto Fanelli, and Biagio Laguzzi. 1984. "Quantitative Analysis of Aromatic Amines in Human Urine by Gas Chromatography—Mass Spectrometry—Selected-Ion Monitoring." Journal of Chromatography B: Biomedical Sciences and Applications 311:141–47. https://www.sciencedirect.com/science/article/abs/pii/S0378434700847003.). A peak value of 580 µg/g 6PPD was detected in another biomonitoring study of 341 Italian rubber industry workers (1982–1987). The urine concentration of 6PPD of workers was found to correlate with the level of 6PPD detected in the air, which reached a maximum concentration of 6.6 mg/m^3 (Rimatori and Castellino 1989, as cited in OECD 2004[FCJPCPVW] OECD. 2004. "SIDS Initial Assessment Report for N-(1,3-Dimethylbutyl)-N´-Phenyl-1,4-Phenylenediamine (6PPD), Organisation for Economic Co-Operation and Development (OECD)." https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e.).

2.6 Potential Populations of Concern

Potential Populations of Concern

- Certain populations may be differentially exposed to 6PPD-q, such as those with occupational exposure.
- There may be environmental justice concerns related to 6PPD-q due to the potential for disproportionate exposures to vulnerable communities.
- Additional research is needed to understand the potential for bioaccumulation in fish tissue and to inform the potential for human exposure in populations that rely on subsistence fishing.

People may be more likely to experience health effects from a chemical if they are biologically susceptible, have other health stressors, or are more highly exposed due to either behavioral exposure factors or increased contact with contaminated environmental media. For example, some people may have higher exposures to 6PPD-q and 6PPD than others because of their occupations or where they live. This section identifies some possible populations of concern based on potential exposure patterns, possible vulnerabilities, and populations that engage in subsistence fishing for coho salmon or other impacted species. Relationships between these potential exposures and health outcomes is a data gap.

Some workplaces in the United States contain tires and tire debris. As described by the California Department of Toxic Substances Control (DTSC) (DTSC 2022[2M3Z8Z4F] DTSC. 2022. "Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the California Department of Toxic Substances Control (DTSC)." https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf .), "…[s]ome of these occupations include tire manufacturers, mechanics, highway workers,… street sweepers, car washers, and parking attendants." Workers involved in handling, shredding or otherwise processing waste tires and other products may be at higher risk of exposure due to their direct contact with rubber materials containing 6PPD. These workers may have dermal exposure to the rubber as well as dust and particulate matter inhalation exposures. In addition, workers with prior skin sensitization to 6PPD or other phenylenediamine compounds may be more highly susceptible to allergic skin responses upon exposure to 6PPD. Children who live, play, attend school, and play sports near roadways or in environments that use crumb rubber could be at a heightened risk of exposure to 6PPD and 6PPD-q in TRWPs and road dusts. Children who play on fields amended with crumb rubber or with playground structures made from recycled tires may also be at elevated risk for exposure to 6PPD and 6PPD-q released from these materials, although exposure levels that result from these sources is not yet documented. Children's lower body weight, greater dust ingestion and inhalation rates, and dust to skin adherence factor result in a higher dose from exposure compared to adults, which might make them more vulnerable to any potential adverse effects (Jin et al. 2023[P9WXQJUR] Jin, Ruihe, Yan Wu, Qun He, Pei Sun, Qiqing Chen, Chunjie Xia, Ye Huang, Jing Yang, and Min Liu. 2023. "Ubiquity of Amino Accelerators and Antioxidants in Road Dust from Multiple Land Types: Targeted and Nontargeted Analysis." Environmental Science & Technology 57 (28): 10361–72. https://doi.org/10.1021/acs.est.3c01448.). Additionally, older children may be at higher risk of exposure compared to younger children as indicated by higher urine concentrations of 6PPD-q in 4–13 year olds compared to 1–3 year olds (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. "First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China." Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.).

Those who spend more time near roadways may have increased exposure to 6PPD and 6PPD-q. Likewise, air transport of directly emitted and resuspended tire and road particles containing 6PPD and 6PPD-q could lead to higher local concentrations of these compounds in ambient air and potentially contaminate air and dust in near-road residences, schools, and workplaces, impacting the health of individuals in these communities.

In a biomonitoring study (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. "First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China." Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.) (Section 2.5), 6PPD and 6PPD-q were detected in the urine of pregnant women, children, and general adult populations at varying concentrations in each subpopulation. Environmental justice concerns arise when vulnerable communities, often including low-income and minority populations, are disproportionately exposed to environmental hazards. This can result in unequal health impacts and socioeconomic disparities. Populations living near roadways in the United States are disproportionately nonwhite and low-income (Rowangould 2013[9KKD6N4U] Rowangould, G.M.

2013. “A Census of the US Near-Roadway Population: Public Health and Environmental Justice Considerations.” Transportation Research, Part D: Transport and Environment 2013 (25): 59–67. https://doi.org/10.1016/j.trd.2013.08.003.) and may be at higher risk for exposure and health effects of 6PPD and 6PPD-q.

Tribal members, recreational fishers, and communities that harvest salmon for subsistence in urbanized areas may experience higher exposure if it is found that these chemicals accumulate in edible fish tissue. See Section 1.3.3: Tribal Nations and Section 1.3.4: Potential Economic and Community Health Concerns for further discussion of environmental justice.

3 Chemical Properties

This section reviews the modeled and measured physicochemical properties of 6PPD and 6PPD-quinone. This information is needed to inform analytical field and lab methods, best management practices, and remediation actions. In general, more research is needed to verify the characteristics of tire contaminants.

This section is a review of the current knowledge of physicochemical properties, sources, and transport for 6PPD and 6PPD-q in the environment. This is an emerging and ongoing area of research, and widespread sampling for 6PPD and 6PPD-q has yet to begin. In addition, the presence of 6PPD in many products, transformation to 6PPD-q, and the leaching characteristics of both are not yet clear (see Section 8.2: Occurrence, Fate, Transport, and Exposure to 6PPD and 6PPD-q). Although other emerging contaminants that originate from tires are known to occur in the environment, the scope of this document is limited to discussion of 6PPD and its transformation product 6PPD-q.

A summary of the physicochemical characteristics of 6PPD and 6PPD-q is provided in Table 3-1. Studies highlighted in the table were performed with an isolated 6PPD-q standard in a lab setting and not with field-collected samples (for example, stormwater or tire leachate) unless otherwise specified. Therefore, the physicochemical properties of 6PPD-q may be different in the environment.

Table 3-1. Properties of 6PPD and 6PPD-q

Property	6PPD	6PPD-q	Reference
Molecular Formula	$C_{18}H_{24}N_2$	$C_{18}H_{22}N_2O_2$	(Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. “A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon.” Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.PubChem 2021[H3YIMDF9] PubChem. 2021. “N-(1,3-Dimethylbutyl)-N’-Phenyl-p-Phenylenediamine.” January 2021. https://pubchem.ncbi.nlm.nih.gov/compound/13101.Tian et al. 2022[BICQHLBC] Tian, Zhenyu, Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C. Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej. 2022. “6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard.” Environmental Science & Technology Letters, January, acs.estlett.1c00910. https://doi.org/10.1021/acs.estlett.1c00910.)
CAS Number	793-24-8	2754428-18-5	CompTox: 6PPD, 6PPD-q
SMILES	CC(C)CC(C)NC1=CC=C(C=C1)NC2=CC=CC=C2	CC(C)CC(C)NC1=CC(=O)C(=CC1=O)NC2=CC=CC=C2	CompTox: 6PPD, 6PPD-q
Molecular Name	N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine	2-((4-Methylpentan-2-yl)amino)-5-(phenylamino)cyclohexa-2,5-diene-1,4-dione	(Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone.” Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.PubChem 2021[H3YIMDF9] PubChem. 2021. “N-(1,3-Dimethylbutyl)-N’-Phenyl-p-Phenylenediamine.” January 2021. https://pubchem.ncbi.nlm.nih.gov/compound/13101.)
Molecular Weight	268.402 g/mol	298.39 g/mol	CompTox: 6PPD, 6PPD-q
Solubility	500 – 2,000 µg/L at 50°C	38 +/- 10 µg/L	(Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone.” Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. “Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update).” Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.)
Physical State	Solid (brown or violet)	Solid (from dark red/deep yellow red/dark orange to black)	CompTox: 6PPD, 6PPD-q
Melting Point	49.2°C	66.0°C	CompTox: 6PPD, 6PPD-q
Boiling Point	163–165°C	341°C	CompTox: 6PPD, 6PPD-q
Vapor Pressure	3.35×10^{-6} Pa at 25°C (estimated)	2.11×10^{-5} Pa at 25°C (estimated)	CompTox: 6PPD, 6PPD-q
Dissociation constant	pKa=6.7 at 20°C	pKa=9.14 (estimated)	CompTox: 6PPD, 6PPD-q
Octanol-Water Partition Coefficient, $\log(K_{ow})$	4.68	4.3 ± 0.02	(Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone.” Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.PubChem 2021[H3YIMDF9] PubChem. 2021. “N-(1,3-Dimethylbutyl)-N’-Phenyl-p-Phenylenediamine.” January 2021. https://pubchem.ncbi.nlm.nih.gov/compound/13101.)
Organic Carbon-Water Partition coefficient ($K_{oc)}$.	K_{oc}: 11,000 L/kg	K_{oc}: 2400 L/kg	CompTox: 6PPD, 6PPD-q
Organic Carbon-Water Partition Coefficient, $\log(K_{oc})$	4.84	3.928	(USEPA 2023[8EAETLIA] USEPA. 2023. Estimation Programs Interface SuiteTM for Microsoft® Windows, v 4.11 (EPISuite) (version v 4.11). https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface.OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. “Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update).” Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.);
Bioaccumulation	Low to moderate bioaccumulation (see Section 3.5 for study details)	Limited information & data available (see Section 3.5 for study details)	CompTox: 6PPD, 6PPD-q (Nair et al. 2023[9V5ES4MI] Nair, Pranav, Jianxian Sun, Linna Xie, Lisa Kennedy, Derek Kozakiewicz, Sonya Kleywegt, Chunyan Hao, et al. 2023. “In Process: Synthesis and Toxicity Evaluation of Tire Rubber–Derived Quinones.” Preprint. Chemistry. https://doi.org/10.26434/chemrxiv-2023-pmxvc.Fang et al. 2023[FFFKR3MY] Fang, Chanlin, Liya Fang, Shanshan Di, Yundong Yu, Xinquan Wang, Caihong Wang, and Yuanxiang Jin. 2023. “Characterization of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD)-Induced Cardiotoxicity in Larval Zebrafish (Danio Rerio).” Science of the Total Environment 882 (July):163595. https://doi.org/10.1016/j.scitotenv.2023.163595.Hiki and Yamamoto 2022[VQE4EZWI] Hiki, Kyoshiro, and Hiroshi Yamamoto. 2022. “The Tire-Derived Chemical 6PPD-Quinone Is Lethally Toxic to the White-Spotted Char Salvelinus leucomaenis pluvius but Not to Two Other Salmonid Species.” Environmental Science & Technology Letters 9 (12): 1050–55. https://doi.org/10.1021/acs.estlett.2c00683.Grasse et al. 2023[WJHX578U] Grasse, Nico, Bettina Seiwert, Riccardo Massei, Stefan Scholz, Qiuguo Fu, and Thorsten Reemtsma. 2023. “Uptake and Biotransformation of the Tire Rubber–Derived Contaminants 6-PPD and 6-PPD Quinone in the Zebrafish Embryo (Danio rerio).” Environmental Science & Technology 57 (41): 15598–607. https://doi.org/10.1021/acs.est.3c02819.Zhang et al. 2023[3FCHDXBN] Zhang, Shu-Yun, Xiufeng Gan, Baoguo Shen, Jian Jiang, Huimin Shen, Yuhang Lei, Qiuju Liang, et al. 2023. “6PPD and Its Metabolite 6PPDQ Induce Different Developmental Toxicities and Phenotypes in Embryonic Zebrafish.” Journal of Hazardous Materials 455 (August):131601. https://doi.org/10.1016/j.jhazmat.2023.131601.)
Sorption	Readily sorbs to organics and soils	Readily sorbs to organics and soils; high sorption losses are observed during sampling and lab analysis	(Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone.” Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. “Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update).” Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.)

Half-life	Less than 1 day (aerobic conditions and dissolved)	Days (aerobic conditions and dissolved) to weeks; characteristics suggest more persistent if bound to soils/ organics	(DTSC 2022[2M3Z8Z4F] DTSC. 2022. “Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the California Department of Toxic Substances Control (DTSC).” https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf.OECD 2004[FCJPCPVW] OECD. 2004. “SIDS Initial Assessment Report for N-(1,3-Dimethylbutyl)-N´-Phenyl-1,4-Phenylenediamine (6PPD), Organisation for Economic Co-Operation and Development (OECD).” https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e.Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone.” Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. “Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update).” Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.) (Section 3.2)
Stability in Water	Abiotic half-life less than a day under most conditions; faster degradation in biologically active water	Half-life=33 hours in 23°C tap water; approx. 25+/-10% loss over 47 days at pH 5, 7, and 9	(Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone.” Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.Hiki et al. 2021[WZF69GXC] Hiki, Kyoshiro, Kenta Asahina, Kota Kato, Takahiro Yamagishi, Ryo Omagari, Yuichi Iwasaki, Haruna Watanabe, and Hiroshi Yamamoto. 2021. “Acute Toxicity of a Tire Rubber–Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species.” Environmental Science & Technology Letters 8 (9): 779–84. https://doi.org/10.1021/acs.estlett.1c00453.Johannessen et al. 2022[E9K7U5U3] Johannessen, Cassandra, Paul Helm, Brent Lashuk, Viviane Yargeau, and Chris D. Metcalfe. 2022. “The Tire Wear Compounds 6PPD-Quinone and 1,3-Diphenylguanidine in an Urban Watershed.” Archives of Environmental Contamination and Toxicology 82 (2): 171–79. https://doi.org/10.1007/s00244-021-00878-4.OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. “Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update).” Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.)

Notes: µg/L=micrograms per liter, g/mol=grams per mole, L/kg=liter per kilogram

3.1 Solubility

Solubility

- 6PPD is more soluble than 6PPD-q in water (mg/L vs. ug/L).
- 6PPD-q preferentially binds to organic matter and can sorb to containers, so it has some hydrophobic properties.
- Conversely, 6PPD-q is sufficiently soluble to be transported by water until it is captured by an organic medium.

One notable characteristic is the solubility of 6PPD and 6PPD-q. 6PPD needs to be unbound and mobile in the rubber of tires. The migration rate from inside the tire to the outside layer where it will react with ozone is vital to its performance (Huntink, N.M. and Datta, R.N. 2003[RTIIEIBC] Huntink, N.M., and Datta, R.N. 2003. “A Novel Slow Release Antidegradant for the Rubber Industry—Part 1: Migration Behavior of Newly Developed Anti-Ozonant Compared to Conventional Antidegradants.” Kautschuk Gummi Kunststoffe 56 (6): 310–15.Razumovskii and Batashova 1970[JRUTALHF] Razumovskii, S. D., and L. S. Batashova. 1970. “Mechanism of Protection against Ozone by N-Phenyl-N′-Isopropyl-p-Phenylenediamine.” Rubber Chemistry and Technology 43 (6): 1340–48. https://doi.org/10.5254/1.3547334.). The solubility of 6PPD in water is between 0.5 and 2 mg per liter (mg/L) (Hiki et al. 2021[WZF69GXC] Hiki, Kyoshiro, Kenta Asahina, Kota Kato, Takahiro Yamagishi, Ryo Omagari, Yuichi Iwasaki, Haruna Watanabe, and Hiroshi Yamamoto. 2021. “Acute Toxicity of a Tire Rubber–Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species.” Environmental Science & Technology Letters 8 (9): 779–84. https://doi.org/10.1021/acs.estlett.1c00453.DTSC 2022[MK5W6W3J] DTSC. 2022. “The Impact of California’s Brake Pad Law: Report to the Legislature. Department of Toxic Substances Control and State Water Resources Control Board.” https://dtsc.ca.gov/wp-content/uploads/sites/31/2023/08/Brake-Pad-Legislative-Report-Accessible.pdf.ECHA 2022[Z9UAAF4F] ECHA. 2022. “6PPD: 1,4-Benzenediamine, N1-(1,3-Dimethylbutyl)-N4-Phenyl- Registration Dossier - European Chemicals Agency (ECHA).” https://echa.europa.eu/registration-dossier/-/registered-dossier/15367/1/2.Seiwert et al. 2020[XRNTFZ69] Seiwert, Bettina, Philipp Klöckner, Stephan Wagner, and Thorsten Reemtsma. 2020. “Source-Related Smart Suspect Screening in the Aqueous Environment: Search for Tire-Derived Persistent and Mobile Trace Organic Contaminants in Surface Waters.” Analytical and Bioanalytical Chemistry 412 (20): 4909–19. https://doi.org/10.1007/s00216-020-02653-1.). Although isolated 6PPD-q is modeled to be more soluble, testing a 6PPD-q commercial standard has shown that it is much less soluble than 6PPD, with reported solubilities ranging from 0.04–0.07 mg/L (Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone.” Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.DTSC 2022[MK5W6W3J] DTSC. 2022. “The Impact of California’s Brake Pad Law: Report to the Legislature. Department of Toxic Substances Control and State Water Resources Control Board.” https://dtsc.ca.gov/wp-content/uploads/sites/31/2023/08/Brake-Pad-Legislative-Report-Accessible.pdf.).[5] This has consequences on the toxicity and transport of these compounds in aquatic environments, as well as analytical methods, where they are often dissolved in other solvents such as methanol or acetonitrile before use in the lab. 6PPD-q preferentially binds to organic matter and can sorb to containers, so it has some hydrophobic properties (Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone.” Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.).

3.2 Half-life

Half-life

- 6PPD-q is more stable than 6PPD in water (half-life of weeks vs. less than 1 day).
- More research is needed to understand the half-life under variable conditions and formations.

6PPD and 6PPD-q also have different stabilities. In water, 6PPD has a half-life of less than a day under aerobic conditions (OECD 2004[FCJPCPVW] OECD. 2004. "SIDS Initial Assessment Report for N-(1,3-Dimethylbutyl)-N´-Phenyl-1,4-Phenylenediamine (6PPD), Organisation for Economic Co-Operation and Development (OECD)." https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e.), whereas 6PPD-q has been shown to be relatively stable in water. The half-life for 6PPD-q has been reported to range from 33 hours at 23°C in dechlorinated tap water (Hiki et al. 2021[WZF69GXC] Hiki, Kyoshiro, Kenta Asahina, Kota Kato, Takahiro Yamagishi, Ryo Omagari, Yuichi Iwasaki, Haruna Watanabe, and Hiroshi Yamamoto. 2021. "Acute Toxicity of a Tire Rubber–Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species." Environmental Science & Technology Letters 8 (9): 779–84. https://doi.org/10.1021/acs.estlett.1c00453.) to longer than 47 days (approximately 25% degradation) (DTSC 2022[2M3Z8Z4F] DTSC. 2022. "Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the California Department of Toxic Substances Control (DTSC)." https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf .Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. "Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone." Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. "Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update)." Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.ECHA 2021[Y79Z3ZWV] ECHA. 2021. "Substance Infocard: N-1,3-Dimethylbutyl-N'-Phenyl-p-Phenylenediamine. European Chemicals Agency (ECHA)." April 7, 2021. https://echa.europa.eu/substance-information/-/substanceinfo/100.011.222.). The half-lives of 6PPD and 6PPD-q have been shown to change with temperature and pH and also be affected by sunlight and biological processes (Qian et al. 2023[KRT88TMQ] Qian, Yiguang, Ziyu Chen, Jiahui Wang, Man Peng, Shenghua Zhang, Xiaoyu Yan, Xiaole Han, et al. 2023. "H/D Exchange Coupled with 2H-Labeled Stable Isotope–Assisted Metabolomics Discover Transformation Products of Contaminants of Emerging Concern." Analytical Chemistry 95 (33): 12541–49. https://doi.org/10.1021/acs.analchem.3c02833.Hiki et al. 2021[WZF69GXC] Hiki, Kyoshiro, Kenta Asahina, Kota Kato, Takahiro Yamagishi, Ryo Omagari, Yuichi Iwasaki, Haruna Watanabe, and Hiroshi Yamamoto. 2021. "Acute Toxicity of a Tire Rubber–Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species." Environmental Science & Technology Letters 8 (9): 779–84. https://doi.org/10.1021/acs.estlett.1c00453.Redman et al. 2023[YJE933XT] Redman, Zachary C., Jessica L. Begley, Isabel Hillestad, Brian P. DiMento, Ryan S. Stanton, Alon R. Aguaa, Michael C. Pirrung, and Patrick L. Tomco. 2023. "Reactive Oxygen Species and Chromophoric Dissolved Organic Matter Drive the Aquatic Photochemical Pathways and Photoproducts of 6PPD-Quinone under Simulated High-Latitude Conditions." Environmental Science & Technology 57 (49): 20813–21. https://doi.org/10.1021/acs.est.3c05742.). More research is needed to predict stability under variable environmental conditions (for example, anaerobic, temperature, pH) and matrices (for example, air, water, soil, sediment).

3.3 Transformation Products and Processes

6PPD in Tires and Transformation to 6PPD-q

- Motor vehicle tires contain approximately 1–2% 6PPD (DTSC 2022[2M3Z8Z4F] DTSC. 2022. "Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the California Department of Toxic Substances Control (DTSC)." https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf.).
- The amount of 6PPD in tires decreases with age of the tire.
- 6PPD in solution transforms to 6PPD-q when exposed to ultraviolet radiation.
- 10% of the 6PPD transforms to 6PPD-q when exposed to ozone (Zhao et al. 2023[ENE6F3HC] Zhao, Haoqi Nina, Ximin Hu, Zhenyu Tian, Melissa Gonzalez, Craig A. Rideout, Katherine T. Peter, Michael C. Dodd, and Edward P.

Kolodziej. 2023. “Transformation Products of Tire Rubber Antioxidant 6PPD in Heterogeneous Gas-Phase Ozonation: Identification and Environmental Occurrence.” Environmental Science & Technology 57 (14): 5621–32. https://doi.org/10.1021/acs.est.2c08690.).

- More research is needed to characterize additional PPDs and their transformation products.

The physicochemical properties that impact fate and transport of 6PPD and several transformation products from TRWP (fresh and weathered/aged) have been investigated under various benchtop leaching and sediment incubator conditions (Unice et al. 2015[NS59BGK2] Unice, K.M., Jennifer Bare, Marisa Kreider, and Julie Panko. 2015. “Experimental Methodology for Assessing the Environmental Fate of Organic Chemicals in Polymer Matrices Using Column Leaching Studies and OECD 308 Water/Sediment Systems: Application to Tire and Road Wear Particles.” Science of the Total Environment 533 (July):476–87. https://doi.org/10.1016/j.scitotenv.2015.06.053.). 6PPD-q was estimated to be 10% of the transformation products when 6PPD was exposed to gas-phase ozone in a column study with a total runtime of approximately 50 hours (Zhao et al. 2023[ENE6F3HC] Zhao, Haoqi Nina, Ximin Hu, Zhenyu Tian, Melissa Gonzalez, Craig A. Rideout, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Transformation Products of Tire Rubber Antioxidant 6PPD in Heterogeneous Gas-Phase Ozonation: Identification and Environmental Occurrence.” Environmental Science & Technology 57 (14): 5621–32. https://doi.org/10.1021/acs.est.2c08690.). Ozonation of 6PPD to 6PPD-q has been found to depend on the ozone dose (Seiwert et al. 2022[QDRRVWMW] Seiwert, Bettina, Maolida Nihemaiti, Mareva Troussier, Steffen Weyrauch, and Thorsten Reemtsma. 2022. “Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater.” Water Research 212:118122. https://doi.org/10.1016/j.watres.2022.118122.). Other transformation products have been identified in roadway-impacted environmental samples, and 6PPD-q was found to further transform by ozone (Seiwert et al. 2022[QDRRVWMW] Seiwert, Bettina, Maolida Nihemaiti, Mareva Troussier, Steffen Weyrauch, and Thorsten Reemtsma. 2022. “Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater.” Water Research 212:118122. https://doi.org/10.1016/j.watres.2022.118122.). Unice et al. (Unice et al. 2015[NS59BGK2] Unice, K.M., Jennifer Bare, Marisa Kreider, and Julie Panko. 2015. “Experimental Methodology for Assessing the Environmental Fate of Organic Chemicals in Polymer Matrices Using Column Leaching Studies and OECD 308 Water/Sediment Systems: Application to Tire and Road Wear Particles.” Science of the Total Environment 533 (July):476–87. https://doi.org/10.1016/j.scitotenv.2015.06.053.) investigated 6PPD in all ages of TRWP (up to 3.3 years of simulated aging) where there was a decrease in mass detected as the age increased; the largest difference occurred between fresh (0 years) and 0.1 years of aging. As expected, there was limited leaching of 6PPD to water from the TRWP (i.e., low solubility) and a higher fraction that was released to sediment. This study was conducted prior to the discovery of 6PPD-q.

Rapid photodegradation has been observed when 6PPD (in solution) was exposed to light (especially in the ultraviolet wavelength, which is less than 400 nm) in lab water experiments (Li et al. 2023[3EFLHAGA] Li, Chenguang, Yanlei Zhang, Shiqi Yin, Qin Wang, Yuanyuan Li, Qiang Liu, Liuqingqing Liu, et al. 2023. “First Insights into 6PPD-Quinone Formation from 6PPD Photodegradation in Water Environment.” Journal of Hazardous Materials 459 (October):132127. https://doi.org/10.1016/j.jhazmat.2023.132127.). The photodegradation of 6PPD was observed to be accelerated under acidic conditions due to the increased absorption of long wavelength irradiation by ionized 6PPD. Li et al. (Li et al. 2023[3EFLHAGA] Li, Chenguang, Yanlei Zhang, Shiqi Yin, Qin Wang, Yuanyuan Li, Qiang Liu, Liuqingqing Liu, et al. 2023. “First Insights into 6PPD-Quinone Formation from 6PPD Photodegradation in Water Environment.” Journal of Hazardous Materials 459 (October):132127. https://doi.org/10.1016/j.jhazmat.2023.132127.) identified nine photodegradation products, as identified by ultra-high-performance LC quadrupole time-of-flight MS (UHPLC-QTOF-MS). Reported mechanisms involved in photodegradation include photoexcitation, direct photolysis, self-sensitized photodegradation, and O_2 oxidation (Li et al. 2023[3EFLHAGA] Li, Chenguang, Yanlei Zhang, Shiqi Yin, Qin Wang, Yuanyuan Li, Qiang Liu, Liuqingqing Liu, et al. 2023. “First Insights into 6PPD-Quinone Formation from 6PPD Photodegradation in Water Environment.” Journal of Hazardous Materials 459 (October):132127. https://doi.org/10.1016/j.jhazmat.2023.132127.). Sunlight has been shown to transform 6PPD in water to 6PPD-q with a molar yield of approximately 1.01% within 90 minutes at pH 7.0 under simulated sunlight irradiation (Zhou et al. 2023[QGKYMZ6J] Zhou, Yangjian, Lacuo Yixi, Qingqing Kong, Jianglin Peng, Yanheng Pan, Junlang Qiu, and Xin Yang. 2023. “Sunlight-Induced Transformation of Tire Rubber Antioxidant N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) to 6PPD-Quinone in Water.” Environmental Science & Technology Letters 10 (9): 798–803. https://doi.org/10.1021/acs.estlett.3c00499.). Research suggests that the degradation of 6PPD-q by sunlight is temperature dependent. This is an area of active research, and the formation pathways and mechanisms of formation of these transformation products in the environment are still considered largely unknown. Evaluating the photodegradation pathway will help us understand the fate of 6PPD and 6PPD-q in the environment.

3.4 Volatility

Significant knowledge gaps exist concerning contaminants associated with TRWP that may be present in the gas phase (Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. "Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers." Environmental Pollution 314 (December):120206. https://doi.org/10.1016/j.envpol.2022.120206.). 6PPD and 6PPD-q have low vapor pressures (reported as 3.35×10^{-6} Pa and 2.11×10^{-5} Pa, respectively, at 25°C), which means these chemicals are unlikely to volatilize at typical conditions in the natural environment (Washington State Department of Ecology 2022[K2CG7KTE] Washington State Department of Ecology. 2022. "6PPD in Road Runoff Assessment and Mitigation Strategies." 22-03–020. Olympia, Washington: Environmental Assessment and Water Quality Programs. https://apps.ecology.wa.gov/publications/documents/2203020.pdf.). Due to the tendency for 6PPD to sorb to soil, sediments, and suspended particulates, 6PPD can be present on suspended particles in the air (OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. "Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update)." Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.). Based on an estimated Henry's Law constant of 7.43×10^{-4} at 25°C, 6PPD has moderate potential to volatilize from surface water (OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. "Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update)." Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.). Research summarized by OSPAR (OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. "Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update)." Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.) did not indicate gaseous emissions of 6PPD from tires, but it is unclear whether the absence of these emissions is due to lack of volatility from tires or rapid degradation of 6PPD after release.

3.5 Biological Uptake

The bioconcentration factor (BCF) for 6PPD is predicted to range from 617 to 801 (USEPA n.d.[NU4F8BLR] USEPA. n.d. "CompTox Chemicals Dashboard: 6PPD - Chemical Details." n.d. https://comptox.epa.gov/dashboard/chemical/details/DTXSID9025114.OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. "Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update)." Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.), suggesting a low to moderate potential for bioaccumulation. For 6PPD-q, the bioconcentration factor has been predicted to be 20.9 (USEPA n.d.[H2B8TI2W] USEPA. n.d. "CompTox Chemicals Dashboard: 6PPD-Quinone - Chemical Details." n.d. https://comptox.epa.gov/dashboard/chemical/details/DTXSID301034849.), but more research is needed to confirm its bioavailability and bioaccumulation. For context, the USEPA's Sustainable Futures / P2 Framework Manual has defined the following levels of a chemical's bioaccumulation in *fish*: not bioaccumulative if BCF less than 1,000; bioaccumulative if BCF greater than or equal to 1,000; and very bioaccumulative if BCF greater than or equal to 5,000 (USEPA 2012[METDU9H5] USEPA. 2012. "7. Estimating Persistence, Bioaccumulation, and Toxicity Using the PBT Profiler." EPA-748-B12-001. Sustainable Futures / P2 Framework Manual. https://www.epa.gov/sites/default/files/2015-05/documents/07.pdf.).

BCFs of 6PPD-q in rainbow trout were calculated at 2.9, 19, 25, and 17.2 liters per kg (L/kg) at water concentrations of 0.8, 3, 12, and 25 µg/L, respectively, and concentrations of 6PPD in tissue were similar at the same water concentrations (Nair et al. 2023[9V5ES4MI] Nair, Pranav, Jianxian Sun, Linna Xie, Lisa Kennedy, Derek Kozakiewicz, Sonya Kleywegt, Chunyan Hao, et al. 2023. "In Process: Synthesis and Toxicity Evaluation of Tire Rubber–Derived Quinones." Preprint. Chemistry. https://doi.org/10.26434/chemrxiv-2023-pmxvc.). These BCF factors are 1 to 2 orders of magnitude lower than other contaminants with similar K_{ow} values, suggesting that 6PPD-q may be rapidly metabolized in rainbow trout (and other susceptible salmonids). Several studies have demonstrated moderate uptake of 6PPD and 6PPD-q in zebrafish from laboratory water, with uptake levels generally higher with 6PPD compared to 6PPD-q (Fang et al. 2023[FFFKR3MY] Fang, Chanlin, Liya Fang, Shanshan Di, Yundong Yu, Xinquan Wang, Caihong Wang, and Yuanxiang Jin. 2023. "Characterization of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD)-Induced Cardiotoxicity in Larval Zebrafish (Danio Rerio)." Science of the Total Environment 882 (July):163595. https://doi.org/10.1016/j.scitotenv.2023.163595.Grasse et al. 2023[WJHX578U] Grasse, Nico, Bettina Seiwert, Riccardo Massei, Stefan Scholz, Qiuguo Fu, and Thorsten Reemtsma. 2023. “Uptake and Biotransformation of the Tire Rubber–Derived Contaminants 6-PPD and 6-PPD Quinone in the Zebrafish Embryo (Danio rerio).” Environmental Science & Technology 57 (41): 15598–607. https://doi.org/10.1021/acs.est.3c02819.Zhang et al. 2023[3FCHDXBN] Zhang, Shu-Yun, Xiufeng Gan, Baoguo Shen, Jian Jiang, Huimin Shen, Yuhang Lei, Qiuju Liang, et al. 2023. “6PPD and Its Metabolite 6PPDQ Induce Different Developmental Toxicities and Phenotypes in Embryonic Zebrafish.” Journal of Hazardous Materials 455 (August):131601. https://doi.org/10.1016/j.jhazmat.2023.131601.). Fang et al. (Fang et al. 2022[69WA3QCX] Fang, Chanlin, Liya Fang, Shanshan Di, Yundong Yu, Xinquan Wang, Caihong Wang, and Yuanxiang Jin. 2022. “Not yet Peer Reviewed: Bioaccumulation of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and Its Potential Cardiotoxicity in Larval Zebrafish (Danio Rerio).” SSRN Scholarly Paper. Rochester, NY. https://papers.ssrn.com/abstract=4166691.) estimated accumulation factors for 6PPD in zebrafish larvae of 265 and 103 based on concentrations in water of 1.35 and 28.2 µg/L, respectively. Grasse et al. (Grasse et al. 2023[WJHX578U] Grasse, Nico, Bettina Seiwert, Riccardo Massei, Stefan Scholz, Qiuguo Fu, and Thorsten Reemtsma. 2023. “Uptake and Biotransformation of the Tire Rubber–Derived Contaminants 6-PPD and 6-PPD Quinone in the Zebrafish Embryo (Danio rerio).” Environmental Science & Technology 57 (41): 15598–607. https://doi.org/10.1021/acs.est.3c02819.) estimated accumulation concentration factors of 6PPD and 6PPD-q in zebrafish embryo over 96 hours of exposure. Analytically determined exposure concentrations were 1.28 and 6.3 µg/L for 6PPD and 4.8, 11.3, and 20.9 µg/L for 6PPD-q. At 72 hours (when 6PPD reached steady state in all experiments), the concentration factors ranged from 142 to 2,447 for 6PPD. 6PPD-q never reached steady state; however, the concentration factors associated with the highest internal concentrations (at 48 hours) ranged from 75 to 216. The mean maximum concentration factor (135.8 ± 64.9) occurred between 24 and 48 hours before decreasing after 96 hours (55.5 ± 29.84). Overall, the decrease in internal concentration of 6PPD-q suggested that biotransformation reactions were occurring in the zebrafish embryos. Specifically, semi-quantification methods found that 50% of 6PPD and 95% 6PPD-q were detoxified through biotransformation in the zebrafish embryos within 96 hours of exposure, suggesting that zebrafish embryos have greater tolerance to 6PPD-q than other species (Grasse et al. 2023[WJHX578U] Grasse, Nico, Bettina Seiwert, Riccardo Massei, Stefan Scholz, Qiuguo Fu, and Thorsten Reemtsma. 2023. “Uptake and Biotransformation of the Tire Rubber–Derived Contaminants 6-PPD and 6-PPD Quinone in the Zebrafish Embryo (Danio rerio).” Environmental Science & Technology 57 (41): 15598–607. https://doi.org/10.1021/acs.est.3c02819.).

Biological Uptake

- 6PPD is predicted to have a low to moderate potential for bioaccumulation.
- Research supports the biological uptake of both 6PPD and 6PPD-q.
- See Section 2: Effects Characterization and Toxicity for more information on the mode of action.
- More research is needed to confirm bioaccumulation of 6PPD-q.

Uptake studies published to date have occurred primarily in lab settings. Additional studies are needed to evaluate biological uptake for conditions outside the lab where variability in environmental (and stormwater) conditions over the range of concentrations measured in the field is considered and incorporated.

S.-Y. Zhang et al. (Zhang et al. 2023[3FCHDXBN] Zhang, Shu-Yun, Xiufeng Gan, Baoguo Shen, Jian Jiang, Huimin Shen, Yuhang Lei, Qiuju Liang, et al. 2023. “6PPD and Its Metabolite 6PPDQ Induce Different Developmental Toxicities and Phenotypes in Embryonic Zebrafish.” Journal of Hazardous Materials 455 (August):131601. https://doi.org/10.1016/j.jhazmat.2023.131601.) observed statistically significant accumulation of 6PPD and 6PPD-q in zebrafish embryos following exposures of 0.2 and 0.8 mg/L of each compound from 8 to 120 hours post fertilization, with 6PPD having a greater magnitude of accumulation. There was no statistically significant accumulation of either compound at an exposure concentration of 0.025 mg/L. With the exception of the minimum exposure concentrations in Fang et al. (Zhang et al. 2023[3FCHDXBN] Zhang, Shu-Yun, Xiufeng Gan, Baoguo Shen, Jian Jiang, Huimin Shen, Yuhang Lei, Qiuju Liang, et al. 2023. “6PPD and Its Metabolite 6PPDQ Induce Different Developmental Toxicities and Phenotypes in Embryonic Zebrafish.” Journal of Hazardous Materials 455 (August):131601. https://doi.org/10.1016/j.jhazmat.2023.131601.) and Grasse et al. (Grasse et al. 2023[WJHX578U] Grasse, Nico, Bettina Seiwert, Riccardo Massei, Stefan Scholz, Qiuguo Fu, and Thorsten Reemtsma. 2023. “Uptake and Biotransformation of the Tire Rubber–Derived Contaminants 6-PPD and 6-PPD Quinone in the Zebrafish Embryo (Danio rerio).” Environmental Science & Technology 57 (41): 15598–607. https://doi.org/10.1021/acs.est.3c02819.), these experimental exposure levels were higher than those detected in surface water. Uptake has also been detected in lettuce in hydroponic solution in a laboratory (Castan et al. 2023[3RBDETGD] Castan, Stephanie, Anya Sherman, Ruoting Peng, Michael T. Zumstein, Wolfgang Wanek, Thorsten Hüffer, and Thilo Hofmann. 2023. “Uptake, Metabolism, and Accumulation of Tire Wear Particle–Derived Compounds in

Lettuce." Environmental Science & Technology 57 (1): 168–78. https://doi.org/10.1021/acs.est.2c05660.) and in fish purchased at a local market in China (Ji et al. 2022[LDBNLUJS] Ji, Jiawen, Changsheng Li, Bingjie Zhang, Wenjuan Wu, Jianli Wang, Jianhui Zhu, Desheng Liu, et al. 2022. "Exploration of Emerging Environmental Pollutants 6PPD and 6PPDQ in Honey and Fish Samples." Food Chemistry 396:133640. https://doi.org/10.1016/j.foodchem.2022.133640.).

Another study assessed the toxicity and accumulation of 6PPD-q at environmentally relevant concentrations in three different fish species (Hiki and Yamamoto 2022[VQE4EZWI] Hiki, Kyoshiro, and Hiroshi Yamamoto. 2022. "The Tire-Derived Chemical 6PPD-Quinone Is Lethally Toxic to the White-Spotted Char Salvelinus leucomaenis pluvius but Not to Two Other Salmonid Species." Environmental Science & Technology Letters 9 (12): 1050–55. https://doi.org/10.1021/acs.estlett.2c00683.). The concentration of 6PPD-q in the target tissues (brain and gills) increased with exposure concentration in the most sensitive species tested (*S. leucomaenis pluvius*), yielding internal median lethal concentration (ILC_{50}) estimates of "…4.0 µg/kg wet weight in brain and 6.2 µg/kg wet weight in gill for *S. leucomaenis pluvius*, while the tissue concentration of 6PPD-q in the two other non-surviving species (*S. curilus* and *O. masou masou*) exceeded the ILC_{50} value for *S. leucomaenis pluvius"* (Hiki and Yamamoto 2022[VQE4EZWI] Hiki, Kyoshiro, and Hiroshi Yamamoto. 2022. "The Tire-Derived Chemical 6PPD-Quinone Is Lethally Toxic to the White-Spotted Char Salvelinus leucomaenis pluvius but Not to Two Other Salmonid Species." Environmental Science & Technology Letters 9 (12): 1050–55. https://doi.org/10.1021/acs.estlett.2c00683.).

As stated by Grasse et al. (Grasse et al. 2023[WJHX578U] Grasse, Nico, Bettina Seiwert, Riccardo Massei, Stefan Scholz, Qiuguo Fu, and Thorsten Reemtsma. 2023. "Uptake and Biotransformation of the Tire Rubber–Derived Contaminants 6-PPD and 6-PPD Quinone in the Zebrafish Embryo (Danio rerio)." Environmental Science & Technology 57 (41): 15598–607. https://doi.org/10.1021/acs.est.3c02819.), "…[c]ross-species internal concentrations and biotransformation of [6PPD-q] provide an important contribution to the characterization of species-specific toxicity" and it "is still unknown whether toxicokinetics (TK) plays a role in the observed species-specific [6PPD-q] toxicity." The toxicological significance of any accumulation is currently unknown (see Section 8.1). See Section 2.3: Potential for Bioaccumulation and Adduct Formation in the toxicity section for more information about the mode of action.

3.6 Biodegradation

More research is needed to understand the biodegradation processes of tires, TRWP), and related contaminants. Whole tires, tire debris, and TRWP are all potential sources of 6PPD and 6PPD-q in the environment. Biodegradation of tire-related compounds, including 6PPD and 6PPD-q, may occur within the TRWP itself or in the environment after leaching (Calarnou et al. 2023[2RFJ5BLH] Calarnou, Laurie, Mounir Traïkia, Martin Leremboure, Lucie Malosse, Séverin Dronet, Anne-Marie Delort, Pascale Besse-Hoggan, and Boris Eyheraguibel. 2023. "Assessing Biodegradation of Roadway Particles via Complementary Mass Spectrometry and NMR Analyses." Science of the Total Environment 900 (November):165698. https://doi.org/10.1016/j.scitotenv.2023.165698.). Some studies on the biodegradation of TWP or tire-related compounds have been done; however, these did not assess the leaching or biodegradation of 6PPD or 6PPD-q (Saifur and Gardner 2023[9WDMIAY3] Saifur, Sumaiya, and Courtney M Gardner. 2023. "Evaluation of Stormwater Microbiomes for the Potential Biodegradation of Tire Wear Particle Contaminants." Journal of Applied Microbiology 134 (5): lxad086. https://doi.org/10.1093/jambio/lxad086.Klun, Rozman, and Kalčíková 2023[VS4VQ4A6] Klun, Barbara, Ula Rozman, and Gabriela Kalčíková. 2023. "Environmental Aging and Biodegradation of Tire Wear Microplastics in the Aquatic Environment." Journal of Environmental Chemical Engineering 11 (5): 110604. https://doi.org/10.1016/j.jece.2023.110604.).

A recent study by Foscari et al. (Foscari et al. 2024[JBUK7E3P] Foscari, Aurelio, Bettina Seiwert, Daniel Zahn, Matthias Schmidt, and Thorsten Reemtsma. 2024. "Leaching of Tire Particles and Simultaneous Biodegradation of Leachables." Water Research 253 (April):121322. https://doi.org/10.1016/j.watres.2024.121322.) evaluated biodegradation during and following leaching of suspended cryo-milled tire tread (CMTT). The first experiment (Phase I) simulated heterogeneous environmental conditions consisting of suspended CMTT, an aqueous phase (i.e., leaching), and microorganisms (i.e., biodegradation). The second experiment (Phase II) assessed just the biodegradation of the particle-free supernatant. To assess the impact of biotic versus abiotic degradation processes, Phase I experiments included test vessels without sludge, and the subsequent Phase II experiments included the supernatant of the sludge-free vessels. The authors concluded that microbial degradation of 6PPD was only observed in Phase I and suggested that abiotic transformation via hydrolysis was dominant in Phase II. In contrast, 6PPD-q showed a strong increasing trend in both sets of Phase I test vessels at the beginning of the study before leveling out in concentration, suggesting that an equilibrium was reached between 6PPD-q released or transformation of

6PPD to 6PPD-q. The equilibrium concentration was lower in the sludge test vessels, suggesting that microbial degradation was significant. Similarly, in Phase II, the sludge test supernatant had a faster decrease in concentration compared to the sludge-free test supernatant, but the observed decrease in concentration in the sludge-free test supernatant supported the impact of abiotic transformation of leached 6PPD-q. These study designs added to the experimental evidence that 6PPD-q is more stable than 6PPD.

6PPD-q has been shown to be formed in wetted soil from 6PPD, presumably by bacteria (Qian et al. 2023[KRT88TMQ] Qian, Yiguang, Ziyu Chen, Jiahui Wang, Man Peng, Shenghua Zhang, Xiaoyu Yan, Xiaole Han, et al. 2023. “H/D Exchange Coupled with 2H-Labeled Stable Isotope–Assisted Metabolomics Discover Transformation Products of Contaminants of Emerging Concern.” Analytical Chemistry 95 (33): 12541–49. https://doi.org/10.1021/acs.analchem.3c02833.). Calarnou et al. (Calarnou et al. 2023[2RFJ5BLH] Calarnou, Laurie, Mounir Traïkia, Martin Leremboure, Lucie Malosse, Séverin Dronet, Anne-Marie Delort, Pascale Besse-Hoggan, and Boris Eyheraguibel. 2023. “Assessing Biodegradation of Roadway Particles via Complementary Mass Spectrometry and NMR Analyses.” Science of the Total Environment 900 (November):165698. https://doi.org/10.1016/j.scitotenv.2023.165698.) investigated the biodegradation of TRWP (of which TWP is a component) and several tire-related compounds, including 6PPD-q. They found a significant decrease in 6PPD-q in the presence of *S. phaeofaciens* (NRRL 8092) (Calarnou et al. 2023[2RFJ5BLH] Calarnou, Laurie, Mounir Traïkia, Martin Leremboure, Lucie Malosse, Séverin Dronet, Anne-Marie Delort, Pascale Besse-Hoggan, and Boris Eyheraguibel. 2023. “Assessing Biodegradation of Roadway Particles via Complementary Mass Spectrometry and NMR Analyses.” Science of the Total Environment 900 (November):165698. https://doi.org/10.1016/j.scitotenv.2023.165698.). Similarly, Xu et al. (Xu et al. 2023[4P2E4JLJ] Xu, Qiao, Gang Li, Li Fang, Qian Sun, Ruixia Han, Zhe Zhu, and Yong-Guan Zhu. 2023. “Enhanced Formation of 6PPD-Q during the Aging of Tire Wear Particles in Anaerobic Flooded Soils: The Role of Iron Reduction and Environmentally Persistent Free Radicals.” Environmental Science & Technology, March. https://doi.org/10.1021/acs.est.2c08672.) suggested that the decrease of 6PPD-q in soil under wet conditions was attributable to biodegradation compared to anaerobic flooded conditions (Xu et al. 2023[4P2E4JLJ] Xu, Qiao, Gang Li, Li Fang, Qian Sun, Ruixia Han, Zhe Zhu, and Yong-Guan Zhu. 2023. “Enhanced Formation of 6PPD-Q during the Aging of Tire Wear Particles in Anaerobic Flooded Soils: The Role of Iron Reduction and Environmentally Persistent Free Radicals.” Environmental Science & Technology, March. https://doi.org/10.1021/acs.est.2c08672.). Better understanding of the biodegradation and the fate of 6PPD and 6PPD-q is a major data gap, including validating laboratory study outcomes relative to observations, measurements, and other data from the natural and built environments.

Section 4 Tables

Recent studies have investigated the occurrence of 6PPD and 6PPD-q in various environmental matrices across the globe. Section 4 summarizes the current state of knowledge but is not intended to represent a comprehensive review of occurrence data. The following tables, organized by medium, were compiled as an index of peer-reviewed studies that this ITRC team was aware of as of March 2024.

Table Number and Title	**Link to PDF**	**Link to Executable File (Word Processor Format)**
4-1 Surface water		
4-2 Stormwater		
4-3 Wastewater, water treatment plants, and tap water		
4-4 Groundwater		
4-5 Roadside soil		
4-6 Sediment		
4-7 Outdoor air		
4-8 Road dust and roadside snow		
4-9 Indoor and nonroad settled dust		
4-10 Aquatic organisms and food		

PDF versions of each table are provided for the reader to view information in a visual format that is consistent across browsers and platforms. Executable files are provided to allow readers to sort information by the column of their choice, but may appear different visually depending on the software used to view this file. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

4 Occurrence, Fate, Transport, and Exposure Pathways

This chapter reviews the fate, transport, and occurrence of tire particles containing 6PPD and 6PPD-q in the environment. More research is needed on the fate, transport, occurrence, and persistence of 6PPD-q once released from tires and other rubber products to inform toxic reduction actions.

In the context of what is known regarding 6PPD and 6PPD-q occurrence, this section also discusses different pathways by which human or ecological receptors may be exposed to 6PPD and 6PPD-q.

Recent studies have investigated the occurrence of 6PPD and 6PPD-q in various environmental matrices across the globe. This section summarizes the current state of knowledge but is not intended to represent a comprehensive review of occurrence data. Additionally, reliability evaluation and comparison of analytical methods have not been performed for studies discussed in this document. The following index presents tables, organized by medium type, where summaries of peer-reviewed studies can be found.

Table	Media Type	Available Publications	Link to PDF	Link to Executable File (Word Processor Format)
4-1	Surface Water	12		
4-2	Stormwater	9		
4-3	Wastewater, water treatment plants, and tap water	8		
4-4	Groundwater	1		
4-5	Roadside soil	1		
4-6	Sediment	3		
4-7	Outdoor air	8		
4-8	Road dust and roadside snow	7		
4-9	Indoor and nonroad settled dust	6		
4-10	Aquatic organisms and food	9		

Note: PDF versions of each table are provided for the reader to view information in a visual format that is consistent across browsers and platforms. Executable files are provided to allow readers to sort information by the column of their choice, but may appear different visually depending on the software used to view this file. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

The studies listed in these tables are from peer-reviewed literature and do not capture the preliminary monitoring efforts by state, tribal, and local agencies. Some of these studies also measured a range of other PPDs and transformation products, which are not addressed in this document. Recent efforts have been made to summarize occurrence data in peer-reviewed literature (Mayer et al. 2024[ZTAVFS9G] Mayer, Paul, Kelly Moran, Ezra Miller, Susanne Brander, Stacey Harper, Manuel Garcia-Jaramillo, Victor Carrasco-Navarro, et al. 2024. “Where the Rubber Meets the Road: Emerging Environmental Impacts of Tire Wear Particles and Their Chemical Cocktails.” Science of The Total Environment 927 (June):171153.

https://doi.org/10.1016/j.scitotenv.2024.171153.Benis et al. 2023[XXB6GPKJ] Benis, Khaled Zoroufchi, Ali Behnami, Shahab Minaei, Markus Brinkmann, Kerry N. McPhedran, and Jafar Soltan. 2023. “Environmental Occurrence and Toxicity of 6PPD Quinone, an Emerging Tire Rubber–Derived Chemical: A Review.” Environmental Science & Technology Letters, September.

https://doi.org/10.1021/acs.estlett.3c00521.Chen et al. 2023[39YBXWMI] Chen, Xiaoli, Tao He, Xinlu Yang, Yijing Gan, Xian Qing, Jun Wang, and Yumei Huang. 2023. “Analysis, Environmental Occurrence, Fate and Potential Toxicity of Tire Wear Compounds 6PPD and 6PPD-Quinone.” Journal of Hazardous Materials 452 (June):131245.

https://doi.org/10.1016/j.jhazmat.2023.131245.Hua and Wang 2023[3FVXFWPE] Hua, Xin, and Dayong Wang. 2023. “Tire-Rubber Related Pollutant 6-PPD Quinone: A Review of Its Transformation, Environmental Distribution, Bioavailability, and Toxicity.” Journal of Hazardous Materials 459:132265. https://doi.org/10.1016/j.jhazmat.2023.132265.). Given the regional-specific conditions that impact the fate and transport of 6PPD-q (and TRWP and 6PPD), considerations should be made when interpreting these data. Further, the sampling and analytical methods used should be reviewed (for example, collecting and storing material, use of a commercially available standard) given the continued advancements made in quantifying this compound in environmental matrices (see also Section 5: Measuring, Mapping, and Modeling). The transport pathways and exposure risk to aquatic, terrestrial, and human systems is poorly understood (see Section 8.2).

Occurrence, Fate, and Transport

- Friction between the road and a tire during driving, braking, and turning leads to the generation and emission of TRWP.
- TRWP are carried beyond the road surface via stormwater or other pathways, such as air dispersion and deposition, and can enter aquatic or terrestrial systems.
- Fate and transport mechanisms that control occurrence vary among landscapes, geography, climate, and environmental conditions.
- The occurrence and persistence of 6PPD, 6PPD-q, TWP, and TRWP in the environment is poorly understood.
- More research is needed to standardize methods and fill in data gaps because initial studies have only scratched the surface.
- In addition, reused and recycled whole tires are a potential source of 6PPD and 6PPD-q, so more research is needed to understand the half-life of 6PPD in tires across varying environments (marine, freshwater, and terrestrial, etc.).

Understanding the mechanisms of toxic exposure, including the duration and mode of action, is needed to characterize the environmental risk (see also Section 2: Effects Characterization and Toxicity).

6PPD and 6PPD-q can be released to the environment from whole tires, TRWP, and reused/recycled/repurposed consumer products. For example, recycled tires can be used to modify asphalt, and 6PPD and 6PPD-q can be released from or sorbed to that material on the roadways (Lokesh et al. 2023[LBXMIT5W] Lokesh, Srinidhi, Siththarththan Arunthavabalan, Elie Hajj, Edgard Hitti, and Yu Yang. 2023. “Investigation of 6PPD-Quinone in Rubberized Asphalt Concrete Mixtures.” ACS Environmental Au, July. https://doi.org/10.1021/acsenvironau.3c00023.). Although whole-tire reuse and disposal has not been the main focus of the available occurrence data, it is important to note that more research is needed to investigate whole tires as a continued source of 6PPD and 6PPD-q. Whole tires are reused in many ways, such as marine reef structures, boat bumpers on docks, and landscaping materials. Regulation and guidance to provide proper storage, transport, and disposal of tires varies across states and should be evaluated to address 6PPD and 6PPD-q exposure concerns. The following subsections, which discuss environmental media, do not discuss whole-tire pollution, tire piles, or tires submerged or on land; these tires represent a source of 6PPD and 6PPD-q that is not well investigated or understood. See Section 1.2 for a brief discussion of tire life cycle and both Section 1.2 and Section 8.2 for discussion and summary of information needs and data gaps regarding sources of 6PPD and 6PPD-q.

TRWP are heterogeneous particles generated at the road surface by the friction of the tire on the road surface during driving. TRWP can be dispersed into the air or onto the roadway and includes wear particles from both the tire tread (i.e., TWP) and the road surface (i.e., road component) (Baensch-Baltruschat et al. 2020[SG7DEPVC] Baensch-Baltruschat, Beate, Birgit Kocher, Friederike Stock, and Georg Reifferscheid. 2020. “Tyre and Road Wear Particles (TRWP)—A Review of Generation, Properties, Emissions, Human Health Risk, Ecotoxicity, and Fate in the Environment.” Science of the Total Environment 733

(September):137823. https://doi.org/10.1016/j.scitotenv.2020.137823.). The road-wear component of TRWP have an impact on the characteristics and transport of the particles in the environment (Kreider et al. 2010[QCJY4JI9] Kreider, Marisa L., Julie M. Panko, Britt L. McAtee, Leonard I. Sweet, and Brent L. Finley. 2010. “Physical and Chemical Characterization of Tire-Related Particles: Comparison of Particles Generated Using Different Methodologies.” Science of the Total Environment 408 (3): 652–59. https://doi.org/10.1016/j.scitotenv.2009.10.016.). Elsewhere in this document TWP will be referred to as the tire fraction of the overall TRWP. See the Tire and Road-Wear Particle Background and Related Terms inset for more details.

An estimated 4.7 kg/year (equivalent to 10.3 pounds/year) per capita of TRWP is released to the environment in the United States (Kole et al. 2017[NZZMY6WC] Kole, Pieter Jan, Ansje J. Löhr, Frank G. A. J. Van Belleghem, and Ad M. J. Ragas. 2017. “Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment.” International Journal of Environmental Research and Public Health 14 (10): 1265. https://doi.org/10.3390/ijerph14101265.). The mass loading of 6PPD and 6PPD-q in the environment is expected to vary spatially given the differences in 6PPD-q and TRWP release rates, tire manufacturing, tire age, and vehicle attributes and operation (for example, weight, speed, and braking) (Kreider et al. 2010[QCJY4JI9] Kreider, Marisa L., Julie M. Panko, Britt L. McAtee, Leonard I. Sweet, and Brent L. Finley. 2010. “Physical and Chemical Characterization of Tire-Related Particles: Comparison of Particles Generated Using Different Methodologies.” Science of the Total Environment 408 (3): 652–59. https://doi.org/10.1016/j.scitotenv.2009.10.016.Baensch-Baltruschat et al. 2020[SG7DEPVC] Baensch-Baltruschat, Beate, Birgit Kocher, Friederike Stock, and Georg Reifferscheid. 2020. “Tyre and Road Wear Particles (TRWP)—A Review of Generation, Properties, Emissions, Human Health Risk, Ecotoxicity, and Fate in the Environment.” Science of the Total Environment 733 (September):137823. https://doi.org/10.1016/j.scitotenv.2020.137823.Wagner et al. 2018[4UCJI65Q] Wagner, Stephan, Thorsten Hüffer, Philipp Klöckner, Maren Wehrhahn, Thilo Hofmann, and Thorsten Reemtsma. 2018. “Tire Wear Particles in the Aquatic Environment — A Review on Generation, Analysis, Occurrence, Fate and Effects.” Water Research 139 (August):83–100. https://doi.org/10.1016/j.watres.2018.03.051.). Further, once released to roads and parking lots, the fate and transport of 6PPD-q and TRWP depends on many factors including tire particle characteristics (for example, size, shape, and density), road characteristics, regional weather, and environmental characteristics (Unice et al. 2019[TLVMH289] Unice, K.M., M.P. Weeber, M.M. Abramson, R.C.D. Reid, J.A.G. van Gils, A.A. Markus, A.D. Vethaak, and J.M. Panko. 2019. “Characterizing Export of Land-Based Microplastics to the Estuary — Part I: Application of Integrated Geospatial Microplastic Transport Models to Assess Tire and Road Wear Particles in the Seine Watershed.” Science of the Total Environment 646:1639–49. https://doi.org/10.1016/j.scitotenv.2018.07.368.Wagner et al. 2018[4UCJI65Q] Wagner, Stephan, Thorsten Hüffer, Philipp Klöckner, Maren Wehrhahn, Thilo Hofmann, and Thorsten Reemtsma. 2018. “Tire Wear Particles in the Aquatic Environment — A Review on Generation, Analysis, Occurrence, Fate and Effects.” Water Research 139 (August):83–100. https://doi.org/10.1016/j.watres.2018.03.051.). Road characteristics include traffic amount and type, vehicle type (for example, car, truck, electric vehicle), road surface, road size, road type (for example, local roads vs. highways), grade (steepness), and roadside slope and type (Wagner et al. 2018[4UCJI65Q] Wagner, Stephan, Thorsten Hüffer, Philipp Klöckner, Maren Wehrhahn, Thilo Hofmann, and Thorsten Reemtsma. 2018. “Tire Wear Particles in the Aquatic Environment — A Review on Generation, Analysis, Occurrence, Fate and Effects.” Water Research 139 (August):83–100. https://doi.org/10.1016/j.watres.2018.03.051.). Watershed characteristics and stormwater conveyance are expected to influence the transport of TRWP and 6PPD-q, including attributes such as roadside slope and conveyance (curb and gutter, grass ditch, paved ditch, presence/absence of stormwater drain and pipe, presence/absence of stormwater filtration or catchment), land use, seasonal traffic trends, seasonal weather patterns, regional stormwater and wastewater management practices, soil types, watershed size, and flood risk. Section 5.3.5.3 describes how these characteristics can be used in the USEPA Visualizing Ecosystem Land Management Assessments (VELMA) tool to identify potential hotspots of 6PPD-q contamination as a means of prioritizing locations to investigate and potentially mitigate impacts to the environment. Section 5: Measuring, Mapping, and Modeling provides additional discussion on how these factors can be measured, mapped, and used in models of TRWP, 6PPD, and 6PPD-q fate and transport.

Although TRWP containing 6PPD are mostly transported by surface water and stormwater, TRWP are also released and transported by atmospheric processes. In a road dust and sediment study (Klöckner et al. 2020[9B7NCVNZ] Klöckner, Philipp, Bettina Seiwert, Paul Eisentraut, Ulrike Braun, Thorsten Reemtsma, and Stephan Wagner. 2020. “Characterization of Tire and Road Wear Particles from Road Runoff Indicates Highly Dynamic Particle Properties.” Water Research 185 (October):116262. https://doi.org/10.1016/j.watres.2020.116262.), more coarse particles were found closer to the roadway, while smaller particles were more readily transported away from the road. As mentioned previously, TRWP are generally found more frequently and in higher quantities near roadways and in urban areas, particularly those with high-volume traffic patterns (Unice, Kreider, and Panko 2013[EU6MQU9K] Unice, K.M., Marisa L. Kreider, and Julie M. Panko. 2013. “Comparison of Tire and Road Wear Particle Concentrations in Sediment for Watersheds in France, Japan, and the United States by Quantitative Pyrolysis GC/MS Analysis.” Environmental Science & Technology 47 (15): 8138–47. https://doi.org/10.1021/es400871j.). Roadside vegetation and solid structures have been shown to mitigate the dispersion of airborne particles near roadways (Baldauf 2016[I5U5RA8E] Baldauf, Richard W. 2016. “Recommendations for Constructing Roadside Vegetation Barriers to Improve Near-Road Air Quality.” 321772. https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&dirEntryId=321772&simpleSearch=1&searchAll=Recommendations+for+constructing+roadside+vegetation+barriers+to+improve+near+road+air+quality.Greenwald, Sarnat, and Fuller 2024[ECNMWXRZ] Greenwald, Roby, Jeremy A. Sarnat, and Christina H. Fuller. 2024. “The Impact of Vegetative and Solid Roadway Barriers on Particulate Matter Concentration in Urban Settings.” PLOS ONE 19 (1): e0296885. https://doi.org/10.1371/journal.pone.0296885.) (see also Section 6.4: Air Particulate Migration). By volume, most TRWP are less than 100 µm (Kreider et al. 2010[QCJY4JI9] Kreider, Marisa L., Julie M. Panko, Britt L. McAtee, Leonard I. Sweet, and Brent L. Finley. 2010. “Physical and Chemical Characterization of Tire-Related Particles: Comparison of Particles Generated Using Different Methodologies.” Science of the Total Environment 408 (3): 652–59. https://doi.org/10.1016/j.scitotenv.2009.10.016.). TRWP have been observed in ambient air monitoring stations in the $PM_{2.5}$ fraction (Unice et al. 2019[TLVMH289] Unice, K.M., M.P. Weeber, M.M. Abramson, R.C.D. Reid, J.A.G. van Gils, A.A. Markus, A.D. Vethaak, and J.M. Panko. 2019. “Characterizing Export of Land-Based Microplastics to the Estuary — Part I: Application of Integrated Geospatial Microplastic Transport Models to Assess Tire and Road Wear Particles in the Seine Watershed.” Science of the Total Environment 646:1639–49. https://doi.org/10.1016/j.scitotenv.2018.07.368.Baensch-Baltruschat et al. 2020[SG7DEPVC] Baensch-Baltruschat, Beate, Birgit Kocher, Friederike Stock, and Georg Reifferscheid. 2020. “Tyre and Road Wear Particles (TRWP)—A Review of Generation, Properties, Emissions, Human Health Risk, Ecotoxicity, and Fate in the Environment.” Science of the Total Environment 733 (September):137823. https://doi.org/10.1016/j.scitotenv.2020.137823.Panko et al. 2019[H57M387X] Panko, Julie M., Kristen M. Hitchcock, Gary W. Fuller, and David Green. 2019. “Evaluation of Tire Wear Contribution to PM2.5 in Urban Environments.” Atmosphere 10 (2): 99. https://doi.org/10.3390/atmos10020099.Panko et al. 2013[UQNTNRM4] Panko, Julie M., Jennifer Chu, Marisa L. Kreider, and Ken M. Unice. 2013. “Measurement of Airborne Concentrations of Tire and Road Wear Particles in Urban and Rural Areas of France, Japan, and the United States.” Atmospheric Environment 72 (June):192–99. https://doi.org/10.1016/j.atmosenv.2013.01.040.). Because TRWP (or TWP) are categorized as microplastics, they are also discussed in Section 2.2.2.1 of the ITRC Microplastics Guidance Document (ITRC 2023[LLWEHVCX] ITRC. 2023. “Microplastics.” Washington, D.C.: Interstate Technology & Regulatory Council, MP Team. https://mp-1.itrcweb.org.).

Specific surface area is a key indicator of potential for release and/or transformation of chemicals contained in environmental particles like 6PPD in TRWP (Moran et al. 2023[9FSZ84KX] Moran, Kelly, Alicia Gilbreath, Miguel Mendez, Diana Lin, and Rebecca Sutton. 2023. “Tire Wear: Emissions Estimates and Market Insights to Inform Monitoring Design.” SFEI Technical Report SFEI Contribution #1049. Richmond, CA: San Francisco Estuary Institute.). For example, copper has been shown to leach from vehicle brake-pad wear particles at a high rate compared to some high-copper reference materials, likely because the wear-particle surface area is more than 150 times greater than the powdered reference materials (Hur, Yim, and Schlautman 2003[XN47T74F] Hur, Jin, Soobin Yim, and Mark A. Schlautman. 2003. “Copper Leaching from Brake Wear Debris in Standard Extraction Solutions. Electronic Supplementary Information (ESI) Available: Thermodynamic Equilibrium Speciation Results from the Geochemical Model MINTEQ. See Http://Www.Rsc.Org/Suppdata/Em/B3/B303820c/.” Journal of Environmental Monitoring 5 (5): 837. https://doi.org/10.1039/b303820c.). The greater the surface area, the greater the potential for formation of transformation products, including 6PPD-q, and for chemical release from the particle into the environment. Scanning electron micrographs (such as Figure 1-6) and focused ion beam images of TRWP reveal rough, irregular surfaces, which suggest that TRWP may have high surface areas (Kreider et al. 2010[QCJY4JI9] Kreider, Marisa L., Julie M. Panko, Britt L. McAtee, Leonard I. Sweet, and Brent L. Finley. 2010. “Physical and Chemical Characterization of Tire-Related Particles: Comparison of Particles Generated Using Different Methodologies.” Science of the Total Environment 408 (3): 652–59. https://doi.org/10.1016/j.scitotenv.2009.10.016.Milani et al. 2004[6N5I8G73] Milani, M., F.P. Pucillo, M. Ballerini, M. Camatini, M. Gualtieri, and S. Martino. 2004. “First Evidence of Tyre Debris Characterization at the Nanoscale by Focused Ion Beam.” Materials Characterization 52 (4–5): 283–88. https://doi.org/10.1016/j.matchar.2004.06.001.). Surface area typically has an inverse correlation with particle size (that is, smaller particles typically have greater total surface area per unit mass). The absence of TRWP surface-area data means that the portion of the particle size distribution (and associated transport pathway) with the greatest potential to release tire-related chemicals, including 6PPD and 6PPD-q, into the environment is unknown.

Modeling in the Seattle area found that the correlation between the presence of 6PPD-q in stormwater and vehicle miles traveled in the area's subwatersheds was slightly stronger than the correlation with subwatershed impervious area (Feist et al. 2017[4PSDP2BG] Feist, Blake E., Eric R. Buhle, David H. Baldwin, Julann A. Spromberg, Steven E. Damm, Jay W. Davis, and Nathaniel L. Scholz. 2017. "Roads to Ruin: Conservation Threats to a Sentinel Species across an Urban Gradient." Ecological Applications 27 (8): 2382–96. https://doi.org/https://doi.org/10.1002/eap.1615.). If this correlation is observed in other locations, it would suggest that large tire particles, which deposit near roads, might release more chemicals into surface runoff than tire particles that are PM_{10} or smaller in diameter, which deposit throughout watersheds.

4.1 Water

4.1.1 Surface Water and Stormwater

Surface runoff (Table 4-1) and stormwater (Table 4-2) are presumed to be major transport pathways of TRWP, 6PPD, and 6PPD-q, which can then result in URMS (McIntyre et al. 2021[MVL2LKBM] McIntyre, Jenifer K., Jasmine Prat, James Cameron, Jillian Wetzel, Emma Mudrock, Katherine T. Peter, Zhenyu Tian, et al. 2021. "Treading Water: Tire Wear Particle Leachate Recreates an Urban Runoff Mortality Syndrome in Coho but Not Chum Salmon." Environmental Science & Technology 55 (17): 11767–74. https://doi.org/10.1021/acs.est.1c03569.McIntyre et al. 2023[F7NAIVJ4] McIntyre, Jenifer, Julann Spromberg, James Cameron, John P. Incardona, Jay W. Davis, and Nathaniel L. Scholz. 2023. "Bioretention Filtration Prevents Acute Mortality and Reduces Chronic Toxicity for Early Life Stage Coho Salmon (Oncorhynchus kisutch) Episodically Exposed to Urban Stormwater Runoff." Science of the Total Environment 902 (December):165759. https://doi.org/10.1016/j.scitotenv.2023.165759.McIntyre et al. 2018[G7QW7PSD] McIntyre, Jenifer, Jessica Lundin, James Cameron, Michelle Chow, Jay Davis, John Incardona, and Nathaniel Scholz. 2018. "Interspecies Variation in the Susceptibility of Adult Pacific Salmon to Toxic Urban Stormwater Runoff." Environmental Pollution 238:196–203. https://doi.org/https://doi.org/10.1016/j.envpol.2018.03.012.Hiki et al. 2021[WZF69GXC] Hiki, Kyoshiro, Kenta Asahina, Kota Kato, Takahiro Yamagishi, Ryo Omagari, Yuichi Iwasaki, Haruna Watanabe, and Hiroshi Yamamoto. 2021. "Acute Toxicity of a Tire Rubber–Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species." Environmental Science & Technology Letters 8 (9): 779–84. https://doi.org/10.1021/acs.estlett.1c00453.Johannessen, Helm, and Metcalfe 2021[U9BWIDJ5] Johannessen, Cassandra, Paul Helm, and Chris D. Metcalfe. 2021. "Detection of Selected Tire Wear Compounds in Urban Receiving Waters." Environmental Pollution 287 (October):117659. https://doi.org/10.1016/j.envpol.2021.117659.Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. "A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon." Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.Seiwert et al. 2020[XRNTFZ69] Seiwert, Bettina, Philipp Klöckner, Stephan Wagner, and Thorsten Reemtsma. 2020. "Source-Related Smart Suspect Screening in the Aqueous Environment: Search for Tire-Derived Persistent and Mobile Trace Organic Contaminants in Surface Waters." Analytical and Bioanalytical Chemistry 412 (20): 4909–19. https://doi.org/10.1007/s00216-020-02653-1.French et al. 2022[3GCU2L57] French, B. F., D. H. Baldwin, J. Cameron, J. Prat, K. King, J. W. Davis, J. K. McIntyre, and N. L. Scholz. 2022. "Urban Roadway Runoff Is Lethal to Juvenile Coho, Steelhead, and Chinook Salmonids, But Not Congeneric Sockeye." Environmental Science & Technology Letters 9 (9): 733–38. https://doi.org/10.1021/acs.estlett.2c00467.Chow et al. 2019[7RMZ3UNQ] Chow, Michelle I., Jessica I. Lundin, Chelsea J. Mitchell, Jay W. Davis, Graham Young, Nathaniel L. Scholz, and Jenifer K. McIntyre. 2019. "An Urban Stormwater Runoff Mortality Syndrome in Juvenile Coho Salmon." Aquatic Toxicology 214 (September):105231. https://doi.org/10.1016/j.aquatox.2019.105231.Du et al. 2017[56E8Y27X] Du, Bowen, Jonathan M. Lofton, Katherine T. Peter, Alexander D. Gipe, C. Andrew James, Jenifer K. McIntyre, Nathaniel L. Scholz, Joel E. Baker, and Edward P. Kolodziej. 2017. "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." Environmental Science: Processes & Impacts 19 (9): 1185–96. https://doi.org/10.1039/C7EM00243B.Scholz et al. 2011[S8ASEIXU] Scholz, Nathaniel L., Mark S. Myers, Sarah G. McCarthy, Jana S. Labenia, Jenifer K. McIntyre, Gina M. Ylitalo, Linda D. Rhodes, et al. 2011. "Recurrent Die-Offs of Adult Coho Salmon Returning to Spawn in Puget Sound Lowland Urban Streams." PLOS ONE 6 (12): e28013. https://doi.org/10.1371/journal.pone.0028013.Peter et al. 2020[5CPFCBQT] Peter, Katherine T., Fan Hou, Zhenyu Tian, Christopher Wu, Matt Goehring, Fengmao Liu, and Edward P. Kolodziej. 2020. "More than a First Flush: Urban Creek Storm Hydrographs

Demonstrate Broad Contaminant Pollutographs." Environmental Science & Technology 54 (10): 6152–65.

https://doi.org/10.1021/acs.est.0c00872.Spromberg et al. 2016[GI97QYN4] Spromberg, Julann A., David H. Baldwin, Steven E. Damm, Jenifer K. McIntyre, Michael Huff, Catherine A. Sloan, Bernadita F. Anulacion, Jay W. Davis, and Nathaniel L. Scholz. 2016. "Coho Salmon Spawner Mortality in Western US Urban Watersheds: Bioinfiltration Prevents Lethal Storm Water Impacts." Journal of Applied Ecology 53 (2): 398–407. https://doi.org/https://doi.org/10.1111/1365-2664.12534.). Rain and snow melt (Table 4-8) pick up and transport dissolved and particulate contaminants from impervious surfaces and deliver them to natural waterbodies (Table 4-1), stormwater treatment structures (Table 4-2), or WWTP (Table 4-3) (Seiwert et al. 2022[QDRRVWMW] Seiwert, Bettina, Maolida Nihemaiti, Mareva Troussier, Steffen Weyrauch, and Thorsten Reemtsma. 2022. "Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater." Water Research 212:118122.

https://doi.org/10.1016/j.watres.2022.118122.Challis et al. 2021[T8TEWPCL] Challis, J. K., H. Popick, S. Prajapati, P. Harder, J. P. Giesy, K. McPhedran, and M. Brinkmann. 2021. "Occurrences of Tire Rubber–Derived Contaminants in Cold-Climate Urban Runoff." Environmental Science & Technology Letters 8 (11): 961–67. https://doi.org/10.1021/acs.estlett.1c00682.). Throughout the United States, MS4 are geographically more common, where stormwater is discharged to natural water bodies or stormwater treatment structures. In combined sewer systems, TRWP and associated chemicals are transported to WWTP under normal conditions but may be discharged to natural waterbodies under excessive runoff conditions as combined sewer overflow. In regard to the persistence of 6PPD-q, Foscari et al. (Foscari et al. 2024[JBUK7E3P] Foscari, Aurelio, Bettina Seiwert, Daniel Zahn, Matthias Schmidt, and Thorsten Reemtsma. 2024. "Leaching of Tire Particles and Simultaneous Biodegradation of Leachables." Water Research 253 (April):121322. https://doi.org/10.1016/j.watres.2024.121322.) demonstrated in lab experiments the biodegradation of 6PPD-q and a corresponding concentration decrease when TRWP were not present, while 6PPD-q concentrations are relatively stable or may even increase when particles are present. The development of methods to accurately measure 6PPD and 6PPD-q in surface water (see Section 5.1.5: Sampling 6PPD-q in Water) will help address the fate, transport, and occurrence data gaps to inform management actions (see Section 8.2).

Occurrence in Water

- Surface runoff and stormwater are major mechanisms for transporting TRWP, 6PPD and 6PPD-q to receiving surface water.
- More studies are needed to understand how environmental, landscape, and stormwater characteristics effect the fate and transport of TRWP, 6PPD, and 6PPD-q.
- More studies are needed to understand what stormwater, wastewater and drinking water treatment technologies are most effective at preventing the transport of TRWP, 6PPD, and 6PPD-q.
- More studies are needed to understand if 6PPD or 6PPD-q are transported by surface water and groundwater.

6PPD and 6PPD-q can be released directly from tires and readily bind to particulates (Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. "Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone." Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.); these particulates are transported by stormwater (Seiwert et al. 2022[QDRRVWMW] Seiwert, Bettina, Maolida Nihemaiti, Mareva Troussier, Steffen Weyrauch, and Thorsten Reemtsma. 2022. "Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater." Water Research 212:118122. https://doi.org/10.1016/j.watres.2022.118122.). 6PPD and 6PPD-q can also be released from TRWP that are generated during driving, deposited along roadways, and transported by stormwater to waterbodies or treatment facilities. Detected environmental concentrations of 6PPD and 6PPD-q have been highest in urban runoff (Zhu et al. 2024[WEPL88BC] Zhu, Jianqiang, Ruyue Guo, Shengtao Jiang, Pengfei Wu, and Hangbiao Jin. 2024. "Occurrence of p-Phenylenediamine Antioxidants (PPDs) and PPDs-Derived Quinones in Indoor Dust."

Science of the Total Environment 912:169325. https://doi.org/10.1016/j.scitotenv.2023.169325.Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. "A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon." Science 371 (6525): 185–89.

https://doi.org/10.1126/science.abd6951.Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. "New Evidence of Rubber-Derived Quinones in Water, Air, and Soil."

Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.Zhang et al. 2023[JWRBWTKN] Zhang, Hai-Yan, Zheng Huang, Yue-Hong Liu, Li-Xin Hu, Liang-Ying He, You-Sheng Liu, Jian-Liang Zhao, and Guang-Guo Ying. 2023. "Occurrence and Risks of 23 Tire Additives and Their Transformation Products in an Urban Water System."

Environment International 171 (January):107715. https://doi.org/10.1016/j.envint.2022.107715.). Studies that measure and compare dissolved and suspended fractions of 6PPD and 6PPD-q in water are needed to understand the fate and transport of these contaminants' pathways from impervious surfaces to natural waterbodies.

Potential aquatic ecological receptors, which include freshwater and marine organisms (vertebrates, invertebrates, and plants), may be exposed to 6PPD-q and 6PPD through direct uptake of water through respiratory surfaces, ingestion, and absorption. The route of exposure may vary among species or life stage. People who engage in subsistence or recreational activities such as swimming, fishing, or boating may be exposed to 6PPD and 6PPD-q through incidental ingestion of and dermal contact with water contaminated by surface runoff. Human exposure to 6PPD and 6PPD-q during water-based activities is an emerging area of concern that also needs further study.

Waterbodies located near roadways and used as sources for drinking water may be vulnerable to environmental contamination with 6PPD and 6PPD-q. Surface water in streams and lakes that are drinking water sources may be affected by surface runoff and stormwater or, depending on the setting, effluent from WWTP. Two published studies report analyses of drinking water source samples connected to surface water, one in China and the other in the greater Toronto area in Canada (Table 4-3). As of May 2024, the ITRC Tire Anti-degradants team did not identify reports or studies for 6PPD and 6PPD-q detection in finished drinking water in the United States.

In China, H.-Y. Zhang et al. (Zhang et al. 2023[JWRBWTKN] Zhang, Hai-Yan, Zheng Huang, Yue-Hong Liu, Li-Xin Hu, Liang-Ying He, You-Sheng Liu, Jian-Liang Zhao, and Guang-Guo Ying. 2023. "Occurrence and Risks of 23 Tire Additives and Their Transformation Products in an Urban Water System." Environment International 171 (January):107715. https://doi.org/10.1016/j.envint.2022.107715.) detected 6PPD in 30%–48% of filtered river source water samples and 6PPD-q in 100% of samples. Concentrations were in the low ng/L range, and 6PPD-q concentrations were higher than the parent chemical 6PPD. Within the drinking water treatment plant (DWTP), neither chemical was detected in samples drawn at each of six treatment stages. A Canadian study sampled for 6PPD-q in four WWTP and two DWTPs which use Lake Ontario as the source water (Johannessen and Metcalfe 2022[6AEMVTD8] Johannessen, Cassandra, and Chris D. Metcalfe. 2022. "The Occurrence of Tire Wear Compounds and Their Transformation Products in Municipal Wastewater and Drinking Water Treatment Plants." Environmental Monitoring and Assessment 194 (10): 731. https://doi.org/10.1007/s10661-022-10450-9.). 6PPD-q was detected in WWTP influent and effluent but not in drinking water (pre- or post-treatment).

4.1.2 Groundwater

There is little information regarding the transport of 6PPD and 6PPD-q from surface water to groundwater (Table 4-4). Groundwater contamination by 6PPD and 6PPD-q, along with other PPD chemicals, was reported in a shallow aquifer in China (Zhang et al. 2023[D6T6D4JP] Zhang, Ruiling, Shizhen Zhao, Xin Liu, Lele Tian, Yangzhi Mo, Xin Yi, Shiyang Liu, Jiaqi Liu, Jun Li, and Gan Zhang. 2023. "Aquatic Environmental Fates and Risks of Benzotriazoles, Benzothiazoles, and p-Phenylenediamines in a Catchment Providing Water to a Megacity of China." Environmental Research 216 (January):114721. https://doi.org/10.1016/j.envres.2022.114721.). Samples from civil wells and household water directly connected to groundwater were analyzed as proxies for groundwater samples. The authors describe the hydrogeology of the aquifer as unconfined and highly permeable to the nearby river water. An important data gap in the United States is whether groundwater that serves as drinking water sources could be vulnerable to a similar contamination pathway. The transport potential will ultimately depend on the organic content and soil type present. More research is needed to evaluate the assumptions that 6PPD and 6PPD-q stay bound to particulates and do not readily move through soil (Cunningham and Schalk 2011[N2W34PYI] Cunningham, W.L., and C.W. Schalk. 2011. "Groundwater Technical Procedures of the U.S. Geological Survey: U.S. Geological Survey Techniques and Methods 1–A1." https://pubs.usgs.gov/tm/1a1/.).

4.1.3 Tap Water

One study that analyzed drinking water at the point of exposure (tap water) was identified during preparation of the current document (Table 4-3). In that study, 6PPD was detected in 25% of drinking water samples collected from 20 buildings in Singapore, while 6PPD-q was not detected (Marques dos Santos and Snyder 2023[GEI8HFLB] Marques dos Santos, Mauricius, and Shane Allen Snyder. 2023. "Occurrence of Polymer Additives 1,3-Diphenylguanidine (DPG), N-(1,3-Dimethylbutyl)-N′-Phenyl-1,4-Benzenediamine (6PPD), and Chlorinated Byproducts in Drinking Water: Contribution from Plumbing Polymer Materials." Environmental Science & Technology Letters, September. https://doi.org/10.1021/acs.estlett.3c00446.). The source of 6PPD in the drinking water samples was not identified but may be due to leaching of the chemical from plumbing components (for example, rubber gaskets, O-rings). The original sources of the drinking water sampled in the study were not identified as surface water, groundwater, or otherwise. More research is needed to understand potential exposures from drinking water broadly, including water at the point of use.

4.1.4 Wastewater and Biosolids

In some cities in the United States, stormwater is diverted to WWTP through combined sewer systems. Studies investigating 6PPD-q removal in WWTP have had mixed results (Table 4-3). Several studies showed a strong reduction or removal of 6PPD-q to nondetect levels in water (Seiwert et al. 2022[QDRRVWMW] Seiwert, Bettina, Maolida Nihemaiti, Mareva Troussier, Steffen Weyrauch, and Thorsten Reemtsma. 2022. “Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater.” Water Research 212:118122. https://doi.org/10.1016/j.watres.2022.118122.Maurer et al. 2023[TJQR62IC] Maurer, Loïc, Eric Carmona, Oliver Machate, Tobias Schulze, Martin Krauss, and Werner Brack. 2023. “Contamination Pattern and Risk Assessment of Polar Compounds in Snow Melt: An Integrative Proxy of Road Runoffs.” Environmental Science & Technology 57 (10): 4143–52. https://doi.org/10.1021/acs.est.2c05784.Zhang et al. 2023[JWRBWTKN] Zhang, Hai-Yan, Zheng Huang, Yue-Hong Liu, Li-Xin Hu, Liang-Ying He, You-Sheng Liu, Jian-Liang Zhao, and Guang-Guo Ying. 2023. “Occurrence and Risks of 23 Tire Additives and Their Transformation Products in an Urban Water System.” Environment International 171 (January):107715. https://doi.org/10.1016/j.envint.2022.107715.), and another study showed an increased mass of 6PPD-q in the effluent from the WWTP (Johannessen and Metcalfe 2022[6AEMVTD8] Johannessen, Cassandra, and Chris D. Metcalfe. 2022. “The Occurrence of Tire Wear Compounds and Their Transformation Products in Municipal Wastewater and Drinking Water Treatment Plants.” Environmental Monitoring and Assessment 194 (10): 731. https://doi.org/10.1007/s10661-022-10450-9.). More research is needed to follow up on this.

Biosolids are a necessary byproduct of our WWTP. WWTP may receive TRWP, 6PPD, and 6PPD-q from upstream sources, and as such they can end up in biosolids. Both 6PPD and 6PPD-q were detected in 100% of biosolid samples from WWTP in Hong Kong (Cao et al. 2023[D5FPK9YB] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Han Qiao, Huankai Li, Gefei Huang, Zhu Yang, and Zongwei Cai. 2023. “Occurrence and Fate of Substituted P-Phenylenediamine-Derived Quinones in Hong Kong Wastewater Treatment Plants.” Environmental Science & Technology, October. https://doi.org/10.1021/acs.est.3c03758.), though more research is needed to characterize these occurrences in other localities. 6PPD-q has been detected in biosolids from a WWTP in Irvine, California (35.3±2.9 and 18.8±1.5 µg/kg, n=2) (Dennis, Braun, and Gan 2024[RNAS6357] Dennis, Nicole M., Audrey J. Braun, and Jay Gan. 2024. “A High-Throughput Analytical Method for Complex Contaminant Mixtures in Biosolids.” Environmental Pollution 345:123517. https://doi.org/10.1016/j.envpol.2024.123517.).[6]

Table	Media Type	Link to PDF	Link to Executable File (Word Processor Format)
4-1	Surface Water		
4-2	Stormwater		
4-3	Wastewater, water treatment plants, and tap water		
4-4	Groundwater		

Note: PDF versions of each table are provided for the reader to view information in a visual format that is consistent across browsers and platforms. Executable files are provided to allow readers to sort information by the column of their choice, but may appear different visually depending on the software used to view this file. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

4.2 Soil

Modeled and measured physicochemical characteristics of 6PPD and 6PPD-q suggest that these compounds readily bind to soil and organics (Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. “New Evidence of Rubber-Derived Quinones in Water, Air, and Soil.” Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.OSPAR Commission 2006[SVMKJM7X] OSPAR Commission. 2006. “Hazardous Substances Series 4-(Dimethylbutylamino)Diphenylamine (6PPD) 2005 (2006 Update).” Publication Number: 271/2006. https://www.ospar.org/documents?v=7029.); however, occurrence data are limited and more studies are needed (Table 4-5). Sampling protocols for measuring and understanding the occurrence and persistence of tire contaminants in soils along roadways are needed to address data gaps. Biodegradation of 6PPD and 6PPD-q in soil has been observed (Xu et al. 2023[4P2E4JLJ] Xu, Qiao, Gang Li, Li Fang, Qian Sun, Ruixia Han, Zhe Zhu, and Yong-Guan Zhu. 2023. “Enhanced Formation of 6PPD-Q during the Aging of Tire Wear Particles in Anaerobic Flooded Soils: The Role of Iron Reduction and Environmentally Persistent Free Radicals.” Environmental Science & Technology, March. https://doi.org/10.1021/acs.est.2c08672.). Additional research is needed to understand other degradation pathways and overall stability in soil.

Exposure in terrestrial organisms (vertebrates, invertebrates, and plants) is poorly characterized, but it is possible that terrestrial receptors may be exposed via ingestion, inhalation, or absorption. The primary pathways through which humans may be exposed to 6PPD and 6PPD-q in soil are ingestion and dermal contact. Incidental ingestion can occur when people come into direct contact with contaminated soil and engage in hand-to-mouth behaviors.

An exposure assessment conducted by Cao et al. (Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. “New Evidence of Rubber-Derived Quinones in Water, Air, and Soil.” Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.), using concentrations of total PPD compounds and their quinone transformation products in roadside soil, surface runoff, and air particles in Hong Kong, estimated that ingestion of roadside soil could be the primary contributor of human exposure to PPDs and PPDquinones, followed by dermal contact, and then inhalation of ambient air particulate. The relative importance of the exposure pathway reflected the lower concentrations of PPD chemicals and their transformation products in ambient air particulate as compared to concentrations in roadside soil and roadway runoff samples (Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. “New Evidence of Rubber-Derived Quinones in Water, Air, and Soil.” Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.). It is unknown whether these exposure pathway trends are applicable to people in the United States. Additional research is needed to understand the potential human health impacts from soil exposure pathways.

Beneficial use of biosolids, or land application, returns nutrients to the soil in place of commercial fertilizers. In California, 6PPD-q was detected in biosolids from a WWTP (see Section 4.1.4: Wastewater and Biosolids). More research is needed to understand the fate, transport, and exposure risk of 6PPD-q in biosolids used for agriculture and landscaping.

Table	Media Type	Link to PDF	Link to Executable File (Word Processor Format)
4-5	Roadside soil		

Note: The PDF version of this table is provided for the reader to view information in a visual format that is consistent across browsers and platforms. The executable file is provided to allow readers to sort information by the column of their choice, but may appear different visually depending on the software used to view this file. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

4.3 Sediment

Occurrence in Sediment

- Tire, road, and soil particles are transported by stormwater and surface water. The allocation between what stays suspended in water and what is deposited in the sediments is unknown.

- Standardized methods for measuring small TRWP in water and sediments are challenging. 6PPD q may provide a proxy for tire-derived microplastics that could represent a continued source of 6PPD and 6PPD q.
- More studies are needed to understand the fate and transport of TRWP in sediments including deposition, composition, biodegradation, and transformation processes.

In hydrology practices, sediment often refers to the benthic media at the bottoms of streams, rivers, estuaries, oceans, and lakes. In stormwater practices, the dirt and debris transported from impervious surfaces to stormwater catchments is referred to as sediment as well. In the San Francisco Bay Area alone, an estimated 0.3 to 2.4 million kg of TRWP wash off roads and parking lots into stormwater systems and enter San Francisco Bay via small tributaries annually (Moran et al. 2023[9FSZ84KX] Moran, Kelly, Alicia Gilbreath, Miguel Mendez, Diana Lin, and Rebecca Sutton. 2023. "Tire Wear: Emissions Estimates and Market Insights to Inform Monitoring Design." SFEI Technical Report SFEI Contribution #1049. Richmond, CA: San Francisco Estuary Institute.). These estimates do not include contributions from San Francisco's combined sewer system or from California's Central Valley. Other urban areas likely have similar wash-off rates. As with soil, 6PPD and 6PPD-q will readily bind to sediment instead of the water phase; however, occurrence data are limited, and more studies are needed (Table 4-6). Studies conducted in the Jiaojiang River and the Pearl River Delta and Estuary in China found both 6PPD and 6PPD-q as the most dominant PPD and PPDquinones quantified in a large-scale survey of urban rivers, estuaries, coasts, and deep-sea sediments (Zhu et al. 2024[3FETIQAB] Zhu, Jianqiang, Ruyue Guo, Fangfang Ren, Shengtao Jiang, and Hangbiao Jin. 2024. "Occurrence and Partitioning of p-Phenylenediamine Antioxidants and Their Quinone Derivatives in Water and Sediment." Science of the Total Environment 914 (March):170046. https://doi.org/10.1016/j.scitotenv.2024.170046.Zeng et al. 2023[TK5YR8WJ] Zeng, Lixi, Yi Li, Yuxin Sun, Liang-Ying Liu, Mingjie Shen, and Bibai Du. 2023. "Widespread Occurrence and Transport of p-Phenylenediamines and Their Quinones in Sediments across Urban Rivers, Estuaries, Coasts, and Deep-Sea Regions." Environmental Science & Technology, January, acs.est.2c07652. https://doi.org/10.1021/acs.est.2c07652.). The concentration of 6PPD and 6PPD-q decreased with distance from the urban areas. The detection of 6PPD may suggest TRWP are a source and/or that the half-life of 6PPD varies between air and water, environmental conditions, and chemical phases (dissolved and suspended fractionation) (Zhu et al. 2024[3FETIQAB] Zhu, Jianqiang, Ruyue Guo, Fangfang Ren, Shengtao Jiang, and Hangbiao Jin. 2024. "Occurrence and Partitioning of p-Phenylenediamine Antioxidants and Their Quinone Derivatives in Water and Sediment." Science of the Total Environment 914 (March):170046. https://doi.org/10.1016/j.scitotenv.2024.170046.Zeng et al. 2023[TK5YR8WJ] Zeng, Lixi, Yi Li, Yuxin Sun, Liang-Ying Liu, Mingjie Shen, and Bibai Du. 2023. "Widespread Occurrence and Transport of p-Phenylenediamines and Their Quinones in Sediments across Urban Rivers, Estuaries, Coasts, and Deep-Sea Regions." Environmental Science & Technology, January, acs.est.2c07652. https://doi.org/10.1021/acs.est.2c07652.). More studies are needed to continue understanding the variability in partitioning and other physicochemical characteristics. Klöckner, Seiwert, Wagner, et al. (Klöckner et al. 2021[Y49MVKMM] Klöckner, Philipp, Bettina Seiwert, Stephan Wagner, and Thorsten Reemtsma. 2021. "Organic Markers of Tire and Road Wear Particles in Sediments and Soils: Transformation Products of Major Antiozonants as Promising Candidates." Environmental Science & Technology 55 (17): 11723–32. https://doi.org/10.1021/acs.est.1c02723.) suggested using organic markers (specifically, the 6PPD transformation products N-formyl-6-PPD, hydroxylated N-1,3-dimethylbutyl-N-phenyl quinone diimine, and 6PPD-q) to measure TRWP. For 6PPD, a greater fraction of release was found in sediment compared to water following aging and biodegradation processes; however, more studies are needed to estimate leaching rates (Unice et al. 2015[NS59BGK2] Unice, K.M., Jennifer Bare, Marisa Kreider, and Julie Panko. 2015. "Experimental Methodology for Assessing the Environmental Fate of Organic Chemicals in Polymer Matrices Using Column Leaching Studies and OECD 308 Water/Sediment Systems: Application to Tire and Road Wear Particles." Science of the Total Environment 533 (July):476–87. https://doi.org/10.1016/j.scitotenv.2015.06.053.Xu et al. 2023[4P2E4JLJ] Xu, Qiao, Gang Li, Li Fang, Qian Sun, Ruixia Han, Zhe Zhu, and Yong-Guan Zhu. 2023. "Enhanced Formation of 6PPD-Q during the Aging of Tire Wear Particles in Anaerobic Flooded Soils: The Role of Iron Reduction and Environmentally Persistent Free Radicals." Environmental Science & Technology, March. https://doi.org/10.1021/acs.est.2c08672.). Anaerobic sediment conditions have been shown to produce more 6PPD-q (Xu et al. 2023[4P2E4JLJ] Xu, Qiao, Gang Li, Li Fang, Qian Sun, Ruixia Han, Zhe Zhu, and Yong-Guan Zhu. 2023. "Enhanced Formation of 6PPD-Q during the Aging of Tire Wear Particles in Anaerobic Flooded Soils: The Role of Iron Reduction and Environmentally Persistent Free Radicals." Environmental Science & Technology, March. https://doi.org/10.1021/acs.est.2c08672.).

As with soil, the primary pathways through which humans may be exposed to 6PPD and 6PPD-q in sediment are also ingestion and dermal contact. Sediment disturbance due to human activities such as wading and swimming can resuspend sediment particles in the water column, making them available for dermal contact or incidental ingestion. Incidental ingestion can also occur when people come into direct contact with contaminated sediment and engage in hand-to-mouth behaviors. It is unknown whether skin absorption of the chemicals from these particles is possible. Additional research is needed to understand the potential human health impacts from sediment exposure pathways. Likewise, more research is needed to understand the ecological risks associated with TRWP, 6PPD, and 6PPD-q in sediments.

Table	**Media Type**	**Link to PDF**	**Link to Executable File (Word Processor Format)**
4-6	Sediment		

Note: The PDF version of this table is provided for the reader to view information in a visual format that is consistent across browsers and platforms. The executable file is provided to allow readers to sort information by the column of their choice, but may appear different visually depending on the software used to view this file. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

4.4 Air

Over time, as tires wear down, particles containing 6PPD and 6PPD-q are released into the environment (outdoor air), and present different potential exposure pathways. Additionally, these particles could infiltrate indoor environments, settling as dust on various surfaces. 6PPD and 6PPD-q have been detected in particulate matter in outdoor air; dusts collected from roads, tunnels, and paved parking; and settled indoor dusts. To date, much, but not all, of the data on 6PPD and 6PPD-q in air and dust were collected in China. This section reviews airborne TRWP and associated particle size, dust, 6PPD, and 6PPD-q.

TRWP, 6PPD, and 6PPD-q Occurrence in Air

- 6PPD and 6PPD-q have been observed in outdoor ambient air and fine particulate matter.
- 6PPD and 6PPD-q have been observed in dust along roads and highways, parking lots and garages, rubber playgrounds, recycling facilities, and homes.
- Tire dust has been observed in snow along roadways.
- More research is needed to understand the airborne exposure pathways for tire dust and related chemicals to humans and terrestrial and aquatic ecosystems.

In laboratory simulations of tire wear, TWPs are generated in multiple size fractions, including below 10 µm in diameter, with a large fraction of the total number of particles emitted below 0.1 µm, known as ultrafine particulate matter or $PM_{0.1}$ (Dahl et al. 2006[PTHCYGGU] Dahl, Andreas, Arash Gharibi, Erik Swietlicki, Anders Gudmundsson, Mats Bohgard, Anders Ljungman, Göran Blomqvist, and Mats Gustafsson. 2006. “Traffic-Generated Emissions of Ultrafine Particles from Pavement–Tire Interface.” Atmospheric Environment 40 (7): 1314–23. https://doi.org/10.1016/j.atmosenv.2005.10.029.Park, Kim, and Lee 2018[HIY3Z76P] Park, Inyong, Hongsuk Kim, and Seokhwan Lee. 2018. “Characteristics of Tire Wear Particles Generated in a Laboratory Simulation of Tire/Road Contact Conditions.” Journal of Aerosol Science 124 (October):30–40. https://doi.org/10.1016/j.jaerosci.2018.07.005.). $PM_{0.1}$ can readily be inhaled and can pass directly into the body. Particles, including TRWP, less than 10 µm in diameter are generally recognized to be respirable; the smaller they are, the deeper they can penetrate the lungs. The term “dust” can comprise different particle types and size fractions. We use the term here in the context of human health to indicate particles that are greater than 10 µm in diameter and therefore not respirable into the deep lung.

4.4.1 Outdoor Air

In outdoor air, 6PPD has been observed in respirable fine particulate matter ($PM_{2.5}$), while 6PPD-q has been found in both outdoor ambient air and in the $PM_{2.5}$ fraction (Table 4-7). In $PM_{2.5}$, 6PPD has been observed at concentrations ranging from about 0.02–9,340 pg/m^3 (Zhang et al. 2022[G77DTKD6] Zhang, Yanhao, Caihong Xu, Wenfen Zhang, Zenghua Qi, Yuanyuan Song, Lin Zhu, Chuan Dong, Jianmin Chen, and Zongwei Cai. 2022. “p-Phenylenediamine Antioxidants in PM2.5: The Underestimated Urban Air Pollutants.” Environmental Science & Technology 56 (11): 6914–21.

https://doi.org/https://doi.org/10.1021/acs.est.1c04500.Wang et al. 2022[TMV9VLRS] Wang, Wei, Guodong Cao, Jing Zhang, Pengfei Wu, Yanyan Chen, Zhifeng Chen, Zenghua Qi, Ruijin Li, Chuan Dong, and Zongwei Cai. 2022. "Beyond Substituted p-Phenylenediamine Antioxidants: Prevalence of Their Quinone Derivatives in PM2.5." Environmental Science & Technology, July, acs.est.2c02463. https://doi.org/10.1021/acs.est.2c02463.Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. "New Evidence of Rubber-Derived Quinones in Water, Air, and Soil." Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.). 6PPD has also been observed at concentrations ranging from less than 0.02 to 0.41 pg/m^3 and detected in 70% of ambient air samples (particle size not specified) from Chicago; 6PPD-q was not measured in this study (Wu, Venier, and Hites 2020[F7XN9GAC] Wu, Yan, Marta Venier, and Ronald A. Hites. 2020. "Broad Exposure of the North American Environment to Phenolic and Amino Antioxidants and to Ultraviolet Filters." Environmental Science & Technology 54 (15): 9345–55. https://doi.org/10.1021/acs.est.0c04114.). 6PPD was not detected in ambient air during a three-month study where passive air samplers were deployed across 18 major cities that compose the Global Atmospheric Passive Sampling (GAPS) Network (Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. "Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers." Environmental Pollution 314 (December):120206. https://doi.org/10.1016/j.envpol.2022.120206.). 6PPD-q has been observed at concentrations ranging from about 0.1–7,250 pg/m^3 in $PM_{2.5}$ (Zhang et al. 2022[G77DTKD6] Zhang, Yanhao, Caihong Xu, Wenfen Zhang, Zenghua Qi, Yuanyuan Song, Lin Zhu, Chuan Dong, Jianmin Chen, and Zongwei Cai. 2022. "p-Phenylenediamine Antioxidants in PM2.5: The Underestimated Urban Air Pollutants." Environmental Science & Technology 56 (11): 6914–21. https://doi.org/https://doi.org/10.1021/acs.est.1c04500.Wang et al. 2022[TMV9VLRS] Wang, Wei, Guodong Cao, Jing Zhang, Pengfei Wu, Yanyan Chen, Zhifeng Chen, Zenghua Qi, Ruijin Li, Chuan Dong, and Zongwei Cai. 2022. "Beyond Substituted p-Phenylenediamine Antioxidants: Prevalence of Their Quinone Derivatives in PM2.5." Environmental Science & Technology, July, acs.est.2c02463. https://doi.org/10.1021/acs.est.2c02463.Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. "New Evidence of Rubber-Derived Quinones in Water, Air, and Soil." Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.) and 0.17–1.75 pg/m^3 in ambient air (Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. "Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers." Environmental Pollution 314 (December):120206. https://doi.org/10.1016/j.envpol.2022.120206.). High detection frequencies of 6PPD and 6PPD-q in urban $PM_{2.5}$ indicate a widespread prevalence, but some observed variability suggests that seasonal, geographic, and economic conditions may impact 6PPD and 6PPD-q occurrence in urban air (Zhang et al. 2022[G77DTKD6] Zhang, Yanhao, Caihong Xu, Wenfen Zhang, Zenghua Qi, Yuanyuan Song, Lin Zhu, Chuan Dong, Jianmin Chen, and Zongwei Cai. 2022. "p-Phenylenediamine Antioxidants in PM2.5: The Underestimated Urban Air Pollutants." Environmental Science & Technology 56 (11): 6914–21. https://doi.org/https://doi.org/10.1021/acs.est.1c04500.Wang et al. 2022[TMV9VLRS] Wang, Wei, Guodong Cao, Jing Zhang, Pengfei Wu, Yanyan Chen, Zhifeng Chen, Zenghua Qi, Ruijin Li, Chuan Dong, and Zongwei Cai. 2022. "Beyond Substituted p-Phenylenediamine Antioxidants: Prevalence of Their Quinone Derivatives in PM2.5." Environmental Science & Technology, July, acs.est.2c02463. https://doi.org/10.1021/acs.est.2c02463.Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. "New Evidence of Rubber-Derived Quinones in Water, Air, and Soil." Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.). Y. Zhang et al. (Zhang et al. 2022[G77DTKD6] Zhang, Yanhao, Caihong Xu, Wenfen Zhang, Zenghua Qi, Yuanyuan Song, Lin Zhu, Chuan Dong, Jianmin Chen, and Zongwei Cai. 2022. "p-Phenylenediamine Antioxidants in PM2.5: The Underestimated Urban Air Pollutants." Environmental Science & Technology 56 (11): 6914–21. https://doi.org/https://doi.org/10.1021/acs.est.1c04500.) used standard exposure assumptions to compute average daily inhalation intakes for residents of each city from the measured concentrations in $PM_{2.5}$. Estimated daily inhalation intakes ranged from 0.3–7.2 pg/day for 6PPD and 2.2–18 pg/day for 6PPD-q.

There is some indication that compounds associated with tire particles are more highly associated with coarse particulate matter, though this association was not measured specifically for 6PPD or 6PPD-q (Zhang et al. 2022[GHLGNCHV] Zhang, Ying-Jie, Ting-Ting Xu, Dong-Min Ye, Ze-Zhao Lin, Fei Wang, and Ying Guo. 2022. "Widespread N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine Quinone in Size-Fractioned Atmospheric Particles and Dust of Different Indoor Environments." Environmental Science & Technology Letters 9 (5): 420–25. https://doi.org/https://doi.org/10.1021/acs.estlett.2c00193.Wang et al. 2023[MVLEXF2I] Wang, Xiaoliang, Steven Gronstal, Brenda

Lopez, Heejung Jung, L.-W. Antony Chen, Guoyuan Wu, Steven Sai Hang Ho, et al. 2023. “Evidence of Non-Tailpipe Emission Contributions to PM2.5 and PM10 near Southern California Highways.” Environmental Pollution 317:120691. https://doi.org/10.1016/j.envpol.2022.120691.). More investigation is needed to determine potential human exposure to 6PPD and 6PPD-q due to coarse particulate matter.

TRWP are regularly found in $PM_{2.5}$ air monitoring stations along roadways (USEPA 2023[7MLIS2WE] USEPA. 2023. “Air Data: Air Quality Data Collected at Outdoor Monitors Across the US.” Collections and Lists. November 9, 2023. https://www.epa.gov/outdoor-air-quality-data.). Studies have demonstrated the transport of TRWP by resuspension and deposition along roadways (Mayer et al. 2024[ZTAVFS9G] Mayer, Paul, Kelly Moran, Ezra Miller, Susanne Brander, Stacey Harper, Manuel Garcia-Jaramillo, Victor Carrasco-Navarro, et al. 2024. “Where the Rubber Meets the Road: Emerging Environmental Impacts of Tire Wear Particles and Their Chemical Cocktails.” Science of The Total Environment 927 (June):171153. https://doi.org/10.1016/j.scitotenv.2024.171153.). Air monitoring is needed along transportation corridors and in near-road environments to estimate the mass loading, chemical composition, and transport of TRWP nonexhaust emissions and volatile chemicals from tires.

Measurements of 6PPD and 6PPD-q in respirable particulate matter samples of indoor air were not identified by the ITRC Tire Anti-degradants team during the preparation of this document. The relevance of exposure through indoor air remains a data gap.

Table	Media Type	Link to PDF	Link to Executable File (Word Processor Format)
4-7	Outdoor air		

Note: The PDF version of this table is provided for the reader to view information in a visual format that is consistent across browsers and platforms. The executable file is provided to allow readers to sort information by the column of their choice, but may appear different visually depending on the software used to view this file. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

4.4.2 Road Dust and Roadside Snow

6PPD and 6PPD-q have been observed along roads (Table 4-5 and Table 4-8), including urban roads, a parking garage, and in roadside snow (Deng et al. 2022[Y9G3IQTU] Deng, Chengliang, Jialing Huang, Yunqing Qi, Da Chen, and Wei Huang. 2022. “Distribution Patterns of Rubber Tire–Related Chemicals with Particle Size in Road and Indoor Parking Lot Dust.” Science of the Total Environment 844:157144. https://doi.org/10.1016/j.scitotenv.2022.157144.Huang et al. 2021[EZEWIV8E] Huang, Wei, Yumeng Shi, Jialing Huang, Chengliang Deng, Shuqin Tang, Xiaotu Liu, and Da Chen. 2021. “Occurrence of Substituted p-Phenylenediamine Antioxidants in Dusts.” Environmental Science & Technology Letters 8 (5): 381–85. https://doi.org/10.1021/acs.estlett.1c00148.Hiki and Yamamoto 2022[VQ3M4AFW] Hiki, Kyoshiro, and Hiroshi Yamamoto. 2022. “Concentration and Leachability of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and Its Quinone Transformation Product (6PPD-Q) in Road Dust Collected in Tokyo, Japan.” Environmental Pollution 302 (June):119082. https://doi.org/10.1016/j.envpol.2022.119082.Jin et al. 2023[P9WXQJUR] Jin, Ruihe, Yan Wu, Qun He, Pei Sun, Qiqing Chen, Chunjie Xia, Ye Huang, Jing Yang, and Min Liu. 2023. “Ubiquity of Amino Accelerators and Antioxidants in Road Dust from Multiple Land Types: Targeted and Nontargeted Analysis.” Environmental Science & Technology 57 (28): 10361–72. https://doi.org/10.1021/acs.est.3c01448.Maurer et al. 2023[TJQR62IC] Maurer, Loïc, Eric Carmona, Oliver Machate, Tobias Schulze, Martin Krauss, and Werner Brack. 2023. “Contamination Pattern and Risk Assessment of Polar Compounds in Snow Melt: An Integrative Proxy of Road Runoffs.” Environmental Science & Technology 57 (10): 4143–52. https://doi.org/10.1021/acs.est.2c05784.Wu, Venier, and Hites 2020[F7XN9GAC] Wu, Yan, Marta Venier, and Ronald A. Hites. 2020. “Broad Exposure of the North American Environment to Phenolic and Amino Antioxidants and to Ultraviolet Filters.” Environmental Science & Technology 54 (15): 9345–55. https://doi.org/10.1021/acs.est.0c04114.Klöckner et al. 2021[DDXBMPC5] Klöckner, Philipp, Bettina Seiwert, Steffen Weyrauch, Beate I. Escher, Thorsten Reemtsma, and Stephan Wagner. 2021. “Comprehensive Characterization of Tire and Road Wear Particles in Highway Tunnel Road Dust by Use of Size and Density Fractionation.” Chemosphere. https://doi.org/https://doi.org/10.1016/j.chemosphere.2021.130530.). In road dust, 6PPD concentrations have been found ranging from 11.4–5,359 ng/g, and 6PPD-q concentrations have been found ranging from 4.02–2,369 ng/g (Deng et al. 2022[Y9G3IQTU] Deng, Chengliang, Jialing Huang, Yunqing Qi, Da Chen, and Wei Huang. 2022. “Distribution Patterns of Rubber Tire–Related Chemicals with Particle Size in Road and Indoor Parking Lot Dust.” Science of the Total Environment 844:157144. https://doi.org/10.1016/j.scitotenv.2022.157144.Hiki and Yamamoto 2022[VQ3M4AFW] Hiki, Kyoshiro, and Hiroshi Yamamoto. 2022. “Concentration and Leachability of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and Its Quinone Transformation Product (6PPD-Q) in Road Dust Collected in Tokyo, Japan.” Environmental Pollution 302 (June):119082. https://doi.org/10.1016/j.envpol.2022.119082.). Higher concentrations of 6PPD and 6PPD-q were found on finer particles than coarser particles in road dust collected within a highway tunnel (Klöckner et al. 2021[DDXBMPC5] Klöckner, Philipp, Bettina Seiwert, Steffen Weyrauch, Beate I. Escher, Thorsten Reemtsma, and Stephan Wagner. 2021. “Comprehensive Characterization of Tire and Road Wear Particles in Highway Tunnel Road Dust by Use of Size and Density Fractionation.” Chemosphere. https://doi.org/https://doi.org/10.1016/j.chemosphere.2021.130530.). 6PPD and 6PPD-q were detected in street-sweeping debris in Germany, prior to decantation of water; more research is needed to understand the management of street-sweeping waste and the potential resuspension of fine TRWP during the treatment process (Klöckner, Seiwert, Wagner, et al. 2021). See Section 6.3.1.6: Street Sweeping and Other Road Maintenance Activities for discussion of street sweeping as a mitigation measure for TRWP.

A pilot study was conducted to test whether funnels placed inside near-roadway passive samplers (Sigma-2) could successfully capture TRWP in the approximately 1 µm to 80 µm size range (Olubusoye et al. 2023[R8HSVPUG] Olubusoye, Boluwatife S., James V. Cizdziel, Matthew Bee, Matthew T. Moore, Marco Pineda, Viviane Yargeau, and Erin R. Bennett. 2023. “Toxic Tire Wear Compounds (6PPD-Q and 4-ADPA) Detected in Airborne Particulate Matter Along a Highway in Mississippi, USA.” Bulletin of Environmental Contamination and Toxicology 111 (6): 68. https://doi.org/10.1007/s00128-023-03820-7.). The authors reported that TRWP concentrations increased with proximity to the road with deposition rates (TRWPs/cm^2/day) of 23, 47, and 63 at 30 m, 15 m, and 5 m from the highway, respectively. 6PPD-q was detected in each of the near-road sampling locations, suggesting the possibility of inhalation exposure.

In another study, road dust samples were collected from Guiyu Town, which is an area with extensive e-waste recycling activity, and Haojiang, a neighboring municipality without e-waste recycling activity (Zhang et al. 2024[ZQPREK6H] Zhang, Zhuxia, Xijin Xu, Ziyi Qian, Qi Zhong, Qihua Wang, Machteld N. Hylkema, Harold Snieder, and Xia Huo. 2024. “Association between 6PPD-Quinone Exposure and BMI, Influenza, and Diarrhea in Children.” Environmental Research 247:118201. https://doi.org/10.1016/j.envres.2024.118201.). Median levels in road dust were higher in Haojiang than in Guiyu Town, the e-waste recycling area. The higher levels of 6PPD-q in road dust from Haojiang were presumably due to higher traffic flow in that municipality compared to Guiyu, according to the authors.

Jin et al. (Jin et al. 2023[P9WXQJUR] Jin, Ruihe, Yan Wu, Qun He, Pei Sun, Qiqing Chen, Chunjie Xia, Ye Huang, Jing Yang, and Min Liu. 2023. “Ubiquity of Amino Accelerators and Antioxidants in Road Dust from Multiple Land Types: Targeted and Nontargeted Analysis.” Environmental Science & Technology 57 (28): 10361–72. https://doi.org/10.1021/acs.est.3c01448.) used their measured concentrations of 6PPD-q and 6PPD in dust samples from urban/suburban, agricultural, and forest areas to derive estimates of daily intake from ingestion and dermal contact for adults and children for each of these area types. Using standard exposure factors, Jin et al. estimated that ingestion may be the primary exposure route for roadside dust for all scenarios and age groups. The highest estimated daily intake by both adults and children was predicted to occur in urban/suburban regions (Jin et al. 2023[P9WXQJUR] Jin, Ruihe, Yan Wu, Qun He, Pei Sun, Qiqing Chen, Chunjie Xia, Ye Huang, Jing Yang, and Min Liu. 2023. “Ubiquity of Amino Accelerators and Antioxidants in Road Dust from Multiple Land Types: Targeted and Nontargeted Analysis.” Environmental Science & Technology 57 (28): 10361–72. https://doi.org/10.1021/acs.est.3c01448.).

6PPD and 6PPD-q have also been found in roadside snow (Table 4-8). 6PPD concentrations have been detected up to 783.79 ng/L, and 6PPD-q concentrations have been detected from about 110–428 ng/L (Seiwert et al. 2022[QDRRVWMW] Seiwert, Bettina, Maolida Nihemaiti, Mareva Troussier, Steffen Weyrauch, and Thorsten Reemtsma. 2022. “Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater.” Water Research 212:118122. https://doi.org/10.1016/j.watres.2022.118122.Maurer et al. 2023[TJQR62IC] Maurer, Loïc, Eric Carmona, Oliver Machate, Tobias Schulze, Martin Krauss, and Werner Brack. 2023. “Contamination Pattern and Risk Assessment of Polar Compounds in Snow Melt: An Integrative Proxy of Road Runoffs.” Environmental Science & Technology 57 (10): 4143–52. https://doi.org/10.1021/acs.est.2c05784.). Studies to date have not evaluated the relative contribution in snow between potential atmospheric sources and road dust sources. Snow melt has been shown to transport the road dust deposition into surface water (Challis et al. 2021[T8TEWPCL] Challis, J. K., H. Popick, S. Prajapati, P. Harder, J. P. Giesy, K. McPhedran, and M. Brinkmann. 2021. "Occurrences of Tire Rubber–Derived Contaminants in Cold-Climate Urban Runoff." Environmental Science & Technology Letters 8 (11): 961–67. https://doi.org/10.1021/acs.estlett.1c00682.).

Table	Media Type	Link to PDF	Link to Executable File (Word Processor Format)
4-8	Road dust and roadside snow		

Note: The PDF version of this table is provided for the reader to view information in a visual format that is consistent across browsers and platforms. The executable versions of this table is provided for visitors to this webpage that wish to download and sort compiled information. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

4.4.3 Indoor Settled Dust

We use the term "dust" in the context of human health to indicate particles that are greater than 10 µm in diameter and therefore not respirable into the deep lung. Exposure to chemicals in dust can occur through direct emissions or when wind or turbulence resuspends dust particles in air. Dust particles greater than 10 µm deposit in the upper airways and can cause effects at the site of deposition or can be transported by mucociliary action and swallowed, resulting in ingestion exposure. Dusts can also be ingested when they get onto hands or food, or in the case of young children, objects that are mouthed. Dermal contact with chemicals in dust may also occur.

6PPD and 6PPD-q have been observed in dust in indoor environments, including e-waste facilities, homes, dormitories, buses, and shopping malls (Table 4-9). 6PPD and 6PPD-q in indoor dust have been detected up to 1,020 ng/g and 2,850 ng/g, respectively (Zhu et al. 2024[WEPL88BC] Zhu, Jianqiang, Ruyue Guo, Shengtao Jiang, Pengfei Wu, and Hangbiao Jin. 2024. "Occurrence of p-Phenylenediamine Antioxidants (PPDs) and PPDs-Derived Quinones in Indoor Dust." Science of the Total Environment 912:169325. https://doi.org/10.1016/j.scitotenv.2023.169325.Zhang et al. 2022[GHLGNCHV] Zhang, Ying-Jie, Ting-Ting Xu, Dong-Min Ye, Ze-Zhao Lin, Fei Wang, and Ying Guo. 2022. "Widespread N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine Quinone in Size-Fractioned Atmospheric Particles and Dust of Different Indoor Environments." Environmental Science & Technology Letters 9 (5): 420–25. https://doi.org/https://doi.org/10.1021/acs.estlett.2c00193.Huang et al. 2021[EZEWIV8E] Huang, Wei, Yumeng Shi, Jialing Huang, Chengliang Deng, Shuqin Tang, Xiaotu Liu, and Da Chen. 2021. "Occurrence of Substituted p-Phenylenediamine Antioxidants in Dusts." Environmental Science & Technology Letters 8 (5): 381–85. https://doi.org/10.1021/acs.estlett.1c00148.Liu et al. 2019[TL9MEY5E] Liu, Runzeng, Yiling Li, Yongfeng Lin, Ting Ruan, and Guibin Jiang. 2019. "Emerging Aromatic Secondary Amine Contaminants and Related Derivatives in Various Dust Matrices in China." Ecotoxicology and Environmental Safety 170 (April):657–63. https://doi.org/10.1016/j.ecoenv.2018.12.036.Wu, Venier, and Hites 2020[F7XN9GAC] Wu, Yan, Marta Venier, and Ronald A. Hites. 2020. "Broad Exposure of the North American Environment to Phenolic and Amino Antioxidants and to Ultraviolet Filters." Environmental Science & Technology 54 (15): 9345–55. https://doi.org/10.1021/acs.est.0c04114.Liang et al. 2022[SZPLJY9T] Liang, Bowen, Jiehua Li, Bibai Du, Zibin Pan, Liang-Ying Liu, and Lixi Zeng. 2022. "E-Waste Recycling Emits Large Quantities of Emerging Aromatic Amines and Organophosphites: A Poorly Recognized Source for Another Two Classes of Synthetic Antioxidants." Environmental Science & Technology Letters, June, acs.estlett.2c00366. https://doi.org/10.1021/acs.estlett.2c00366.). The referenced indoor dust studies varied in the sample collection and processing methods they used and so are not directly comparable to each other, but the results taken together serve to illustrate the potential for human exposure via indoor dust.

In four solid waste recycling facilities in China, 6PPD-q was found in airborne particulate matter and settled dusts (Zhang et al. 2022[G77DTKD6] Zhang, Yanhao, Caihong Xu, Wenfen Zhang, Zenghua Qi, Yuanyuan Song, Lin Zhu, Chuan Dong, Jianmin Chen, and Zongwei Cai. 2022. "p-Phenylenediamine Antioxidants in PM2.5: The Underestimated Urban Air Pollutants." Environmental Science & Technology 56 (11): 6914–21. https://doi.org/https://doi.org/10.1021/acs.est.1c04500.). 6PPD was reported in dust samples from electronic waste recycling facilities, one in China and one in Canada (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. "First Report on the Occurrence of N-(1,3-

Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China." Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.Wu, Venier, and Hites 2020[F7XN9GAC] Wu, Yan, Marta Venier, and Ronald A. Hites. 2020. "Broad Exposure of the North American Environment to Phenolic and Amino Antioxidants and to Ultraviolet Filters." Environmental Science & Technology 54 (15): 9345–55. https://doi.org/10.1021/acs.est.0c04114.). Neither of the electronic waste studies analyzed for 6PPD-q. Overall, there is a lack of data relevant to determining occupational exposure levels for U.S. workers with potential exposure to 6PPD-q. Biomonitoring and evaluation of health impacts to worker population groups is a data gap (DTSC 2022[2M3Z8Z4F] DTSC. 2022. "Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the California Department of Toxic Substances Control (DTSC)." https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf .).

6PPD was detected in settled dust collected from the floor of U.S. and Canadian residences in Indiana and Ontario, respectively. Median 6PPD levels in dust were slightly higher in residences located in Indiana compared to Ontario (Wu, Venier, and Hites 2020[F7XN9GAC] Wu, Yan, Marta Venier, and Ronald A. Hites. 2020. "Broad Exposure of the North American Environment to Phenolic and Amino Antioxidants and to Ultraviolet Filters." Environmental Science & Technology 54 (15): 9345–55. https://doi.org/10.1021/acs.est.0c04114.). 6PPD-q was not analyzed in this study, but other studies on indoor dust, as described below, detected 6PPD-q where 6PPD was present.

Composite dust samples collected from 97 residences in a large city in eastern China contained both 6PPD and 6PPD-q, with a 100% detection frequency (Zhu et al. 2024[WEPL88BC] Zhu, Jianqiang, Ruyue Guo, Shengtao Jiang, Pengfei Wu, and Hangbiao Jin. 2024. "Occurrence of p-Phenylenediamine Antioxidants (PPDs) and PPDs-Derived Quinones in Indoor Dust." Science of the Total Environment 912:169325. https://doi.org/10.1016/j.scitotenv.2023.169325.). Average levels in the dust were 17 ng of 6PPD and 14 ng of 6PPD-q per gram of dust. In another study, indoor dust samples were collected from Guiyu Town, which is an area with extensive e-waste recycling activity, and Haojiang, a neighboring municipality without e-waste recycling activity (Zhang et al. 2024[ZQPREK6H] Zhang, Zhuxia, Xijin Xu, Ziyi Qian, Qi Zhong, Qihua Wang, Machteld N. Hylkema, Harold Snieder, and Xia Huo. 2024. "Association between 6PPD-Quinone Exposure and BMI, Influenza, and Diarrhea in Children." Environmental Research 247:118201. https://doi.org/10.1016/j.envres.2024.118201.). Median levels of 6PPD-q in house dust and dust in kindergartens in the e-waste town were 3.2 ng and 7.5 ng per gram of dust, respectively. Median levels in Haojiang were lower, with 1.4 ng and 1.3 ng of 6PPD-q per gram of dust sampled from houses and kindergartens, respectively. The authors conducted an exposure assessment and determined that children living in Guiyu Town have a higher daily intake from ingestion and inhalation of 6PPD-q from house or kindergarten dust than children living in Haojiang. Daily intakes of 6PPD-q were higher from kindergarten dust compared to house dust for both towns.

6PPD and 6PPD-q were detected in settled dust samples (25 µm–250 µm particle size fraction) taken from the interior of 11 vehicles and 18 residences in Guangzhou, China (Huang et al. 2021[EZEWIV8E] Huang, Wei, Yumeng Shi, Jialing Huang, Chengliang Deng, Shuqin Tang, Xiaotu Liu, and Da Chen. 2021. "Occurrence of Substituted p-Phenylenediamine Antioxidants in Dusts." Environmental Science & Technology Letters 8 (5): 381–85. https://doi.org/10.1021/acs.estlett.1c00148.). Median levels of 6PPD in dust samples taken from vehicle interiors were two orders of magnitude higher than median levels of 6PPD in dust samples taken from residences. For 6PPD-q, concentrations were higher in interior vehicle dusts than in dusts sampled outdoors in parking lots and roadways. 6PPD-q was not detected in residences above the limit of quantitation in this study.

In another study relevant to vehicle interiors, 6PPD-q concentrations were higher in dust sampled from surfaces in buses compared to indoor dust sampled from shopping malls, residential bedrooms, and air conditioner filters inside college dormitories and houses (Zhang et al. 2022[GHLGNCHV] Zhang, Ying-Jie, Ting-Ting Xu, Dong-Min Ye, Ze-Zhao Lin, Fei Wang, and Ying Guo. 2022. "Widespread N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine Quinone in Size-Fractioned Atmospheric Particles and Dust of Different Indoor Environments." Environmental Science & Technology Letters 9 (5): 420–25. https://doi.org/https://doi.org/10.1021/acs.estlett.2c00193.).

Table	**Media Type**	**Link to PDF**	**Link to Executable File (Word Processor Format)**

4-9	Indoor and nonroad settled dust		

Note: The PDF version of this table is provided for the reader to view information in a visual format that is consistent across browsers and platforms. The executable file is provided to allow readers to sort information by the column of their choice, but may appear different visually depending on the software used to view this file. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

4.5 Potential Food Sources and Human Consumption of 6PPD and 6PPD-q

The development of consistent and reliable standardized methods for measuring 6PPD and 6PPD-q in biological matrices will allow us to investigate biological uptake and, potentially, exposure history. These methods are still in development. The following section summarizes what is known about the potential for exposure to 6PPD-q and 6PPD from consumption of fish and other potential food sources. Table 4-10 presents the available data relevant to 6PPD and 6PPD-q in aquatic organisms and food. Section 3.5 describes biological uptake and accumulation of 6PPD and 6PPD-q. In general, more research is needed to understand biological uptake and bioaccumulation processes of 6PPD and 6PPD-q (see Section 8.1 for additional detail on information gaps and research needs on this topic).

Table	**Media Type**	**Link to PDF**	**Link to Executable File (Word Processor Format)**
4-10	Aquatic organisms and food		

Note: The PDF version of this table is provided for the reader to view information in a visual format that is consistent across browsers and platforms. The executable file is provided to allow readers to sort information by the column or their choice, but may appear different visually depending on the software used to view this file. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

4.5.1 Aquatic Food Sources

6PPD-q and 6PPD have been detected in the organs of several different species of fish; however, a substantial knowledge gap exists regarding the presence of 6PPD-q and 6PPD within edible fish tissues and other aquatic biota consumed by humans, as well as whether these levels are sufficiently elevated to pose a risk to human health. Additionally, more research is needed to understand human exposure potential to 6PPD-q and 6PPD from consumption of the whole body of the fish. Results described below indicate measurements done on uncooked fish tissue. It is unknown how heat applied during cooking processes may impact 6PPD-q and 6PPD concentrations in fish tissue and other aquatic food sources.

Ji, Li, et al. ([Exploration of emerging environmental pollutants]) analyzed for 6PPD-q and 6PPD in a small sample of fish from a market in China. Freshwater species tested included snakehead fish, mandarin fish, tilapia, crucian, yellow-head catfish, and blunt-snout bream; marine species were Spanish mackerel, weever, silver pomfret, and large yellow croaker. 6PPD was detected in snakehead and weever. 6PPD-q was detected in the Spanish mackerel, but at a level below the limit of quantitation. Ji, Li, et al. ([Exploration of emerging environmental pollutants]) did not indicate which tissue types of the fish were analyzed, nor the source water they were fished from.

Frozen capelin caught in Canada and purchased at a supermarket contained 6PPD-q DNA adducts in liver, gill, and roe (Wu et al. 2023[PYQQU7AG] Wu, Jiabin, Guodong Cao, Feng Zhang, and Zongwei Cai. 2023. “A New Toxicity Mechanism of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine Quinone: Formation of DNA Adducts in Mammalian Cells and Aqueous Organisms.” Science of the Total Environment 866:161373. https://doi.org/10.1016/j.scitotenv.2022.161373.). The authors did not state where in Canada the capelin were caught.

6PPD-q was detected in the brain and gill of white spotted char (*Salvelinus leucomaenis pluvius*), southern Asian Dolly Varden (*Salvelinus curilus)*, and masu (*Oncorhynchus masou masou*) exposed under laboratory conditions (Hiki and Yamamoto 2022[VQE4EZWI] Hiki, Kyoshiro, and Hiroshi Yamamoto. 2022. “The Tire-Derived Chemical 6PPD-Quinone Is Lethally Toxic to the White-Spotted Char Salvelinus leucomaenis pluvius but Not to Two Other Salmonid Species.” Environmental Science & Technology Letters 9 (12): 1050–55. https://doi.org/10.1021/acs.estlett.2c00683.), but the relevance of this finding to human exposure through consumption of these organs is unclear. The monohydroxylated metabolite of 6PPD-q was also detected in the same tissues (Hiki and Yamamoto 2022[VQE4EZWI] Hiki, Kyoshiro, and Hiroshi Yamamoto. 2022. “The Tire-Derived Chemical 6PPD-Quinone Is Lethally Toxic to the White-Spotted Char Salvelinus leucomaenis pluvius but Not to Two Other Salmonid Species.” Environmental Science & Technology Letters 9 (12): 1050–55. https://doi.org/10.1021/acs.estlett.2c00683.). People who consume the whole body of the fish, such as in soup stock, may be exposed to higher concentrations of 6PPD-q due to its concentration in the brain of the fish. It is unknown whether 6PPD-q and/or 6PPD are present in the tissues of fish that are more likely to be consumed, such as the skin and fillet.

In addition to the lack of data concerning 6PPD-q and 6PPD levels in edible fish tissue, a notable data gap concerns other aquatic biota consumed by people, such as shellfish. In addition, limited attention has been directed toward understanding how cooking processes might alter levels in the edible portions of these aquatic organisms. Determining concentrations of 6PPD-q and 6PPD in aquatic food sources and assessing the impact of various cooking techniques is important for evaluating any potential human exposure risks and establishing informed consumption guidelines.

4.5.2 Other Potential Food Sources

Sherman, Hämmerle, et al. (Sherman et al. 2024[QBL568VF] Sherman, Anya, Luzian Elijah Hämmerle, Evyatar Ben Mordechay, Benny Chefetz, Thorsten Hüffer, and Thilo Hofmann. 2024. “Uptake of Tire-Derived Compounds in Leafy Vegetables and Implications for Human Dietary Exposure.” Frontiers in Environmental Science 12 (May). https://doi.org/10.3389/fenvs.2024.1384506.) detected 6PPD in 7 of 28 leafy vegetables sampled from grocery stores in Switzerland and Israel. The average concentration of the seven positive vegetables was 0.26 ng/g; the highest measurement was 0.4 ng/g. 6PPD-q was not detected in the vegetables. The uptake of 6PPD into hydroponically grown lettuce has been examined (Castan et al. 2023[3RBDETGD] Castan, Stephanie, Anya Sherman, Ruoting Peng, Michael T. Zumstein, Wolfgang Wanek, Thorsten Hüffer, and Thilo Hofmann. 2023. “Uptake, Metabolism, and Accumulation of Tire Wear Particle–Derived Compounds in Lettuce.” Environmental Science & Technology 57 (1): 168–78. https://doi.org/10.1021/acs.est.2c05660.). The results provide some general context for whether food crops can uptake 6PPD and translocate it through the plant. Interpretation is limited to the laboratory conditions, however, and are not necessarily relevant for field-grown crops. Exposing corn salad (*Valerianella locusta*) roots to 6PPD and 6PPD-q via tire particulates in hydroponic nutrient solution resulted in the detection of small amounts of 6PPD and 6PPD-q in the leaves of this edible plant. These experiments show that uptake and translocation of 6PPD-q into consumable plants is possible under some conditions. The exposure relevance of this study is limited because hydroponics is not a predominant cultivation method employed in agriculture, so it is uncertain whether the uptake behavior of 6PPD shown in this study would occur similarly in crops grown in agricultural soil (see also Section 4.1.4: Wastewater and Biosolids). Further, dosing levels used in the study were higher than environmentally relevant concentrations. Although a conjugated 6PPD-glucoside form and three stable biotransformation products of 6PPD-q were detected, the human health relevance of these products is unknown (Castan et al. 2023[3RBDETGD] Castan, Stephanie, Anya Sherman, Ruoting Peng, Michael T. Zumstein, Wolfgang Wanek, Thorsten Hüffer, and Thilo Hofmann. 2023. “Uptake, Metabolism, and Accumulation of Tire Wear Particle–Derived Compounds in Lettuce.” Environmental Science & Technology 57 (1): 168–78. https://doi.org/10.1021/acs.est.2c05660.).

Only one other study examining the presence of 6PPD and 6PPD-q in food other than fish was located by the ITRC Tire Anti-degradants team during preparation of this document (Ji et al. 2022[LDBNLUJS] Ji, Jiawen, Changsheng Li, Bingjie Zhang, Wenjuan Wu, Jianli Wang, Jianhui Zhu, Desheng Liu, et al. 2022. “Exploration of Emerging Environmental Pollutants 6PPD and 6PPDQ in Honey and Fish Samples.” Food Chemistry 396:133640. https://doi.org/10.1016/j.foodchem.2022.133640.). Ten samples of honey purchased at a supermarket in Beijing, China, were analyzed for 6PPD and 6PPD-q; neither 6PPD nor 6PPD-q was detected in any of the samples (Ji et al. 2022[LDBNLUJS] Ji, Jiawen, Changsheng Li, Bingjie Zhang, Wenjuan Wu, Jianli Wang, Jianhui Zhu, Desheng Liu, et al. 2022. “Exploration of Emerging Environmental Pollutants 6PPD and 6PPDQ in Honey and Fish Samples.” Food Chemistry 396:133640. https://doi.org/10.1016/j.foodchem.2022.133640.).

It is unknown whether the ingestion of non-aquatic food sources will expose the consumer to 6PPD or 6PPD-q. More studies are needed to fill this knowledge gap.

4.6 Consumer Products

In addition to exposure to tire-derived 6PPD and 6PPD-q via environmental media pathways (air, soil/dust, food, and water), there is also potential for exposure from manufactured consumer products other than tires that can also contain 6PPD and

6PPD-q. Consumer products are manufactured from new materials that contain 6PPD as an additive, as well as from recycled tires. Potential routes of human exposure from contact with consumer products may include dermal contact, inhalation of particles, and incidental ingestion of particles, depending upon the product and usage patterns. Exposure to 6PPD and 6PPD-q from consumer products has not been characterized. Further, testing of consumer products for 6PPD and 6PPD-q may not be comparable among the studies cited herein due to the lack of standardized methods and intra- and inter-laboratory validation procedures. The extent of human exposure and importance of the sources and products discussed below is not known.

4.6.1 Recycled Tire Rubber Products

An estimated five million tons of scrap tires were generated in the United States in 2021 (USTMA 2022[WYGSX5UU] USTMA, U.S. Tire Manufacturers Association. 2022. “2021 US Scrap Tire Management Summary.” October 25. https://www.ustires.org/sites/default/files/21%20US%20Scrap%20Tire%20Management%20Report%20101722.pdf.). Approximately 32% (equal to 1.6 million tons in 2021) of scrap tires are made into ground rubber in the United States. Ground rubber is then repurposed for a range of applications and manufactured products, including asphalt rubber paving, sports surfaces, loose mulch, and automotive and consumer products (USTMA 2022[WYGSX5UU] USTMA, U.S. Tire Manufacturers Association. 2022. “2021 US Scrap Tire Management Summary.” October 25. https://www.ustires.org/sites/default/files/21%20US%20Scrap%20Tire%20Management%20Report%20101722.pdf.).

The U.S. Tire Manufacturers Association (USTMA) estimates that 11% of the ground rubber from scrap tires is used to manufacture molded and extruded consumer and industrial products. Some of these products may be present in indoor environments, including flooring materials such as rubber mats and tiles and accessibility ramps (CalRecycle 2023[9MZ55M8A] CalRecycle. 2023. “California Tire Derived Products Catalog.” 2023. https://www.e-productcatalog.com/TDPCatalog/.). A small sample (n=2) of doormats made from recycled rubber were reported to contain 6PPD at an average of 630 µg/g and 6PPD-q at an average of 18 µg/g (Zhao et al. 2023[NMVDB224] Zhao, Haoqi Nina, Ximin Hu, Melissa Gonzalez, Craig A. Rideout, Grant C. Hobby, Matthew F. Fisher, Carter J. McCormick, et al. 2023. “Screening P-Phenylenediamine Antioxidants, Their Transformation Products, and Industrial Chemical Additives in Crumb Rubber and Elastomeric Consumer Products.” Environmental Science & Technology, February. https://doi.org/10.1021/acs.est.2c07014.).

Some products can also be stamped or cut directly from scrap tire tread. No analytic data on samples of stamped products was located.

As of 2021, 7% of recycled tire rubber is used for sports surfaces, for example as crumb rubber infill material for artificial turf fields and as playground surfaces. The potential for exposure to chemicals bound in recycled tire rubber requires additional investigation.

The U.S. National Toxicology Program detected 6PPD in recycled tire-crumb rubber samples from manufacturing facilities (National Toxicology Program, Public Health Service U.S. Department of Health and Human Services 2019[SAUIHJFK] National Toxicology Program, Public Health Service U.S. Department of Health and Human Services. 2019. “NTP Research Report on the Chemical and Physical Characterization of Recycled Tire Crumb Rubber.” Research Report 11. https://ntp.niehs.nih.gov/go/rr11abs.). The National Toxicology Program did not test for 6PPD-q (6PPD-q had not yet been discovered at the time the study was conducted). In a series of publications from a European study of crumb rubber, 86 samples from playing fields across Europe (Figure 4-1) contained 6PPD at an average concentration of 571 mg/kg for all samples. Levels were higher, averaging 1,000 mg/kg (0.1% by weight), for granules that had not been coated with polyurethane (Schneider et al. 2020[QN7GCPX2] Schneider, Klaus, Manfred De Hoogd, Maria Pelle Madsen, Pascal Haxaire, Anne Bierwisch, and Eva Kaiser. 2020. “ERASSTRI — European Risk Assessment Study on Synthetic Turf Rubber Infill — Part 1: Analysis of Infill Samples.” Science of The Total Environment 718:137174. https://doi.org/10.1016/j.scitotenv.2020.137174.). Again, concentrations of the quinone were not measured. More recently, both 6PPD and 6PPD-q were found in samples of crumb rubber from recreational facilities in Europe (Armada et al. 2023[AHX5WWPV] Armada, Daniel, Antia Martinez-Fernandez, Maria Celeiro, Thierry Dagnac, and Maria Llompart. 2023. “Assessment of the Bioaccessibility of PAHs and Other Hazardous Compounds Present in Recycled Tire Rubber Employed in Synthetic Football Fields.” Science of the Total Environment 857:159485. https://doi.org/10.1016/j.scitotenv.2022.159485.). Further, both compounds could be extracted from crumb-rubber samples with synthetic digestive fluids.

Figure 4-1. Crumb rubber, from recycled tires, is added as a cushioning infill in artificial turf, creating the potential for athletes to be exposed.
Image attribution: Football in the City Stadium, by Steve Daniels, https://commons.wikimedia.org/wiki/File:Football_in_the_City_Stadium_-_geograph.org.uk_-_5459076.jpg

Both 6PPD and 6PPD-q were detected in crumb rubber from a small sample (n=9) of synthetic turf athletic fields in Washington state (Cao et al. 2023[D5FPK9YB] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Han Qiao, Huankai Li, Gefei Huang, Zhu Yang, and Zongwei Cai. 2023. "Occurrence and Fate of Substituted P-Phenylenediamine-Derived Quinones in Hong Kong Wastewater Treatment Plants." Environmental Science & Technology, October. https://doi.org/10.1021/acs.est.3c03758.). Concentrations were highly variable. Median concentrations for 6PPD and 6PPD-q were 1.2 mg/kg and 9.8 mg/kg, respectively. The difference in concentration levels noted in Washington compared to the European samples is not yet understood.

In another study, researchers collected samples of crumb rubber from 40 school artificial turf fields in China. 6PPD and 6PPD-q were detected in fields using classical black rubber but not in fields using ethylene propylene diene monomer or thermoplastic elastomer. The results varied widely among fields using classical black rubber, with 6PPD concentrations ranging from 0.18 to 12.87 µg/g. 6PPD-q was detected in 24 out of 28 fields using classical black rubber, with concentrations ranging from less than the limit of quantitation to 28.05 µg/g (Zhao et al. 2024[LZFSSS5F] Zhao, Feng, Jingzhi Yao, Xinyu Liu, Man Deng, Xiaojia Chen, Changzhi Shi, Lei Yao, Xiaofei Wang, and Mingliang Fang. 2024. "Occurrence and Oxidation Kinetics of Antioxidant p-Phenylenediamines and Their Quinones in Recycled Rubber Particles from Artificial Turf." Environmental Science & Technology Letters 11 (4): 335–41. https://doi.org/10.1021/acs.estlett.3c00948.).

The study of recreational facilities in Europe did not detect 6PPD above the limit of quantitation in air monitoring of particulates conducted at field locations with crumb rubber playing surfaces (Schneider et al. 2020[7AVSU3G7] Schneider, Klaus, Manfred De Hoogd, Pascal Haxaire, Arne Philipps, Anne Bierwisch, and Eva Kaiser. 2020. "ERASSTRI — European Risk Assessment Study on Synthetic Turf Rubber Infill — Part 2: Migration and Monitoring Studies." Science of The Total

Environment 718:137173. https://doi.org/10.1016/j.scitotenv.2020.137173.).

4.6.2 Manufactured Products from New Materials Containing 6PPD

The vast majority of 6PPD in the United States is used in the manufacturing of tires; however, other consumer products made from elastomeric materials may also include 6PPD as an anti-degradant additive. Manufactured products that contain 6PPD and are used indoors could contribute to human exposure to 6PPD-q. People spend most of their time indoors, and young children are particularly vulnerable to exposure from household dusts due to behavioral factors such as crawling and playing on the floor (USEPA 2011[PL79ZTRH] USEPA. 2011. “Exposure Factors Handbook 2011 Edition (Final Report).” U.S. Environmental Protection Agency, Washington, DC.). We were unable to evaluate data on the extent of 6PPD additives in products. The lack of data and of studies that determine the rate of production of 6PPD-q from 6PPD in indoor environments represent information needed to adequately characterize human exposure levels.

A small sample of rubber consumer products including laboratory stoppers (n=3), sneaker soles (n=3), and a rubber garden hose (n=1) were reported to contain 6PPD (Zhao et al. 2023[NMVDB224] Zhao, Haoqi Nina, Ximin Hu, Melissa Gonzalez, Craig A. Rideout, Grant C. Hobby, Matthew F. Fisher, Carter J. McCormick, et al. 2023. “Screening P-Phenylenediamine Antioxidants, Their Transformation Products, and Industrial Chemical Additives in Crumb Rubber and Elastomeric Consumer Products.” Environmental Science & Technology, February. https://doi.org/10.1021/acs.est.2c07014.). The authors also tested for 6PPD-q. The laboratory stoppers and sneaker soles contained detectable levels of 6PPD-q (Zhao et al. 2023[NMVDB224] Zhao, Haoqi Nina, Ximin Hu, Melissa Gonzalez, Craig A. Rideout, Grant C. Hobby, Matthew F. Fisher, Carter J. McCormick, et al. 2023. “Screening P-Phenylenediamine Antioxidants, Their Transformation Products, and Industrial Chemical Additives in Crumb Rubber and Elastomeric Consumer Products.” Environmental Science & Technology, February. https://doi.org/10.1021/acs.est.2c07014.).

Marques dos Santos and Snyder (Marques dos Santos and Snyder 2023[GEI8HFLB] Marques dos Santos, Mauricius, and Shane Allen Snyder. 2023. “Occurrence of Polymer Additives 1,3-Diphenylguanidine (DPG), N-(1,3-Dimethylbutyl)-N′-Phenyl-1,4-Benzenediamine (6PPD), and Chlorinated Byproducts in Drinking Water: Contribution from Plumbing Polymer Materials.” Environmental Science & Technology Letters, September. https://doi.org/10.1021/acs.estlett.3c00446.) analyzed samples of plumbing fittings to determine whether these products can be a source of 6PPD in drinking water. Seven different plumbing devices (o-rings and polymer seals) were tested. An oscillating kit for a faucet filter made of acrylonitrile butadiene rubber leached the highest amount of 6PPD (1 ng/mg of material). Silicone-based seals did not leach 6PPD. 6PPD-q was not detected in these samples.

6PPD and 6PPD-q were found in the dust of e-waste recycling facilities in China (Liang et al. 2022[SZPLJY9T] Liang, Bowen, Jiehua Li, Bibai Du, Zibin Pan, Liang-Ying Liu, and Lixi Zeng. 2022. “E-Waste Recycling Emits Large Quantities of Emerging Aromatic Amines and Organophosphites: A Poorly Recognized Source for Another Two Classes of Synthetic Antioxidants.” Environmental Science & Technology Letters, June, acs.estlett.2c00366. https://doi.org/10.1021/acs.estlett.2c00366.) and Ontario (Wu, Venier, and Hites 2020[F7XN9GAC] Wu, Yan, Marta Venier, and Ronald A. Hites. 2020. “Broad Exposure of the North American Environment to Phenolic and Amino Antioxidants and to Ultraviolet Filters.” Environmental Science & Technology 54 (15): 9345–55. https://doi.org/10.1021/acs.est.0c04114.). Liang et al. suggest that the sources may be materials in consumer electronics (Liang et al. 2022[SZPLJY9T] Liang, Bowen, Jiehua Li, Bibai Du, Zibin Pan, Liang-Ying Liu, and Lixi Zeng. 2022. “E-Waste Recycling Emits Large Quantities of Emerging Aromatic Amines and Organophosphites: A Poorly Recognized Source for Another Two Classes of Synthetic Antioxidants.” Environmental Science & Technology Letters, June, acs.estlett.2c00366. https://doi.org/10.1021/acs.estlett.2c00366.). Whether consumer electronics expose people in the United States to 6PPD or 6PPD-q is unknown as of March 2024.

Section 5 Tables

Section 5 reviews the variety of methods for assessing and measuring 6PPD and 6PPD-q among variable environmental matrices and landscapes. This section also includes discussion on using desktop mapping (GIS) and modeling tools to help focus reconnaissance efforts. Finally, this chapter provides an overview of modeling tools to help visualize potential 6PPD-q hot spots near potentially vulnerable ecosystems.

The following tables compile information recommendations on where and how to measure 6PPD and 6PP-q based on the studies and related research work that this ITRC team was aware of as of March 2024.

Table Number and Title	**Link to HTML**	
5-1 Recommendations for measuring 6PPD and 6PPD q in drinking water supply systems		
	Link to PDF	**Link to Executable File (Word Processor Format)**
5-2 Summary of Sample Collection and Analytical Method Information for Studies of 6PPD		
5-3 Summary of Sample Collection and Analytical Method Information for Studies of 6PPD-q		
5-4 Assessment of 6PPD q Sample Collection Methods		
	Link to HTML	
5-5 Sampling recommendations for 6PPD-q in water		

5-6 Selected mapping tools and other resources that may be useful for visualizing water quality conditions in support of resource and stormwater management	HTML

PDF versions of each table are provided for the reader to view information in a visual format that is consistent across browsers and platforms. Executable files are provided to allow readers to sort information by the column of their choice, but may appear different visually depending on the software used to view this file. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

5 Measuring, Mapping, and Modeling

This chapter reviews the variety of methods for assessing and measuring 6PPD and 6PPD-q among variable environmental matrices and landscapes. The discovery of a new chemical has spurred collaborations and sharing of scientific innovations to develop standard operating procedures in record time. Continued innovations and coordination among technical staff are needed to further develop and evaluate analytical methods to understand the scope and scale of the tire contaminant problem. This chapter includes a section on using desktop mapping (geographic information system [GIS]) and modeling tools to help focus reconnaissance efforts when dealing with such a widespread contaminant. In addition, this chapter provides an overview of modeling tools to help visualize potential 6PPD-q hot spots near potentially vulnerable ecosystems.

5.1 Field Methods

Science and monitoring efforts by local, state, and federal agencies and universities are in the stage of developing methods for sampling and measuring 6PPD-q. More research is needed to assess the many data gaps regarding the exposure and health impacts of TRWP, 6PPD, and 6PPD-q to human, terrestrial, and aquatic life. Defining tire contaminant leaching dynamics, fate, transport, persistence, and occurrence will help us understand exposure risks and environmental impacts. Bulk-based and single-particle–based methods are used to attempt to measure TRWP; however, the complex and variable characteristics of TRWP present analytical challenges (Rødland et al. 2023[SGXM45KB] Rødland, Elisabeth S., Mats Gustafsson, David Jaramillo-Vogel, Ida Järlskog, Kathrin Müller, Cassandra Rauert, Juanita Rausch, and Stephan Wagner. 2023. “Analytical Challenges and Possibilities for the Quantification of Tire-Road Wear Particles.” TrAC Trends in Analytical Chemistry 165:117121. https://doi.org/10.1016/j.trac.2023.117121.).

The ability to reliably measure PPDs and associated transformation products like 6PPD-q is needed to address the many data gaps. The most appropriate sampling method will depend on study objectives, the landscape, and environmental media. The matrix and available laboratories will often determine the analytical method.

The most appropriate study design will depend on the objective. There are many different types of environmental sampling study objectives, including point and nonpoint source identification, status and trends, and effectiveness monitoring. The objective will determine whether a probabilistic design or a stratified nonrandomized design is most appropriate. The intended use of the data will also guide the most effective sampling design; these include exploratory, regulatory, model building, or focusing site reconnaissance (USEPA 2002[AP7FTC43] USEPA. 2002. “Guidance on Choosing a Sampling Design for Environmental Data Collection for Use in Developing a Quality Assurance Project Plan.” EPA QA/G-5S. Washington, DC: Office of Environmental Information. https://www.epa.gov/sites/default/files/2015-06/documents/g5s-final.pdf.).

5.1.1 Natural Landscape Considerations

5.1.1.1 Streams/Rivers

Environmental Data Gaps

- A limited number of published studies have conducted 6PPD or 6PPD-q sampling.
- Most sampling has been along roadways and in streams or rivers.
- More sampling is needed to understand the occurrence, persistence, fate, and transport of TRWP, 6PPD, and 6PPD-q in the terrestrial and aquatic environments.

Of the species studied to date, coho salmon are the most sensitive and acutely impacted by 6PPD-q. The species resides in small streams throughout the lowlands that are often subjected to URMS. Small streams may be the most impacted by roadway runoff and TRWP, 6PPD, and 6PPD-q. Identifying the most appropriate sampling method depends on the size of the stream, accessibility, flow, mixing rates, and sampling duration. For small, well-mixed, shallow streams, a well-timed grab sample from the stream bank or a well-placed autosampler is effective. For larger rivers with higher banks, deep and fast-moving water, and difficult terrain, a cable, bridge, or boat are more appropriate for sampling. For longer-term monitoring, an autonomous stream sampling station with an autosampler triggered by rain and flow metrics is more appropriate in many instances. Autonomous moorings are another great option for larger rivers. The sampler should be aware of upstream and downstream point and nonpoint sources such as highway bridges, stormwater, or wastewater treatment discharges when choosing the best site to sample or deploy sampling equipment. The goal is to collect a sample that is representative of the whole stream; however, streams and rivers with stormwater and wastewater discharges are not always homogenous (

Shelton 1994[7NMALZXW] Shelton, Larry R. 1994. “Field Guide for Collecting and Processing Stream-Water Samples for the National Water-Quality Assessment Program.” USGS Numbered Series Open-File Report 94–455. U.S. Geological Survey.). The timing and location of exposure to TRWP, 6PPD, and 6PPD-q is poorly understood, and more research is needed.

5.1.1.2 Lakes/Ponds

The land use around a lake or pond and the discharge types to a lake or pond will determine the exposure risk to resident fish species impacted by tire contaminants. Geographic information system (GIS) desktop assessments and communication with the local managing jurisdiction will help identify areas of highest concern when determining where to sample. Lakes can provide an effective record of contamination over time, which can be accessed by collecting and processing sediment cores. Sampling biota, such as fish tissues, is another useful monitoring tool. Methods are being developed for measuring 6PPD-q in fish tissues and plasma to support this type of work. Research is needed to evaluate the presence of TRWPs in lakes and whether they continue leaching over time.

5.1.1.3 Wetlands

The impact and vulnerability of wetlands to tire contaminant exposure is currently unknown. More research is needed to understand the transport of 6PPD and 6PPD-q to wetlands and the toxicity of the contaminants to wetland inhabitants. Analysis of the effluent of wetlands to adjacent streams and estuaries is needed as well.

5.1.1.4 Estuaries

Toxics tend to accumulate in estuaries. Coho salmon are salmonids that are particularly sensitive to 6PPD-q and spend a considerable amount of time in estuaries. The juveniles spend several months to years getting ready to leave their natal watershed before they venture out to sea. Thus, the juveniles are exposed to the toxics while in the estuaries (Carey et al. 2023[TADJGUPJ] Carey, Andrea, Alex Gipe, William Hobbs, and Sandra O’Neill. 2023. “Investigating the Source of PBDE Contaminant Exposure in Steelhead Trout within the Major Tributaries of the Nisqually River Basin.” Final Contract Report Submitted to the Nisqually Indian Tribe WDFW Report Number FPT 23-02. Washington Department of Fish and Wildlife — Toxics Biological Observation System (TBiOS) and Washington Department of Ecology — Environmental Assessment Program. https://wdfw.wa.gov/sites/default/files/publications/02440/wdfw02440.pdf.). Sampling of water, sediments, and biota in estuaries is needed to evaluate the fate and transport of tire contaminants. Like streams and rivers, the characteristics of the estuary will determine the best sampling method.

5.1.1.5 Marine

TRWPs are a major component of microplastic pollution in the marine environment (Kole et al. 2017[NZZMY6WC] Kole, Pieter Jan, Ansje J. Löhr, Frank G. A. J. Van Belleghem, and Ad M. J. Ragas. 2017. “Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment.” International Journal of Environmental Research and Public Health 14 (10): 1265. https://doi.org/10.3390/ijerph14101265.Sieber, Kawecki, and Nowack 2020[LENES5UC] Sieber, Ramona, Delphine Kawecki, and Bernd Nowack. 2020. “Dynamic Probabilistic Material Flow Analysis of Rubber Release from Tires into the Environment.” Environmental Pollution 258:113573. https://doi.org/10.1016/j.envpol.2019.113573.Boucher and Friot 2017[KK2RJVQ6] Boucher, Julien, and Damien Friot. 2017. “Primary Microplastics in the Oceans: A Global Evaluation of Sources.” Gland, Switzerland: IUCN.). The fate and transport of these particles and their ability to continue leaching 6PPD and 6PPD-q is unknown. More research is needed to evaluate the presence of 6PPD and 6PPD-q in the marine environment. Coastal marine environments are logistically more complex to sample and often require boats to support collections. Sediments and biota are effective methods for measuring contaminant exposure. Methods for measuring 6PPD-q in marine matrices are being evaluated.

5.1.2 Built Landscape Considerations

5.1.2.1 Drinking Water

Data Gaps in Water and Wastewater Treatment

- Minimal studies have been published regarding the efficacy of current drinking water, wastewater, and stormwater filtration technologies.
- More sampling is needed to determine whether 6PPD and 6PPD-q are properly mitigated with current technology or new treatment technologies are needed.

Human exposure to 6PPD-q has been documented by biomonitoring studies (see Section 2.5). However, the routes of exposure are still unknown. The possibility of exposure through drinking water remains a data gap. To help close the data gaps related to 6PPD and 6PPD-q in drinking water, Table 5-1 recommends locations and provides the rationale for collecting and analyzing samples for these chemicals.

Table 5-1. Recommendations for measuring 6PPD and 6PPD-q in drinking water supply systems

Description	Recommended Sample Collection Location(s)	Rationale for Sample Collection and Analysis
Source Water (Rivers, Streams, Lakes, Reservoirs, Springs, Groundwater)	• point(s) of intake • upstream (or upgradient) from the point of intake	• identify potential sources of 6PPD • measure the effectiveness of surface water treatment devices (if present)
Treatment Plant (DWTP)	• point(s) of intake • effluent (finished drinking water)	• evaluate how effectively treatment plant processes remove 6PPD and 6PPD-q from source water
End Use	• point of entry to household, business, government building, etc. • point of use (faucets, etc.)	• determine whether sources of 6PPD or 6PPD-q are impacting the treated water distribution system • identify potential sources of 6PPD or 6PPD-q within the end user’s pipes or on-site treatment/conditioning systems

5.1.2.2 Wastewater

WWTP receive wastewater from sanitary sewers or combined sewer systems. The type of sewer system depends on geographic location, local management guidance, and age of infrastructure. Each type of system has pros and cons. Some municipal and industrial stormwater systems discharge to WWTP. A study conducted in Toronto, Canada, detected 6PPD-q in the influent and effluent of a municipal WWTP (Johannessen and Metcalfe 2022[6AEMVTD8] Johannessen, Cassandra, and Chris D. Metcalfe. 2022. “The Occurrence of Tire Wear Compounds and Their Transformation Products in Municipal Wastewater and Drinking Water Treatment Plants.” Environmental Monitoring and Assessment 194 (10): 731. https://doi.org/10.1007/s10661-022-10450-9.). Many transportation operation centers and car-washing sites collect their gray water and send it to WWTP. More research is needed to measure how effectively WWTP remove CEC, including newly discovered organic contaminants like 6PPD-q. Sampling methods will depend on the study goal and available resources. Choosing between autosamplers and grab samples will partially depend on the residence time of the influent prior to discharge (McHugh 2023[ZITFDETV] McHugh, Chris. 2023. “Wastewater Sampling.” LSASDPROC-306-R6 042223. Athens, Georgia: Region 4 U.S. Environmental Protection Agency Laboratory Services & Applied Science Division. https://www.epa.gov/sites/default/files/2017-07/documents/wastewater_sampling306_af.r4.pdf.).

5.1.2.3 Hatcheries

Water Quality of Hatcheries

- Some larger hatcheries have developed filtration systems to protect salmon and trout populations from contaminants.
- Do these filtration methods remove 6PPD and 6PPD-q?
- More studies are needed to determine whether filtration removes 6PPD-q and whether hatcheries can act as refugia from urban pollution.
- Smaller tribal hatcheries do not have the same institutional support as state and federal hatcheries.
- Hatcheries near urban areas are likely to be more vulnerable to 6PPD-q exposure, and sampling is needed to detect 6PPD-q toxicity.

The initial coho salmon mass mortality events were observed in a fish hatchery in Washington State. The hatchery used diverted stream water that ran through a moderately urbanized area. Unexplained mass die offs would occur among coho salmon, but not other salmonids. WA Ecology conducted a three-year ecoforensic investigation and determined that the mortality events occurred during or after storm events (Kendra and Willms 1990[BQ4XP54V] Kendra, Will, and Roger Willms. 1990. “Recurrent Coho Salmon Mortality at Maritime Heritage Fish Hatchery, Bellingham: A Synthesis of Data Collected from

1987–1989." Washington State Department of Ecology, Environmental Services Program, Surface Water Investigations Section. https://apps.ecology.wa.gov/publications/documents/90e54.pdf.). At that time, the analytical ability to pinpoint the contaminant causing the mortality had not yet been established. The hatchery switched from using stream water to well water, and the URMS events stopped. Any hatcheries that use creek or river water that are impacted by urbanization or transportation runoff are at risk of exposing sensitive species to tire contaminants. There may be a need to sample the influent of hatcheries that observe URMS occurrences or learn from the effectiveness of their filtration systems.

Hatcheries have been proposed as a refuge for salmon and trout populations that are impacted by urbanization. For example, Elwha hatcheries on the Olympic Peninsula in Washington provided a refuge after the Elwha River dam was removed and built-up sediment smothered spawning grounds. Eventually the sediment was transported out of the river, but the hatcheries helped sustain the population in the interim.

In the case of 6PPD and 6PPD-q, the hatcheries often have outdated infrastructure that may need to be retrofitted to control toxic exposures. Studies that coordinate fish population trends and 6PPD-q are needed to understand the impact on the populations at each life history stage.

5.1.3 Stormwater Considerations

Stormwater Management Efficacy

- Stormwater management is customized to land uses.
- Standardized methods are needed to identify effective stormwater management practices to protect aquatic life from 6PPD-q.

Stormwater management technologies can be designed to mimic natural filtration processes to capture TRWP and bind pollutants from roadways (McIntyre et al. 2023[F7NAIVJ4] McIntyre, Jenifer, Julann Spromberg, James Cameron, John P. Incardona, Jay W. Davis, and Nathaniel L. Scholz. 2023. "Bioretention Filtration Prevents Acute Mortality and Reduces Chronic Toxicity for Early Life Stage Coho Salmon (Oncorhynchus kisutch) Episodically Exposed to Urban Stormwater Runoff." Science of the Total Environment 902 (December):165759. https://doi.org/10.1016/j.scitotenv.2023.165759.Rodgers et al. 2023[LZXSW5WM] Rodgers, Timothy F. M., Yanru Wang, Cassandra Humes, Matthew Jeronimo, Cassandra Johannessen, Sylvie Spraakman, Amanda Giang, and Rachel C. Scholes. 2023. "Bioretention Cells Provide a 10-Fold Reduction in 6PPD-Quinone Mass Loadings to Receiving Waters: Evidence from a Field Experiment and Modeling." Environmental Science & Technology Letters, June. https://doi.org/10.1021/acs.estlett.3c00203.Spromberg et al. 2016[GI97QYN4] Spromberg, Julann A., David H. Baldwin, Steven E. Damm, Jenifer K. McIntyre, Michael Huff, Catherine A. Sloan, Bernadita F. Anulacion, Jay W. Davis, and Nathaniel L. Scholz. 2016. "Coho Salmon Spawner Mortality in Western US Urban Watersheds: Bioinfiltration Prevents Lethal Storm Water Impacts." Journal of Applied Ecology 53 (2): 398–407. https://doi.org/https://doi.org/10.1111/1365-2664.12534.McIntyre et al. 2014[G79YZJGX] McIntyre, J. K., J. W. Davis, J. P. Incardona, John D. Stark, B. F. Anulacion, and N. L. Scholz. 2014. "Zebrafish and Clean Water Technology: Assessing Soil Bioretention as a Protective Treatment for Toxic Urban Runoff." Science of the Total Environment 500:173–80. https://doi.org/10.1016/j.scitotenv.2014.08.066.). Customized treatment trains that employ multiple methods to reduce and control TRWPs and other contaminants is another potential effective strategy. Further research is needed to study the effectiveness of new and existing stormwater control devices and features.

The conveyance and presence or absence of SCMs will determine the discharge of 6PPD-q to potentially vulnerable aquatic habitats (see also Section 6.3.3). Inventories of these discharge outfalls and the types of conveyance and stormwater control devices will help identify areas to conduct pollution identification and correction studies.

Tire-derived contaminants are washed into waterbodies during storm events, which lead to temporary peaks in 6PPD-q concentrations (Johannessen et al. 2022[E9K7U5U3] Johannessen, Cassandra, Paul Helm, Brent Lashuk, Viviane Yargeau, and Chris D. Metcalfe. 2022. "The Tire Wear Compounds 6PPD-Quinone and 1,3-Diphenylguanidine in an Urban Watershed." Archives of Environmental Contamination and Toxicology 82 (2): 171–79. https://doi.org/10.1007/s00244-021-00878-4.). Single time-point grab samples may not represent an ecologically relevant concentration due to 6PPD-q mobility through the aquatic environment. In larger rivers and watersheds, peak concentration of 6PPD-q may not be observed for many hours after peak discharge (Johannessen et al. 2022[E9K7U5U3] Johannessen, Cassandra, Paul Helm, Brent Lashuk, Viviane Yargeau, and Chris D. Metcalfe. 2022. "The Tire Wear Compounds 6PPD-Quinone and 1,3-Diphenylguanidine in an Urban Watershed." Archives of Environmental Contamination and Toxicology 82 (2): 171–79. https://doi.org/10.1007/s00244-021-00878-4.). In smaller tributaries with high amounts of impervious surfaces that impair water quality, referred to as urban stream syndrome (Walsh et al. 2005[CQ74T2RQ] Walsh, Christopher J., Allison H. Roy, Jack W. Feminella, Peter D. Cottingham, Peter M. Groffman, and Raymond P. Morgan. 2005. “The Urban Stream Syndrome: Current Knowledge and the Search for a Cure.” Journal of the North American Benthological Society 24 (3): 706–23. https://doi.org/10.1899/04-028.1.), peak concentrations may occur in the first hour. The greater the percent of impervious surface within the stream catchment, the flashier the stream and the more difficult it is to capture the pollutant peak (Gulliver, Erickson, and Weiss 2010[7SGTZFB7] Gulliver, J. S., A. J. Erickson, and P. T. Weiss, eds. 2010. Stormwater Treatment: Assessment and Maintenance. University of Minnesota, St. Anthony Falls Laboratory. Minneapolis, MN. https://stormwaterbook.safl.umn.edu/.).

5.1.3.1 Stormwater Effectiveness Sampling

In some cases, paired influent and effluent sampling is useful for SCM effectiveness evaluations. Paired sampling is most appropriate for SCMs with a relatively short (on the order of minutes) detention time. Alternative sampling methods are suggested for longer detention time SCMs or treatment trains (ponds, etc.), as indicated by the Technology Assessment Protocol–Ecology (TAPE). TAPE is WA Ecology’s process for evaluating and approving emerging stormwater treatment BMPs (https://www.wastormwatercenter.org/stormwater-technologies/tape/).

5.1.3.2 Selecting a Stormwater Control Measure

Stormwater Control Measure Efficacy

- There are prescribed methods for testing and approving new technologies. These methods help avoid unintended consequences and maximize the treatment co-benefits for other pollutants of concern.
- In addition, exploratory sampling is needed for existing infrastructure and will require less stringent efficacy methods. Understanding the inventory of existing conveyance and treatment are recommended first steps.

This section presents a typical stormwater effectiveness sampling protocol. When choosing an SCM to monitor be sure to get permission from the property owner and/or jurisdiction. It is also best to do the following:

- Find an SCM that is in an area that does not have a safety hazard such as steep slopes, in a roadway, or similar.
- Avoid sites affected by backwater, tidal influence, or high groundwater.
- Ensure the land use/drainage basin will produce enough pollutants of interest to evaluate the effectiveness of the measure.

Sampling equipment will require dedicated, solar, or battery power. When selecting an SCM to monitor, consider whether staff will need to carry batteries and sample bottles a long distance. It is also best to avoid sites that require confined space entry for sample collection or other routine activities.

5.1.3.2.1 SCM Information

The following information about the SCM should be recorded/documented, where applicable:

- If this is an existing SCM, how long has the system been in operation?
- If this is an existing SCM, how frequently has it needed maintenance or been maintained?
- Was the SCM sized following the regional stormwater management guidance?
- What is the design flow rate?
- What are the treatment mechanisms (high-density sludge, sand filter, membrane filter, media filter, etc.)?
- What is the size of the system (area of filter bed, number of cartridges, etc.)? For media filters, what type of media is it?
- What is the primary land use in the drainage basin?
- How big is the drainage basin?

5.1.3.3 Precipitation Monitoring

Rainfall should be measured within the drainage basin or adjacent to the monitoring equipment. Rainfall monitoring should be performed to measure and record rainfall continuously throughout the study duration (Washington State Department of Ecology 2018[8VMVK98Y] Washington State Department of Ecology. 2018. “Technical Guidance Manual for Evaluating Emerging Stormwater Treatment Technologies.” Washington State Department of Ecology.

https://apps.ecology.wa.gov/publications/documents/1810038.pdf.). Section 5.1.3.6 summarizes a typical best practice for qualifying participation events in terms of storm size, storm duration, and antecedent conditions, although one or more of these parameters can be adjusted as necessary to meet study objectives.

5.1.3.4 Flow Monitoring

The following recommendations on current best practices for treatment system flow monitoring are summarized from technical guidance from Washington State Department of Ecology (Washington State Department of Ecology 2018[8VMVK98Y] Washington State Department of Ecology. 2018. "Technical Guidance Manual for Evaluating Emerging Stormwater Treatment Technologies." Washington State Department of Ecology. https://apps.ecology.wa.gov/publications/documents/1810038.pdf.). It is important to continuously monitor influent, effluent, and bypass flow rates throughout the duration of each project or study.

Influent and effluent flows should be measured as close as practicable to the inlet and outlet, respectively, to ensure that the recorded depth and flow rate represent actual conditions experienced by the system. It is important to select an effluent monitoring location that avoids measuring effluent flow rates in portions of the conveyance system where this flow mixes with bypass flow.

Stormwater that goes around the treatment system should be measured in areas that represent only the water circumventing the treatment system. It is best practice to avoid bypass flow measurement in the portions of the conveyance system where bypass flow mixes with effluent (treated) flow.

Each flow measurement device should be installed in a place that is both secure and convenient to access. The equipment needs to be properly calibrated and maintained on a regular basis and should be easily accessible for the entire duration of monitoring activities.

5.1.3.5 Water Quality Sampling

Technical guidance from WA Ecology recommends collecting a minimum of 15 pairs of samples from the influent and effluent of the treatment system during separate storm events (Washington State Department of Ecology 2018[8VMVK98Y] Washington State Department of Ecology. 2018. "Technical Guidance Manual for Evaluating Emerging Stormwater Treatment Technologies." Washington State Department of Ecology. https://apps.ecology.wa.gov/publications/documents/1810038.pdf.). That guidance also recommends use of automated samplers for sample collection for target analytes unless that analyte requires manual grab samples (for example, NWTPH-Dx, fecal coliform, *E. coli*).

When choosing monitoring locations, keep in mind that insufficient mixing may cause stratification across the flow column for settleable or floating solids and the bound pollutants associated with these solids. Best practice is to gather influent and effluent samples where stormwater flow is well mixed and unaffected by pollutants that have accumulated or been stored in stagnant areas. When an automated sampler is used, the sampling locations should be located sufficiently far from the flow-monitoring apparatus to prevent skewed depth and flow measurements (Washington State Department of Ecology 2018[8VMVK98Y] Washington State Department of Ecology. 2018. "Technical Guidance Manual for Evaluating Emerging Stormwater Treatment Technologies." Washington State Department of Ecology. https://apps.ecology.wa.gov/publications/documents/1810038.pdf.).

Influent samples should be collected as close as possible to the treatment system inlet to ensure that the samples are representative of actual conditions. Effluent samples should be collected as close as practicable to the outlet for the treatment system to ensure collection of samples that are representative of treated water. Samples should not be collected from locations where the conveyance system and bypass flow mix (Washington State Department of Ecology 2018[8VMVK98Y] Washington State Department of Ecology. 2018. "Technical Guidance Manual for Evaluating Emerging Stormwater Treatment Technologies." Washington State Department of Ecology. https://apps.ecology.wa.gov/publications/documents/1810038.pdf.).

Additional national guidance for stormwater sampling is available for urban stormwater BMP performance, NPDES compliance, and industrial stormwater (USEPA 2017[PFTF5ZRM] USEPA. 2017. "NPDES Compliance Inspection Manual Chapter 5 — Sampling." Interim Revised Version.

https://www.epa.gov/sites/default/files/2017-03/documents/npdesinspect-chapter-05.pdf.USEPA 2004[3JZH9WJS] USEPA. 2004.

“NPDES Compliance Inspection Manual.” EPA 305-X-04-001. Office of Enforcement and Compliance Assurance.

https://www.epa.gov/sites/default/files/2013-09/documents/npdesinspect_0.pdf.USEPA 2021[HSPCRKFU] USEPA. 2021. “Industrial Stormwater Monitoring and Sampling Guide.” EPA 832-B-09-003. https://www.epa.gov/sites/default/files/2015-11/documents/msgp_monitoring_guide.pdf.Geosyntec Consultants and Wright Water Engineers, Inc. 2009[BZIBLH7F] Geosyntec Consultants, and Wright Water Engineers, Inc. 2009. “Urban Stormwater BMP Performance Monitoring.” https://static1.squarespace.com/static/5f8dbde10268ab224c895ad7/t/604926dae8a36b0ee128f8ac/1615406817379/2009MonitoringManualSingleFile.pdf.).

5.1.3.6 An Example of Valid Sample/Storm Event

The list below is an example of current best practice for samples and storms to be considered an Event Mean Concentration and a valid sample:

- Storm Size: ≥0.15 inches
- Antecedent dry period: 6 hours with less than 0.04 inches
- Storm duration: ≥1 hour
- Range of rainfall intensities
- Number of aliquots per sample: ≥10
- Storm coverage: aliquots should be collected over ≥75% of the first 24 hours of the hydrograph
- Sample duration: ≤36 hours
- Number of samples (paired effluent and influent when possible): 15 each

5.1.3.7 Study Duration

The duration of the sample should span at least one and one-half maintenance cycles or, for systems with more than a 2-year maintenance cycle, two wet seasons (Washington State Department of Ecology 2018[8VMVK98Y] Washington State Department of Ecology. 2018. “Technical Guidance Manual for Evaluating Emerging Stormwater Treatment Technologies.” Washington State Department of Ecology. https://apps.ecology.wa.gov/publications/documents/1810038.pdf.).

For a storm event meeting the criteria of Section 5.1.3.6, collection of a minimum of 15 pairs of influent and effluent samples within a 36-hour period is recommended.

5.1.3.8 Maintenance Inspections and Activities

The study should include regular maintenance inspections to track and record the maintenance needs of the test system. Maintenance indicators are generally specific to the BMP, but typical indicators include an accumulation of sediment and a reduction in effluent (treated) flow rate through the system. All maintenance inspections and activities should be documented.

5.1.4 Comparison of Sampling 6PPD and 6PPD-q

Most laboratories have chosen to measure 6PPD-q because it is more stable and has a longer half-life than 6PPD. This fact has resulted in fewer studies of 6PPD (Table 5-2) relative to 6PPD-q (Table 5-3). If measurement of 6PPD is important to the study objectives, timely extraction of 6PPD after sample collection (within hours) is necessary.

Table	Media Type	Link to PDF	Link to Executable File (Word Processor Format)
5-2	Summary of sample collection and analytical method information for studies of 6PPD	PDF	W
5-3	Summary of sample collection and analytical method information for studies of 6PPD-q	PDF	W

Note: PDF versions of each table are provided for the reader to view information in a visual format that is consistent across browsers and platforms. Executable files are provided to allow readers to sort information by the column of their choice, but may appear different visually depending on the software used to view this file. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

The pros and cons of commonly used sampling methods for 6PPD-q in various media are presented in Table 5-4.

Table	**Media Type**	**Link to PDF**	**Link to Executable File (Word Processor Format)**
5-4	Assessment of 6PPD-q sample collection methods		

Note: The PDF version of this table is provided for the reader to view information in a visual format that is consistent across browsers and platforms. The executable file is provided to allow readers to sort information by the column of their choice, but may appear different visually depending on the software used to view this file. Instructions on how to sort information in a document formatted for a word processor format are widely available by internet search.

5.1.5 Sampling 6PPD-q in Water

Capturing the peak (the highest concentration) of 6PPD-q is essential when determining the exposure impact to sensitive organisms. The sampling objectives also drive the type of sampler used so that exposure to 6PPD-q can be accurately measured over a given period and agencies can assess the risk of URMS occurrences.

Table 5-5 presents recommended approaches and materials to minimize or avoid when collecting samples for 6PPD-q in water.

Table 5-5. Sampling recommendations for 6PPD-q in water

Category	**Recommended**	**Minimize or Avoid**
Pump Tubing	PTFE tubing	Silicon tubing
Sample Container	Amber glass bottle with PTFE-lined cap; cleaned and certified	Plastic containers
Sample Splitters or Funnels	Metal or PTFE	Other plastics
Gloves	Nitrile	
Sample Storage	On ice until delivered to lab for analysis	

Note: PTFE=polytetrafluoroethylene

The remainder of this section describes different ways to collect water samples for 6PPD-q.

5.1.5.1 Grab Sampling

Grab samples can be an effective sampling method when screening for 6PPD-q given its flexibility and low cost. Yet, 6PPD-q grab samples often require logistically challenging storm chasing at all hours and days of the week and can result in false nondetects when pollutant peaks are missed. Amber glass bottles are recommended to prevent 6PPD-q loss from binding and photodegradation, and polyurethane bottles can be used for short hold times (hours); samples should be transferred to glass for longer hold times (Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone.” Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.).

To date, there are no 6PPD-q–specific sampling considerations for drinking water collection. Use existing drinking water protocols and the general 6PPD-q water sampling recommendations.

5.1.5.2 Active Sampling in Water

Autosampler Considerations

- PTFE tubing and glass bottles are preferred to minimize 6PPD-q loss due to affinity to some plastics.
- If polyethylene containers are used, the sample should be transferred to amber glass bottles or extracted as soon as possible.
- Store samples on ice until transferred to the lab.
- Remotely triggered or programmed samplers are an effective method that reduce logistically challenging storm chasing.

Autosamplers are an effective active sampling method for measuring organic contaminants in stormwater, but they require an equipment investment and technical staff. Most autosamplers can be programmed to composite the samples into one jar or collect discrete, sequential samples in separate containers. The ability to trigger the autosampler to capture a water sample at the right time is an effective way to capture the pollutant peak, whereas other methods are averaging or integrative.

Special considerations for 6PPD-q autosampling include tubing and bottle-type choices. The preferred bottle type is amber glass; however, polyurethane bottles are acceptable for short periods of time based on the measured stickiness of lab and field equipment (Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. "Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone." Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.). If polyurethane bottles are used, samples should be transferred to amber glass bottles as soon as possible. The preferred tubing is polytetrafluoroethylene (PTFE)-lined tubing, as 6PPD-q has been shown to readily adhere to other types of tubing (Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. "Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone." Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.). Samples should be kept on ice until transported from the field to the lab for extractions.

According to Gulliver et al. (Gulliver, Erickson, and Weiss 2010[7SGTZFB7] Gulliver, J. S., A. J. Erickson, and P. T. Weiss, eds. 2010. Stormwater Treatment: Assessment and Maintenance. University of Minnesota, St. Anthony Falls Laboratory. Minneapolis, MN. https://stormwaterbook.safl.umn.edu/.), "…[r]emote sampler capabilities reduce collection costs and make it possible to obtain many more samples per storm event than is possible with current manual sampling techniques." For example, USEPA has created an in-stream remote sampling tool that uses a micropump to collect water samples (Kahl et al. 2014[X5ZATENS] Kahl, Michael D., Daniel L. Villeneuve, Kyle Stevens, Anthony Schroeder, Elizabeth A. Makynen, Carlie A. LaLone, Kathleen M. Jensen, et al. 2014. "An Inexpensive, Temporally Integrated System for Monitoring Occurrence and Biological Effects of Aquatic Contaminants in the Field: Novel System for in Situ Testing." Environmental Toxicology and Chemistry 33 (7): 1584–95. https://doi.org/10.1002/etc.2591.). Other groups have developed similar remote samplers (for example, Schönenberger et al. 2020[6Q9QTYR8] Schönenberger, Urs, Michael Patrick, Simon Wullschleger, and Christian Stamm. 2020. "A Water-Level Proportional Water Sampler for Remote Areas." Zenodo. https://zenodo.org/records/4280534.). These types of samplers may prove more practical for stormwater monitoring needs because they cost less while offering greater flexibility on sampling location relative to traditional approaches using manual sampling.

5.1.5.3 Passive Sampling in Water

Passive Samplers

- Passive samplers provide a cost-effective method for assessing the most bioavailable dissolved form of a contaminant. Passive samplers for 6PPD-q are being evaluated.

Passive samplers have gained popularity over the last decade as an effective method for assessing the spatial and temporal occurrence of organic contaminants. The passive samplers are deployed in the field and left for days to weeks; many are relatively affordable, and some mimic the bioavailable form of contaminants. This is particularly useful for 6PPD-q that is transported during storm events and persists for only hours to days in surface water before settling to the benthic environment or being transported downstream; such contaminants are difficult to reliably measure. Preliminary investigations are underway to evaluate the efficacy of several passive samplers for quantifying 6PPD-q. To date, state and federal agencies are working to estimate sampling rates and produce standard operating procedures to support local passive sampling research.

5.1.5.4 Size Partitioning (Filtering)

Considering the affinity of 6PPD-q to stick to filters, total bulk sampling is recommended unless the study design objective is to understand the size-class partitioning or method development loss of 6PPD-q during filtration and sampling. When filters are employed to separate dissolved and total fractions, the filters should be extracted for 6PPD-q.

Passive sampler media and types are designed to sorb to different size molecules and polarities. The type of passive sampler selected should be the one most appropriate for the objective of the study. See Table 5-4 for a comparison of several passive sampler types.

5.1.6 Sampling 6PPD-q in Soil

Few studies to date have measured 6PPD-q in soils and sediments. Most studies were conducted within a laboratory setting to test how effective various biofiltration media are at removing 6PPD-q transported by roadway runoff (McIntyre et al. 2023[F7NAIVJ4] McIntyre, Jenifer, Julann Spromberg, James Cameron, John P. Incardona, Jay W. Davis, and Nathaniel L. Scholz. 2023. "Bioretention Filtration Prevents Acute Mortality and Reduces Chronic Toxicity for Early Life Stage Coho Salmon (Oncorhynchus kisutch) Episodically Exposed to Urban Stormwater Runoff." Science of the Total Environment 902 (December):165759. https://doi.org/10.1016/j.scitotenv.2023.165759.Spromberg et al. 2016[GI97QYN4] Spromberg, Julann A., David H. Baldwin, Steven E. Damm, Jenifer K. McIntyre, Michael Huff, Catherine A. Sloan, Bernadita F. Anulacion, Jay W. Davis, and Nathaniel L. Scholz. 2016. "Coho Salmon Spawner Mortality in Western US Urban Watersheds: Bioinfiltration Prevents Lethal Storm Water Impacts." Journal of Applied Ecology 53 (2): 398–407. https://doi.org/https://doi.org/10.1111/1365-2664.12534.). Many data gaps exist regarding how long 6PPD and 6PPD-q persist in soils at the side of the road and whether 6PPD-q remains bound once filtered by soils.

5.1.7 Sampling 6PPD-q in Sediments

Zeng et al. (Zeng et al. 2023[TK5YR8WJ] Zeng, Lixi, Yi Li, Yuxin Sun, Liang-Ying Liu, Mingjie Shen, and Bibai Du. 2023. "Widespread Occurrence and Transport of p-Phenylenediamines and Their Quinones in Sediments across Urban Rivers, Estuaries, Coasts, and Deep-Sea Regions." Environmental Science & Technology, January, acs.est.2c07652. https://doi.org/10.1021/acs.est.2c07652.) conducted a survey of PPDs in riverine, estuarine, and marine sediments. 6PPD-q was observed in these waterways. Samples of the top 10 cm of sediment were collected from a research vessel using a grab sampler. Three samples were collected and mixed as a composite sample and frozen for transport to the laboratory. The samples were freeze-dried, weighed, sieved through a 1.0 mm mesh screen to remove debris and stored at −80°C until analysis. Holding times and methods are discussed further in Section 5.2: Laboratory Methods. Standard operating procedures are being developed for sediment collection and analysis, see Table 5-4 for a comparison of additional sediment collection methods. The most appropriate method and study design will depend on the study objective.

5.1.8 Sampling 6PPD-q in Organisms

5.1.8.1 Tissues and Plasma

The measurement of 6PPD and 6PPD-q in biotic materials may provide an effective measure of exposure to aquatic and terrestrial organisms, including humans. URMS occurrences can be difficult to catch given the short exposure duration period and low concentrations required to cause mortality. The ability to measure 6PPD and 6PPD-q in biota may help us understand the occurrence, exposure, sublethal, and chronic impacts to more tolerant species and whether there are any exposures though the food chain, including to humans.

5.1.8.2 Bioassays/Biomarkers

Most ambient water contains several to thousands of chemicals forming complex and dynamic mixtures in rivers and streams; this situation is challenging because many of the co-occurring chemicals have not been toxicologically tested and the way that chemicals in mixtures interact is highly challenging to predict. Therefore, bioassays can be used alone or in conjunction with 6PPD-q analysis to provide an integrated means of assessing mixtures and their dynamic behavior. Several bioassay types exist that vary in complexity and logistical demands. Depending on the goals of a monitoring event or study, careful consideration of their pros and cons is essential to produce data responsive to the question being addressed. Table 5-4 provides a set of common approaches that may be considered for research or regulatory purposes.

5.1.9 Bioassessments

Biological assessments are evaluations of the condition of waterbodies using surveys and other direct measurements of resident biological organisms (macroinvertebrates, fish, and plants). Biological assessment results are used to answer the question of whether waterbodies support survival and reproduction of desirable fish, shellfish, and other aquatic species—in other words, whether the waterbodies meet their designated aquatic life uses.

Monitoring the status and trends of water quality and habitat indicators is an important type of assessment that tracks whether overall water quality and habitat conditions are improving or degrading and is most appropriate when done on a regional scale over a long period of time (decades). Biological assessments have become a widely accepted metric of overall stream health; however, it can be a challenging metric to connect to a single contaminant over a short period of time (Larson et al. 2019[UMIHZC75] Larson, Chad A., Glenn Merritt, Jack Janisch, Jill Lemmon, Meghan Rosewood-Thurman, Brian Engeness, Stacy Polkowske, and George Onwumere. 2019. “The First Statewide Stream Macroinvertebrate Bioassessment in Washington State with a Relative Risk and Attributable Risk Analysis for Multiple Stressors.” Ecological Indicators 102 (July):175–85. https://doi.org/10.1016/j.ecolind.2019.02.032.). For agencies or programs that rely on bioassessments, it might be advantageous to revisit past studies that used biological assessments that were unable to determine a cause of poor stream health; such instances may correlate with 6PPD-q detections or storm events. Road crossings are popular places to access streams for bioassessments, and road proximity should be considered when selecting site assessment locations. In general, reference sites should be located upstream of roads, and impact sites should be located downstream.

5.1.10 Sampling 6PPD-q in Air

Methods for monitoring particles in air have been available for decades; the first studies monitoring TRWP in air were published in the 1970s (Johannessen et al. 2022[YXQSYBCM] Johannessen, Cassandra, John Liggio, Xianming Zhang, Amandeep Saini, and Tom Harner. 2022. “Composition and Transformation Chemistry of Tire-Wear Derived Organic Chemicals and Implications for Air Pollution.” Atmospheric Pollution Research 13 (9): 101533. https://doi.org/10.1016/j.apr.2022.101533.). Methods for sampling 6PPD and 6PPD-q in air are much the same.

5.1.10.1 Active Sampling in Air

Active sampling of particulate matter is commonly achieved using a quartz fiber filter or series of filters coupled with a low-, medium-, or high-volume air sampler. Most ambient air monitoring of particulates follows the Federal Reference Method for the Determination of Particulate Matter as PM_{10} in the Atmosphere (40 CFR, Chapter 1, part 50, Appendix M, as published in 62 Federal Register, 38753, July 18, 1997) and as $PM_{2.5}$ (40 CFR, Chapter 1, part 50, Appendix L, as published in 62 Federal Register, 38714, July 18, 1997 and as amended in 64 Federal Register, 19717, April 22, 1999). Variations of these methods have been successfully used to sample TRWP, 6PPD, and 6PPD-q (for example, Zhang et al. 2022[G77DTKD6] Zhang, Yanhao, Caihong Xu, Wenfen Zhang, Zenghua Qi, Yuanyuan Song, Lin Zhu, Chuan Dong, Jianmin Chen, and Zongwei Cai. 2022. “p-Phenylenediamine Antioxidants in PM2.5: The Underestimated Urban Air Pollutants.” Environmental Science & Technology 56 (11): 6914–21. https://doi.org/https://doi.org/10.1021/acs.est.1c04500.Zhang et al. 2022[GHLGNCHV] Zhang, Ying-Jie, Ting-Ting Xu, Dong-Min Ye, Ze-Zhao Lin, Fei Wang, and Ying Guo. 2022. “Widespread N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine Quinone in Size-Fractioned Atmospheric Particles and Dust of Different Indoor Environments.” Environmental Science & Technology Letters 9 (5): 420–25. https://doi.org/https://doi.org/10.1021/acs.estlett.2c00193.Wang et al. 2022[TMV9VLRS] Wang, Wei, Guodong Cao, Jing Zhang, Pengfei Wu, Yanyan Chen, Zhifeng Chen, Zenghua Qi, Ruijin Li, Chuan Dong, and Zongwei Cai. 2022. “Beyond Substituted p-Phenylenediamine Antioxidants: Prevalence of Their Quinone Derivatives in PM2.5.” Environmental Science & Technology, July, acs.est.2c02463. https://doi.org/10.1021/acs.est.2c02463.Panko et al. 2019[H57M387X] Panko, Julie M., Kristen M. Hitchcock, Gary W. Fuller, and David Green. 2019. “Evaluation of Tire Wear Contribution to PM2.5 in Urban Environments.” Atmosphere 10 (2): 99. https://doi.org/10.3390/atmos10020099.Panko et al. 2013[UQNTNRM4] Panko, Julie M., Jennifer Chu, Marisa L. Kreider, and Ken M. Unice. 2013. “Measurement of Airborne Concentrations of Tire and Road Wear Particles in Urban and Rural Areas of France, Japan, and the United States.” Atmospheric Environment 72 (June):192–99. https://doi.org/10.1016/j.atmosenv.2013.01.040.).

Settled dust can be collected using a precleaned brush and dustbin or shovel.

5.1.10.2 Passive Sampling in Air

Passive sampling of 6PPD and 6PPD-q in air is accomplished using the same PUF-based passive air samplers (PUF-PAS) that are used to sample other airborne organic and inorganic contaminants (for example, Gaga et al. 2019[5HHJMIKX] Gaga, Eftade O., Tom Harner, Ewa Dabek-Zlotorzynska, Valbona Celo, Greg Evans, Cheol-Heon Jeong, Sabina Halappanavar, Narumol

Jariyasopit, and Yushan Su. 2019. “Polyurethane Foam (PUF) Disk Samplers for Measuring Trace Metals in Ambient Air.” Environmental Science & Technology Letters 6 (9): 545–50. https://doi.org/10.1021/acs.estlett.9b00420.Saini et al. 2020[2B4BLHGY] Saini, Amandeep, Tom Harner, Sita Chinnadhurai, Jasmin K. Schuster, Alan Yates, Andrew Sweetman, Beatriz H. Aristizabal-Zuluaga, et al. 2020. “GAPS-Megacities: A New Global Platform for Investigating Persistent Organic Pollutants and Chemicals of Emerging Concern in Urban Air.” Environmental Pollution 267 (December):115416. https://doi.org/10.1016/j.envpol.2020.115416.Rauert et al. 2018[Q65D2KZM] Rauert, Cassandra, Jasmin K. Schuster, Anita Eng, and Tom Harner. 2018. “Global Atmospheric Concentrations of Brominated and Chlorinated Flame Retardants and Organophosphate Esters.” Environmental Science & Technology 52 (5): 2777–89. https://doi.org/10.1021/acs.est.7b06239.). This method involves the deployment of PUF disks for anywhere from 24 hours to several months, depending on expected atmospheric concentrations. These samplers can gather samples representing the whole air mixture because they collect both gas- and particle-phase chemicals with an equivalent air sampling rate of about 4 m^3/day. After the PUF disk is extracted and contaminants on the disk are quantified, air concentrations can be estimated by dividing the chemical mass in each sample by the corresponding equivalent air volume, which is calculated by multiplying the number of days that the passive samplers were exposed by the generic sampling rate of 4 m^3/day. This method has been successfully used for sampling 6PPD and 6PPD-q (for example, Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. “Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers.” Environmental Pollution 314 (December):120206. https://doi.org/10.1016/j.envpol.2022.120206.).

5.2 Laboratory Methods

This section summarizes published analytical methods and laboratory approaches for the analysis of 6PPD and 6PPD-q; this is intended to provide a starting point for information about laboratory methods as of April 2024. Detection limits of the analytical methods will continue to evolve to provide relevant low-level data as toxicity thresholds are established.

Laboratory Methods

Commercial, public, and research laboratories are developing methods for the analysis of 6PPD and 6PPD-q in a range of environmental matrices and consumer products.

When selecting a laboratory, aspects to consider for data quality and reproducibility include method accreditation, detection limits, sample holding times, and quality control parameters.

Stormwater and surface water can have high turbidities and, because 6PPD and 6PPD-q sorb to organic material, it is important to use a method that provides whole-water analysis.

This document does not address methods for analyzing TRWP in the environment because in part, that is beyond the scope, and in part because quantifying the actual particles in environmental matrices poses analytical challenges. Even sampling TRWP in water is difficult because the density of TRWP changes as the particles age and sink to the sediment (Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. “Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers.” Environmental Pollution 314 (December):120206. https://doi.org/10.1016/j.envpol.2022.120206.). Chemicals associated with tire rubber have been proposed as markers to estimate TRWP. For example, N-formyl-6-PPD, hydroxylated N-1,3- dimethylbutyl-N-phenyl quinone diamine, and 6PPD-q are potential organic markers for TRWPs in the environment, but further research is needed to confirm the relationship between TRWP and the chemicals (Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. “Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers.” Environmental Pollution 314 (December):120206. https://doi.org/10.1016/j.envpol.2022.120206.).

5.2.1 Physicochemical Property Considerations in the Laboratory

Physicochemical properties are discussed in Section 3 and summarized in Table 3-1. Rubber laboratory materials should be avoided to prevent contamination of 6PPD or 6PPD-q.

6PPD: The main considerations for 6PPD analysis are the relatively short half-life of several hours in aqueous solution (Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. “Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers.” Environmental Pollution 314

(December):120206. https://doi.org/10.1016/j.envpol.2022.120206.), solubility of 0.5 to 2 mg/L, and relatively high log K_{ow} and log K_{oc} (DTSC 2022[2M3Z8Z4F] DTSC. 2022. “Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the California Department of Toxic Substances Control (DTSC).” https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf .Hiki et al. 2021[WZF69GXC] Hiki, Kyoshiro, Kenta Asahina, Kota Kato, Takahiro Yamagishi, Ryo Omagari, Yuichi Iwasaki, Haruna Watanabe, and Hiroshi Yamamoto. 2021. “Acute Toxicity of a Tire Rubber–Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species.” Environmental Science & Technology Letters 8 (9): 779–84. https://doi.org/10.1021/acs.estlett.1c00453.Klöckner et al. 2020[9B7NCVNZ] Klöckner, Philipp, Bettina Seiwert, Paul Eisentraut, Ulrike Braun, Thorsten Reemtsma, and Stephan Wagner. 2020. “Characterization of Tire and Road Wear Particles from Road Runoff Indicates Highly Dynamic Particle Properties.” Water Research 185 (October):116262. https://doi.org/10.1016/j.watres.2020.116262.ECHA 2021[Y79Z3ZWV] ECHA. 2021. “Substance Infocard: N-1,3-Dimethylbutyl-N’-Phenyl-p-Phenylenediamine. European Chemicals Agency (ECHA).” April 7, 2021. https://echa.europa.eu/substance-information/-/substanceinfo/100.011.222.). If 6PPD is present in environmental water samples, there is a short window of analysis time before the compound degrades. Even though the solubility of 6PPD is greater (mg/L) than 6PPD-q (µg/L range), because of its short half-life, 6PPD is anticipated to be detected less frequently in the dissolved phase than 6PPD-q in waterways. When investigating the leaching of 6PPD directly from tire particles or TWPs, the solvent for leaching studies and approach used can influence the rate and number of tire-related compounds leached (Foscari et al. 2023[EHDIWG3V] Foscari, Aurelio, Natascha Schmidt, Bettina Seiwert, Dorte Herzke, Richard Sempéré, and Thorsten Reemtsma. 2023. “Leaching of Chemicals and DOC from Tire Particles under Simulated Marine Conditions.” Frontiers in Environmental Science 11 (June). https://doi.org/10.3389/fenvs.2023.1206449.Zhao et al. 2023[ENE6F3HC] Zhao, Haoqi Nina, Ximin Hu, Zhenyu Tian, Melissa Gonzalez, Craig A. Rideout, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Transformation Products of Tire Rubber Antioxidant 6PPD in Heterogeneous Gas-Phase Ozonation: Identification and Environmental Occurrence.” Environmental Science & Technology 57 (14): 5621–32. https://doi.org/10.1021/acs.est.2c08690.). The inclusion of 4-hydroxydiphenylamine (4-HDPA) and other transformation products of 6PPD in the monitoring may provide a more comprehensive view on 6PPD leaching, particularly in long-term studies.

6PPD-q: A challenging aspect for 6PPD-q analysis is the relatively high log K_{ow} and log K_{oc}, which cause it to partition to organic or solid materials. Materials used by the laboratories should be investigated to be sure sorption is minimized when filtering or processing samples and that laboratory carryover is minimized on equipment. 6PPD-q is observed in the aqueous phase before binding to organic or solid materials and can remain in the aqueous phase for days in tap water, laboratory stock solutions, and stormwater (Lane et al. 2024[Q3DSSIIU] Lane, Rachael F., Kelly L. Smalling, Paul M. Bradley, Justin B. Greer, Stephanie E. Gordon, John D. Hansen, Dana W. Kolpin, Andrew R. Spanjer, and Jason R. Masoner. 2024. “Tire-Derived Contaminants 6PPD and 6PPD-Q: Analysis, Sample Handling, and Reconnaissance of United States Stream Exposures.” Chemosphere, July, 142830. https://doi.org/10.1016/j.chemosphere.2024.142830.Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone.” Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.Hiki et al. 2021[WZF69GXC] Hiki, Kyoshiro, Kenta Asahina, Kota Kato, Takahiro Yamagishi, Ryo Omagari, Yuichi Iwasaki, Haruna Watanabe, and Hiroshi Yamamoto. 2021. “Acute Toxicity of a Tire Rubber–Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species.” Environmental Science & Technology Letters 8 (9): 779–84. https://doi.org/10.1021/acs.estlett.1c00453.). With observations of sorption to organic material (Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone.” Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.), methods that provide a whole-water analysis (Zhang et al. 2023[D6T6D4JP] Zhang, Ruiling, Shizhen Zhao, Xin Liu, Lele Tian, Yangzhi Mo, Xin Yi, Shiyang Liu, Jiaqi Liu, Jun Li, and Gan Zhang. 2023. “Aquatic Environmental Fates and Risks of Benzotriazoles, Benzothiazoles, and p-Phenylenediamines in a Catchment Providing Water to a Megacity of China.” Environmental Research 216 (January):114721. https://doi.org/10.1016/j.envres.2022.114721.) are important as a filtered direct-inject water method could miss concentrations in the sorbed fraction. Additional research is needed to understand rates of adsorption and the fate and transport of the dissolved versus suspended particle fractions of 6PPD-q and 6PPD.

5.2.2 Bottle Types and Laboratory Holding Times

6PPD: A thorough bottle comparison study has not been performed for 6PPD as this is challenging to investigate due to the short half-life. Approaches that have been investigated to prolong the 6PPD half-life include the use of free ozone scavengers, such as ascorbic acid, but the preservatives can cause stability issues during the analysis of 6PPD-q (Woudneh 2023[6S8L3YFK] Woudneh, Million. 2023. "Best Practices in the Analysis of 6PPD-Quinone." Presented at the ITRC Tire Anti-Degradants 6PPD Team Meeting, May 16.).

6PPD-q: For holding times of more than a day, glass is recommended, and plastics should be avoided; stainless steel and PTFE can be used for shorter holding times under a day (Lane et al. 2024[Q3DSSIIU] Lane, Rachael F., Kelly L. Smalling, Paul M. Bradley, Justin B. Greer, Stephanie E. Gordon, John D. Hansen, Dana W. Kolpin, Andrew R. Spanjer, and Jason R. Masoner. 2024. "Tire-Derived Contaminants 6PPD and 6PPD-Q: Analysis, Sample Handling, and Reconnaissance of United States Stream Exposures." Chemosphere, July, 142830. https://doi.org/10.1016/j.chemosphere.2024.142830.Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. "Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone." Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.). If plastic containers are used, the bottles can be rinsed with organic solvents to recover some sorbed 6PPD-q, but glass is recommended to avoid the losses and work of trying to recover the sorbed fraction. A U.S. Geological Survey (USGS) 5-month holding-time study with laboratory-generated 6PPD-q solutions showed significant sorption to high-density polyethylene, polypropylene, and polystyrene, with no significant sorption to glass. Holding times in laboratory solutions can be significantly different from environmental water samples, and in 75-day stormwater holding times there was variability in the stability with differences noted for headspace and storage temperature. Based on that data, the recommended storage conditions are glass bottles with minimal headspace and refrigeration (5°C). 6PPD-q was frozen and thawed five times in half-full amber glass bottles with no significant decrease in 6PPD-q concentrations (Lane et al. 2024[Q3DSSIIU] Lane, Rachael F., Kelly L. Smalling, Paul M. Bradley, Justin B. Greer, Stephanie E. Gordon, John D. Hansen, Dana W. Kolpin, Andrew R. Spanjer, and Jason R. Masoner. 2024. "Tire-Derived Contaminants 6PPD and 6PPD-Q: Analysis, Sample Handling, and Reconnaissance of United States Stream Exposures." Chemosphere, July, 142830. https://doi.org/10.1016/j.chemosphere.2024.142830.).

5.2.3 Abiotic and Biotic Laboratory Extraction Techniques for 6PPD and 6PPD-q

A variety of preparation techniques have been used to prepare abiotic and biotic samples for 6PPD and 6PPD-q analysis and are summarized and referenced in Table 5-2 and Table 5-3, respectively. This is intended to provide preliminary information about reported laboratory extraction techniques as of April 2024. Filtration, liquid/liquid extraction, and solid-phase extraction (SPE) can be used to clean up and concentrate surface water, stormwater, groundwater, surface runoff, snowmelt, and WWTP influent and effluent samples for 6PPD and 6PPD-q analysis. For laboratory solutions of 6PPD-q, the filter material with the highest reported recovery is glass-fiber filters (Lane et al. 2024[Q3DSSIIU] Lane, Rachael F., Kelly L. Smalling, Paul M. Bradley, Justin B. Greer, Stephanie E. Gordon, John D. Hansen, Dana W. Kolpin, Andrew R. Spanjer, and Jason R. Masoner. 2024. "Tire-Derived Contaminants 6PPD and 6PPD-Q: Analysis, Sample Handling, and Reconnaissance of United States Stream Exposures." Chemosphere, July, 142830. https://doi.org/10.1016/j.chemosphere.2024.142830.). The extraction of water-deployed passive samplers depends on the material that has been deployed and should follow manufacturer recommendations for extraction.

Air has been sampled for 6PPD and 6PPD-q using PUF to collect gas- and particle-phase chemicals with the airborne particulate matter using Sigma-2 passive samplers and with particles collected on quartz fiber filters and then solvent extracted before analysis (Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. "Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers." Environmental Pollution 314 (December):120206. https://doi.org/10.1016/j.envpol.2022.120206.Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. "New Evidence of Rubber-Derived Quinones in Water, Air, and Soil." Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.Liang et al. 2022[SZPLJY9T] Liang, Bowen, Jiehua Li, Bibai Du, Zibin Pan, Liang-Ying Liu, and Lixi Zeng. 2022. "E-Waste Recycling Emits Large Quantities of Emerging Aromatic Amines and Organophosphites: A Poorly Recognized Source for Another Two Classes of Synthetic Antioxidants." Environmental Science & Technology Letters, June, acs.estlett.2c00366. https://doi.org/10.1021/acs.estlett.2c00366.). $PM_{2.5}$ can be collected on quartz fiber filters, extracted by serial sonication, and filtered using PTFE, polyethersulfone, or nylon filters (see Table 5-2 and Table 5-3). Soil and sediments have been extracted with serial ultrasonication and then filtered (through PTFE or nylon) prior to analysis (see Table 5-2 and Table 5-3).

Fish-tissue samples are prepared for 6PPD and 6PPD-q analysis by homogenization and then an extraction, such as QuEChERS (a SPE method that is quick, easy, cheap, effective, rugged, and safe) or sonication, followed by centrifugation and filtering (Nair et al. 2023[9V5ES4MI] Nair, Pranav, Jianxian Sun, Linna Xie, Lisa Kennedy, Derek Kozakiewicz, Sonya Kleywegt, Chunyan Hao, et al. 2023. "In Process: Synthesis and Toxicity Evaluation of Tire Rubber–Derived Quinones." Preprint. Chemistry. https://doi.org/10.26434/chemrxiv-2023-pmxvc.Fang et al. 2023[FFFKR3MY] Fang, Chanlin, Liya Fang, Shanshan Di, Yundong Yu, Xinquan Wang, Caihong Wang, and Yuanxiang Jin. 2023. "Characterization of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD)-Induced Cardiotoxicity in Larval Zebrafish (Danio Rerio)." Science of the Total Environment 882 (July):163595. https://doi.org/10.1016/j.scitotenv.2023.163595.Hiki and Yamamoto 2022[VQE4EZWI] Hiki, Kyoshiro, and Hiroshi Yamamoto. 2022. "The Tire-Derived Chemical 6PPD-Quinone Is Lethally Toxic to the White-Spotted Char Salvelinus leucomaenis pluvius but Not to Two Other Salmonid Species." Environmental Science & Technology Letters 9 (12): 1050–55. https://doi.org/10.1021/acs.estlett.2c00683.Grasse et al. 2023[WJHX578U] Grasse, Nico, Bettina Seiwert, Riccardo Massei, Stefan Scholz, Qiuguo Fu, and Thorsten Reemtsma. 2023. "Uptake and Biotransformation of the Tire Rubber–Derived Contaminants 6-PPD and 6-PPD Quinone in the Zebrafish Embryo (Danio rerio)." Environmental Science & Technology 57 (41): 15598–607. https://doi.org/10.1021/acs.est.3c02819.Zhang et al. 2023[3FCHDXBN] Zhang, Shu-Yun, Xiufeng Gan, Baoguo Shen, Jian Jiang, Huimin Shen, Yuhang Lei, Qiuju Liang, et al. 2023. "6PPD and Its Metabolite 6PPDQ Induce Different Developmental Toxicities and Phenotypes in Embryonic Zebrafish." Journal of Hazardous Materials 455 (August):131601. https://doi.org/10.1016/j.jhazmat.2023.131601.Ji et al. 2022[LDBNLUJS] Ji, Jiawen, Changsheng Li, Bingjie Zhang, Wenjuan Wu, Jianli Wang, Jianhui Zhu, Desheng Liu, et al. 2022. "Exploration of Emerging Environmental Pollutants 6PPD and 6PPDQ in Honey and Fish Samples." Food Chemistry 396:133640. https://doi.org/10.1016/j.foodchem.2022.133640.). Fish plasma, blood, and bile are extracted by SPE or vortex-sonication/centrifuged prior to analysis for 6PPD and 6PPD-q (Hägg et al. 2023[9C6TC8JJ] Hägg, Fanny, Dorte Herzke, Vladimir A. Nikiforov, Andy M. Booth, Kristine Hopland Sperre, Lisbet Sørensen, Mari Egeness Creese, and Claudia Halsband. 2023. "Ingestion of Car Tire Crumb Rubber and Uptake of Associated Chemicals by Lumpfish (Cyclopterus Lumpus)." Frontiers in Environmental Science 11 (October):1219248. https://doi.org/10.3389/fenvs.2023.1219248.Mahoney et al. 2022[V5HSELRG] Mahoney, Hannah, Francisco C. da Silva Junior, Catherine Roberts, Matthew Schultz, Xiaowen Ji, Alper James Alcaraz, David Montgomery, et al. 2022. "Exposure to the Tire Rubber-Derived Contaminant 6PPD-Quinone Causes Mitochondrial Dysfunction In Vitro." Environmental Science & Technology Letters 9 (9): 765–71. https://doi.org/10.1021/acs.estlett.2c00431.). Human urine has been prepared for analysis using salting-out–assisted liquid−liquid extraction (Du et al. 2022[DWFYR89F] Du, Bibai, Bowen Liang, Yi Li, Mingjie Shen, Liang-Ying Liu, and Lixi Zeng. 2022. "First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China." Environmental Science & Technology Letters, November. https://doi.org/10.1021/acs.estlett.2c00821.). Lettuce has been prepared for analysis with serial bead beating followed by solvent extraction and nylon filtering (Castan et al. 2023[3RBDETGD] Castan, Stephanie, Anya Sherman, Ruoting Peng, Michael T. Zumstein, Wolfgang Wanek, Thorsten Hüffer, and Thilo Hofmann. 2023. "Uptake, Metabolism, and Accumulation of Tire Wear Particle–Derived Compounds in Lettuce." Environmental Science & Technology 57 (1): 168–78. https://doi.org/10.1021/acs.est.2c05660.). Honey has been extracted with modified QuEChERS (Ji et al. 2022[LDBNLUJS] Ji, Jiawen, Changsheng Li, Bingjie Zhang, Wenjuan Wu, Jianli Wang, Jianhui Zhu, Desheng Liu, et al. 2022. "Exploration of Emerging Environmental Pollutants 6PPD and 6PPDQ in Honey and Fish Samples." Food Chemistry 396:133640. https://doi.org/10.1016/j.foodchem.2022.133640.).

5.2.4 Analytical Method Approaches for 6PPD and 6PPD-q

After the preparation of biotic and abiotic samples, the most frequently applied analytical technique for 6PPD and 6PPD-q is liquid chromatography with mass spectrometry (LC-MS) (see Table 5-2 and Table 5-3). Gas chromatography / MS (GC/MS) (Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. "A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon." Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.Rauert et al. 2022[9WERCXNS] Rauert, Cassandra, Nathan Charlton, Elvis D. Okoffo, Ryan S. Stanton, Alon R. Agua, Michael C. Pirrung, and Kevin V. Thomas. 2022. "Concentrations of Tire Additive Chemicals and Tire Road Wear Particles in an Australian Urban Tributary." Environmental Science & Technology, January. https://doi.org/10.1021/acs.est.1c07451.) can also be used but has not been as widely applied. LC-MS is frequently used because of low ng/L method detection limits, the ability to analyze a variety of biological and environmental samples, flexibility in quantitation, and the ability to provide structural elucidation for other unknow chemicals (Cao et al. 2022[LT2AYSFX] Cao, Guodong, Jing Zhang, Wei Wang, Pengfei Wu, Yi Ru, and Zongwei Cai. 2022. "Mass Spectrometry Analysis of a Ubiquitous Tire Rubber–Derived Quinone in the Environment." TrAC Trends in Analytical Chemistry, 116756. https://doi.org/10.1016/j.trac.2022.116756.). LC-MS is used to analyze 6PPD and 6PPD-q from abiotic and biotic matrices. 6PPD-q has been analyzed, but not always detected (for occurrences see Tables 4-1 through 4-10), in surface water; stormwater; groundwater; road runoff, snow; suspended particles; dust; $PM_{2.5}$; influent and effluent from WWTP and drinking water treatment plants; soil; sediment; biosolids; human urine; mammalian cells; fish or mollusk tissues, fish bile, and fish plasma; and food (including lettuce and honey). with corresponding reporting limits listed in Table 5-2 and Table 5-3. 6PPD has been analyzed, but not always detected (for occurrences see Tables 4-1 through 4-10), in the same or similar media as were measured for 6PPD-q, with corresponding reporting limits listed in Table 5-2 and Table 5-3.

5.2.4.1 MS2 Targeted and Nontargeted

Liquid chromatography (LC) or GC with targeted analysis, semi-targeted analysis, suspect screening, and nontargeted analysis has been used in the analysis of 6PPD-q and 6PPD. Commonly monitored ions for 6PPD and 6PPD-q during multiple reaction monitoring and targeted screenings are listed in Table 5-2 and Table 5-3, respectively. High-resolution MS (HRMS) can be used for targeted analysis and is an MS technique that is gaining popularity because a full scan is collected (even during a targeted analysis), which results in capturing additional information so that transformation products of unknown compounds related to 6PPD, 6PPD-q, or tire chemicals can be elucidated (Seiwert et al. 2022[QDRRVWMW] Seiwert, Bettina, Maolida Nihemaiti, Mareva Troussier, Steffen Weyrauch, and Thorsten Reemtsma. 2022. "Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater." Water Research 212:118122. https://doi.org/10.1016/j.watres.2022.118122.Cao et al. 2022[LT2AYSFX] Cao, Guodong, Jing Zhang, Wei Wang, Pengfei Wu, Yi Ru, and Zongwei Cai. 2022. "Mass Spectrometry Analysis of a Ubiquitous Tire Rubber–Derived Quinone in the Environment." TrAC Trends in Analytical Chemistry, 116756. https://doi.org/10.1016/j.trac.2022.116756.). As was demonstrated by Müller et al. (Müller et al. 2022[QJXVBLCK] Müller, Kathrin, Daniel Hübner, Sven Huppertsberg, Thomas P. Knepper, and Daniel Zahn. 2022. "Probing the Chemical Complexity of Tires: Identification of Potential Tire-Borne Water Contaminants with High-Resolution Mass Spectrometry." Science of The Total Environment 802:149799. https://doi.org/10.1016/j.scitotenv.2021.149799.), this can be advantageous in screening a large number of unknowns related to tire chemicals while also identifying 6PPD and 6PPD-q.

5.2.4.2 Other Techniques

Other techniques that have been investigated for the sampling or detection of 6PPD-q and 6PPD but not widely applied. For the sampling of 6PPD-q condensed phase membrane introduction mass spectrometry (CP-MIMS) with a semipermeable polydimethylsiloxane capillary hollow fiber membrane has been used (Monaghan et al. 2021[RKMTS6DI] Monaghan, Joseph, Angelina Jaeger, Alon R. Agua, Ryan S. Stanton, Michael Pirrung, Chris G. Gill, and Erik T. Krogh. 2021. "A Direct Mass Spectrometry Method for the Rapid Analysis of Ubiquitous Tire-Derived Toxin N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine Quinone (6-PPDQ)." Environmental Science & Technology Letters 8 (12): 1051–56. https://doi.org/10.1021/acs.estlett.1c00794.). The ASTM-D5666 standard method is available for ascertaining the purity of PPDs by high-performance liquid chromatography (HPLC) ultraviolet detection (ASTM International 2023[JGR7UE66] ASTM International. 2023. "ASTM-D5666 | Standard Test Method for Rubber Chemical Antidegradants; Purity of p-Phenylenediamine (PPD) Antidegradants by High Performance Liquid Chromatography." ASTM-D5666-95R23. https://www.document-center.com/standards/show/ASTM-D5666.). Ultraviolet-visible spectrometry analysis has been used for some 6PPD research and in the identification of transformation products (Cataldo et al. 2015[JFXS3CPR] Cataldo, Franco, Brad Faucette, Semone Huang, and Warren Ebenezer. 2015. "On the Early Reaction Stages of Ozone with N,N′-Substituted p-Phenylenediamines (6PPD, 77PD) and N,N′,N″-Substituted-1,3,5-Triazine 'Durazone®': An Electron Spin Resonance (ESR) and Electronic Absorption Spectroscopy Study." Polymer Degradation and Stability 111 (January):223–31. https://doi.org/10.1016/j.polymdegradstab.2014.11.011.Li et al. 2023[3EFLHAGA] Li, Chenguang, Yanlei Zhang, Shiqi Yin, Qin Wang, Yuanyuan Li, Qiang Liu, Liuqingqing Liu, et al. 2023. "First Insights into 6PPD-Quinone Formation from 6PPD Photodegradation in Water Environment." Journal of Hazardous Materials 459 (October):132127. https://doi.org/10.1016/j.jhazmat.2023.132127.Zhao et al. 2023[ENE6F3HC] Zhao, Haoqi Nina, Ximin Hu, Zhenyu Tian, Melissa Gonzalez, Craig A. Rideout, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. "Transformation Products of Tire Rubber Antioxidant 6PPD in Heterogeneous Gas-Phase Ozonation: Identification and Environmental Occurrence."

Environmental Science & Technology 57 (14): 5621–32. https://doi.org/10.1021/acs.est.2c08690.) and in measurement of 6PPD-q standards (Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. “A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon.” Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.).

5.2.4.3 Rubber Products

Analytical techniques have been applied to understand the leaching of chemicals from rubber products. When preparing rubber products for analysis, consideration should be given to the preparation technique; techniques such as sample grinding can increase surface area and the formation of 6PPD-q. Differences have been observed in chemicals leaching from TWPs and CMTT; TWP leachates were dominated by transformation products, while CMTT was dominated by rubber parent materials (6PPD), diphenylguanidine, and mercaptobenzothiazole (Weyrauch et al. 2023[T89H6LNJ] Weyrauch, Steffen, Bettina Seiwert, Milena Voll, Stephan Wagner, and Thorsten Reemtsma. 2023. “Accelerated Aging of Tire and Road Wear Particles by Elevated Temperature, Artificial Sunlight and Mechanical Stress — A Laboratory Study on Particle Properties, Extractables and Leachables.” Science of the Total Environment 904 (December):166679. https://doi.org/10.1016/j.scitotenv.2023.166679.). Aging of rubber materials, especially sunlight photodegradation, further changes the leached chemicals to more transformation products (Weyrauch et al. 2023[T89H6LNJ] Weyrauch, Steffen, Bettina Seiwert, Milena Voll, Stephan Wagner, and Thorsten Reemtsma. 2023. “Accelerated Aging of Tire and Road Wear Particles by Elevated Temperature, Artificial Sunlight and Mechanical Stress — A Laboratory Study on Particle Properties, Extractables and Leachables.” Science of the Total Environment 904 (December):166679. https://doi.org/10.1016/j.scitotenv.2023.166679.). See Section 3.6 for additional information about biodegradation of CMTT.

To analyze the bioavailable fraction of crumb rubber used on synthetic turf sport fields, researchers used ultrasound-assisted extraction coupled with an in vitro simulation of mammalian digestion. The researchers optimized this approach for polyaromatic hydrocarbons and also analyzed for the bioavailable fraction of 6PPD-q with GC/MS suspect screening. (Armada et al. 2023[AHX5WWPV] Armada, Daniel, Antia Martinez-Fernandez, Maria Celeiro, Thierry Dagnac, and Maria Llompart. 2023. “Assessment of the Bioaccessibility of PAHs and Other Hazardous Compounds Present in Recycled Tire Rubber Employed in Synthetic Football Fields.” Science of the Total Environment 857:159485. https://doi.org/10.1016/j.scitotenv.2022.159485.). Tire particles have also been investigated with the fish in vitro digestive model and co-ingestion experiments to create digestate solutions that were analyzed by UHPLC-HRMS (Masset et al. 2022[UGNACB4V] Masset, Thibault, Benoit J. D. Ferrari, William Dudefoi, Kristin Schirmer, Alan Bergmann, Etienne Vermeirssen, Dominique Grandjean, Luke Christopher Harris, and Florian Breider. 2022. “Bioaccessibility of Organic Compounds Associated with Tire Particles Using a Fish In Vitro Digestive Model: Solubilization Kinetics and Effects of Food Coingestion.” Environmental Science & Technology 56 (22): 15607–16. https://doi.org/10.1021/acs.est.2c04291.). Leaching from crumb rubber has also been explored with solvent and water extractions and analyzed by LC-MS/MS (Zhao et al. 2023[ENE6F3HC] Zhao, Haoqi Nina, Ximin Hu, Zhenyu Tian, Melissa Gonzalez, Craig A. Rideout, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. “Transformation Products of Tire Rubber Antioxidant 6PPD in Heterogeneous Gas-Phase Ozonation: Identification and Environmental Occurrence.” Environmental Science & Technology 57 (14): 5621–32. https://doi.org/10.1021/acs.est.2c08690.).

5.2.5 Considerations for Measuring 6PPD

Methods for measuring 6PPD have not been as widely reported due to the relatively short half-life of 6PPD in both environmental and laboratory conditions. Transformation products (including hydrolysis products) are quickly formed once 6PPD is in water or, to a lesser degree, in organic solvents (for example, methanol, acetonitrile, toluene). Limited information is available on the transformation products of 6PPD, but 6PPD-q is known to occur as a transformation product in the environment (Seiwert et al. 2022[QDRRVWMW] Seiwert, Bettina, Maolida Nihemaiti, Mareva Troussier, Steffen Weyrauch, and Thorsten Reemtsma. 2022. “Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater.” Water Research 212:118122. https://doi.org/10.1016/j.watres.2022.118122.Zeng et al. 2023[TK5YR8WJ] Zeng, Lixi, Yi Li, Yuxin Sun, Liang-Ying Liu, Mingjie Shen, and Bibai Du. 2023. “Widespread Occurrence and Transport of p-Phenylenediamines and Their Quinones in Sediments across Urban Rivers, Estuaries, Coasts, and Deep-Sea Regions.” Environmental Science & Technology, January, acs.est.2c07652. https://doi.org/10.1021/acs.est.2c07652.Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. “New Evidence of Rubber-Derived Quinones in Water, Air, and Soil." Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.). Therefore, due to the relative reactivity of 6PPD, the methods can only generate an estimated level of 6PPD in environmental samples. Preservatives and pH modifiers have been investigated as ways to stabilize 6PPD, but these additives negatively impact the analysis of 6PPD-q, compromising the sample; the current recommendation for 6PPD analysis by LC-MS is to minimize holding times and direct-injection to minimize both processing and losses (Woudneh 2023[6S8L3YFK] Woudneh, Million. 2023. "Best Practices in the Analysis of 6PPD-Quinone." Presented at the ITRC Tire Anti-Degradants 6PPD Team Meeting, May 16.). Monitoring the ions for 6PPD in MS spectrometry methods can provide presence/absence information in consumer goods and TRWP-laden samples that show positive detections for 6PPD that can act as a reservoir for increased 6PPD-q formation.

5.2.5.1 Standard or Approved Methods for 6PPD

Currently there are no standardized or approved methods for measuring 6PPD. The National Oceanic and Atmospheric Administration (NOAA) and the USGS have included 6PPD in their 6PPD-q methods and provide an estimate of 6PPD concentrations (Lane et al. 2024[Q3DSSIIU] Lane, Rachael F., Kelly L. Smalling, Paul M. Bradley, Justin B. Greer, Stephanie E. Gordon, John D. Hansen, Dana W. Kolpin, Andrew R. Spanjer, and Jason R. Masoner. 2024. "Tire-Derived Contaminants 6PPD and 6PPD-Q: Analysis, Sample Handling, and Reconnaissance of United States Stream Exposures." Chemosphere, July, 142830. https://doi.org/10.1016/j.chemosphere.2024.142830.Mahoney et al. 2022[V5HSELRG] Mahoney, Hannah, Francisco C. da Silva Junior, Catherine Roberts, Matthew Schultz, Xiaowen Ji, Alper James Alcaraz, David Montgomery, et al. 2022. "Exposure to the Tire Rubber-Derived Contaminant 6PPD-Quinone Causes Mitochondrial Dysfunction In Vitro." Environmental Science & Technology Letters 9 (9): 765–71. https://doi.org/10.1021/acs.estlett.2c00431.).

5.2.5.2 Detecting 6PPD in Consumer Products

Techniques that can be applied to identify 6PPD in consumer products include HPLC (Ikarashi and Kaniwa 2000[8KFPXSNG] Ikarashi, Yoshiaki, and Masa-aki Kaniwa. 2000. "Determination of P-Phenylenediamine and Related Antioxidants in Rubber Boots by High Performance Liquid Chromatography. Development of an Analytical Method for N-(1-Methylheptyl)-N'-Phenyl-p-Phenylenediamine." Journal of Health Science 46 (6): 467–73. https://doi.org/10.1248/jhs.46.467.Poldushova, Kandyrin, and Reznichenko 2016[6S6C5F9Z] Poldushova, G.A., K.L. Kandyrin, and S.V. Reznichenko. 2016. "The Effect of the Structure of p - Phenylenediamine Antiagers on the Physicomechanical and Hysteresis Properties of Filled Rubber Compounds." International Polymer Science and Technology 43 (2): 19–22. https://doi.org/10.1177/0307174X1604300205.Lokesh et al. 2023[LBXMIT5W] Lokesh, Srinidhi, Siththarththan Arunthavabalan, Elie Hajj, Edgard Hitti, and Yu Yang. 2023. "Investigation of 6PPD-Quinone in Rubberized Asphalt Concrete Mixtures." ACS Environmental Au, July. https://doi.org/10.1021/acsenvironau.3c00023.), LC-MS (Ikarashi and Kaniwa 2000[8KFPXSNG] Ikarashi, Yoshiaki, and Masa-aki Kaniwa. 2000. "Determination of P-Phenylenediamine and Related Antioxidants in Rubber Boots by High Performance Liquid Chromatography. Development of an Analytical Method for N-(1-Methylheptyl)-N'-Phenyl-p-Phenylenediamine." Journal of Health Science 46 (6): 467–73. https://doi.org/10.1248/jhs.46.467.Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. "New Evidence of Rubber-Derived Quinones in Water, Air, and Soil." Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.), GC/MS (Shetye and Ambare 2018[YK73YHYB] Shetye, Sugandha S., and Satish N. Ambare. 2018. "Pyrolysis Gas Chromatography Mass Spectrometry: A Efficient Technique for Identification and Quantification of Rubber Antioxident P-Phenylene Diamine (6PPD)." International Journal of Research and Analytical Reviews 5 (2): 949–54. http://ijrar.com/upload_issue/ijrar_issue_920.pdf.Armada et al. 2022[XZYEATEB] Armada, Daniel, Maria Celeiro, Thierry Dagnac, and Maria Llompart. 2022. "Green Methodology Based on Active Air Sampling Followed by Solid Phase Microextraction and Gas Chromatography-Tandem Mass Spectrometry Analysis to Determine Hazardous Substances in Different Environments Related to Tire Rubber." Journal of Chromatography A 1668:462911. https://doi.org/10.1016/j.chroma.2022.462911.Skoczyńska et al. 2021[THG8LDSG] Skoczyńska, Ewa, Pim E.G. Leonards, Maria Llompart, and Jacob de Boer. 2021. "Analysis of Recycled Rubber: Development of an Analytical Method and Determination of Polycyclic Aromatic Hydrocarbons and Heterocyclic Aromatic Compounds in Rubber Matrices." Chemosphere 276:130076. https://doi.org/10.1016/j.chemosphere.2021.130076.), QTOF/MS (Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. "New Evidence of Rubber-Derived Quinones in Water, Air, and Soil." Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.), thermal desorption (TD), and pyrolysis-GC/MS (pryo-GC/MS) (Shetye and Ambare 2018[YK73YHYB] Shetye, Sugandha S., and Satish N. Ambare. 2018. "Pyrolysis Gas Chromatography Mass Spectrometry: A Efficient Technique for Identification and Quantification of Rubber Antioxident P-Phenylene Diamine (6PPD)." International Journal of Research and Analytical Reviews

5 (2): 949–54. http://ijrar.com/upload_issue/ijrar_issue_920.pdf.More et al. 2023[28DQ7TYQ] More, Sharlee L., Julie V. Miller, Stephanie A. Thornton, Kathy Chan, Timothy R. Barber, and Kenneth M. Unice. 2023. "Refinement of a Microfurnace Pyrolysis-GC–MS Method for Quantification of Tire and Road Wear Particles (TRWP) in Sediment and Solid Matrices." Science of the Total Environment 874 (May):162305. https://doi.org/10.1016/j.scitotenv.2023.162305.).

The following description of 6PPD analysis in consumer products was compiled from the references cited in the preceding paragraph. Consumer products are cut down to micro-sized particles via cryogenic grinding (or cyromilling) to a length less than 5 mm. The subsequent apparatus used depends on the specific instrumentation used. For example, inductively coupled plasma / MS (ICP/MS) uses glass vials and then the particles would be transferred into polyethylene sample holders for analysis. As another example, TD would use quartz sampling tubes. Density separation is not necessary when working with a known consumer product. Procedural steps are based on which specific instrumentation is used to analyze the sample. One of the least complicated methods is pyro-GC/MS. For example, with HPLC, LC-MS, and ICP/MS, acid digestion may be a necessary first step depending upon the type of polymer rubber of the consumer product; this adds time to the analysis process and is less environmentally friendly.

For LC-MS, the milled consumer sample is prepared with solvent extraction via centrifugation, shaking, or sonication and concentrated via blowdown, solvent accelerator extraction, or plastic-free stream with nitrogen. Cleanup steps can include syringe filter or SPE. With TD and pyro-GC/MS, there are three types of quartz sample tubes to choose from depending on the volatility of the consumer sample: the double open-ended, single open-ended, and slit. The tube is conditioned by passing through a hot flame, such as a Bunsen burner or butane flame, and a small amount of consumer sample is added to the quartz tube and pyrolyzed. A well-characterized National Institute of Standards and Technology rubber sample is used as a reference, and a total ion count chromatogram is used to identify patterns of ions and major chemical markers of tire rubber.

5.2.5.3 6PPD Commercial Standards and Isotopically Labeled Surrogate or Internal Standards

6PPD is available from a range of commercial vendors as a solid standard and is stable in this solid form until the use-by date provided by the manufacturer. An isotopically labeled 6PPD internal standard is not commercially available, and the following chemicals have been used as surrogate and internal standards: D5-6PPD-q, 6PPD-q-$^{13}C_6$, aniline-d_5, atrazine-d_5, benzophenone-d10, benzothiazole-d4, caffeine-$^{13}C_3$, coumaphos-d10, 16diphenylamine-d10, diphenylurea-d10, 5-methylbenzotriazole-d6, melamine-$^{13}C_3$, progesterone-d9, and pyrene-d10 (see Table 5-2).

5.2.6 Considerations for Measuring 6PPD-q

During the discovery and purification of 6PPD-q (Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. "A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon." Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.), a variety of analytical techniques were used to isolate and identify 6PPD-q. Because stormwater is so complex, Z. Tian et al. fractionated the stormwater using sand filtration, ion exchange, XAD-2 fractionation, silica gel fractionation, parallel HPLC fractionation, and sequential HPLC fractionation, and they tested each fraction for coho salmon toxicity. Z. Tian et al. (Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. "A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon." Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.) elucidated the compounds in the toxic fraction with LC and GC for separation and QTOF and orbitrap HRMS (UPLC-QTOF-MS/MS, UPLC-Orbitrap-MSn, GC-QTOF-HRMS) detection. These techniques for investigating unknown compounds in complex mixtures, along with nuclear magnetic resonance data for confirmation, identified 6PPD-q.

Stormwater and surface water can have high turbidities, and because 6PPD sorbs to organic material (Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. "Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone." Environmental Science: Processes & Impacts 25 (5): 901–11. https://doi.org/10.1039/D3EM00047H.), it is important to use a method that provides whole-water analysis, including suspended materials. Laboratory rubber materials, silicone, and parafilm also have a higher capacity for sorption and should be avoided (Hu et al. 2023[BFCN5BLS] Hu, Ximin, Haoqi (Nina) Zhao, Zhenyu Tian, Katherine T. Peter, Michael C. Dodd, and Edward P. Kolodziej. 2023. "Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber–Derived Toxicant 6PPD-Quinone." Environmental Science: Processes & Impacts 25 (5): 901–11.

https://doi.org/10.1039/D3EM00047H.Woudneh 2023[6S8L3YFK] Woudneh, Million. 2023. “Best Practices in the Analysis of 6PPD-Quinone.” Presented at the ITRC Tire Anti-Degradants 6PPD Team Meeting, May 16.). Rubber laboratory materials should also be avoided to prevent background contamination of 6PPD or 6PPD-q.

5.2.6.1 Finding a Laboratory

Commercial, public, and research laboratories are available for the analysis of 6PPD-q. When selecting a laboratory, be sure it provides the analytical rigor required for project or program goals. Laboratory method accreditation, method detection limits, sample holding times, and quality control parameters (laboratory blanks, laboratory duplicate samples, spike recoveries, method verification standards) should be reviewed to ensure data will meet the desired quality and reproducibility. Analytical method accreditation requirements vary by state, organization, and agency. Laboratory accreditation in the state of Washington is offered by WA Ecology. A list of WA Ecology accredited labs is available at Home – Lab Search (wa.gov)

5.2.6.2 Standard or Approved Methods for 6PPD-q

Options for the analysis of 6PPD-q include commercial, public, and research laboratories. Methods of analysis in water have been published by several organizations and are summarized below.

5.2.6.2.1 USEPA Draft Method 1634

The USEPA’s OW Draft Method 1634 for the analysis of 6PPD-q in storm and surface water specifies headspace-free samples collected in 250-mL amber glass bottles with PTFE-lined caps, with samples stored between 0°C and 6°C but not frozen. These samples, which may be held for up to 14 days, have an aliquot of the extracted internal standard (EIS), 13C6-6PPD-q, and are then extracted using Phenomenex Strata-XL, 100-µm polymeric reversed-phase 200-mg, or equivalent, SPE cartridges. The SPE column is rinsed with a 5-mL aliquot of 50:50 methanol:water and then extracted with two 5-mL aliquots of acetonitrile. The non-EIS, D5-6PPD-q, is added to the 10-mL extract volume, and a 50-uL aliquot injected onto the LC-MS/MS system. Analyte separation is accomplished on a C18 column using a 0.2% formic acid in water and acetonitrile mobile phase that has a 10-minute run time. The isotope dilution method is used to quantitate 6PPD-q. The EIS recoveries are also determined using the NIS and are used as an indicator of analytical data quality. The minimum level of quantification for the method is 2 ng/L and is derived from a single-laboratory validation study.

5.2.6.2.2 Washington State Department of Ecology

“Standard Operating Procedure (SOP): Extraction and Analysis of 6PPD-q” (Mel730136, Version 1.2, approved 6/3/2023) contains procedures for the extraction and analysis of water for 6PPD-q by triple quadrupole MS (Washington State Department of Ecology 2023[HJQ3HEWU] Washington State Department of Ecology. 2023. “Standard Operating Procedure (SOP): Extraction and Analysis of 6PPD-Quinone (Mel730136, Version 1.2).”). Water samples are collected headspace-free in 250-mL amber glass bottles with Teflon™-lined caps according to the Quality Assurance Project Plan: Monitoring of Tire Contaminants in Coho Salmon Watersheds. Samples are stored above freezing to 6°C and may be held for up to 28 days until extraction by SPE. Compounds that can be used as the EIS or injected internal standard are D5-6PPD-q and $^{13}C_6$-6PPD-q. The SPE column is conditioned with a 5-mL aliquot of acetonitrile and 10-mL of Milli-Q water, rinsed with 5-mL of 1:1 methanol:water and 5-mL of hexane, then extracted with two 5-mL aliquots of acetonitrile. Analyte separation is accomplished on a biphenyl column using a 0.1% formic acid/water and 0.1% formic acid/acetonitrile mobile phase that has a 10.5-minute run time. The suggested reporting limit is 1 ng/L and the lower limit of quantitation for the instrument is suggested to be 0.025 ng/mL.

5.2.6.2.3 National Oceanic and Atmospheric Administration

The NOAA method, in development as of May 2024, is an LC-MS/MS method for the detection of 6PPD-q in water, fish bile, fish plasma, blubber, fish tissue, and shellfish (da Silva et al. In preparation). The procedure recommends sample collection in glass vials or bottles. Water samples are prepared with liquid/liquid extraction and concentrated, and the solvent is exchanged. The surrogate standard is D5-6PPD-q, and the internal standard is progesterone-D9. Bile and plasma are diluted and then extracted with SPE. Blubber, fish, and shellfish are extracted with an accelerated solvent extractor (ASE) with gravity-flow column cleanup and fractionation, then GPC cleanup. Analyte separation is accomplished on a C18 column. The detection limit for plasma is 0.0075–0.025 ng/mL, bile is 0.015–0.05 ng/mL, and fish tissue is 0.07 ng/g.

5.2.6.2.4 U.S. Geological Survey

The USGS direct-inject method is a UPLC-MS/MS method for the analysis of 6PPD-q in surface water (Lane et al. 2024[Q3DSSIIU]

Lane, Rachael F., Kelly L. Smalling, Paul M. Bradley, Justin B. Greer, Stephanie E. Gordon, John D. Hansen, Dana W. Kolpin, Andrew R. Spanjer, and Jason R. Masoner. 2024. "Tire-Derived Contaminants 6PPD and 6PPD-Q: Analysis, Sample Handling, and Reconnaissance of United States Stream Exposures." Chemosphere, July, 142830. https://doi.org/10.1016/j.chemosphere.2024.142830.). Samples are collected in headspace-free amber glass bottles with Teflon™-lined caps and stored at 0°C–6°C for less than 14 days or frozen until analysis. Samples are 0.7-micron glass-fiber filtered, and the surrogate internal standard D5-6PPD-q is added. Analyte separation is accomplished on a C18 column using a 0.1% formic acid in water and acetonitrile mobile phase that has a 5-minute run time. The isotope dilution method is used to quantitate 6PPD-q, and the method reporting limit is 2 ng/L.

5.2.6.3 6PPD-q Commercial Standards and Isotopically Labeled Surrogate or Internal Standards

One of the initial limitations of 6PPD-q research was the lack of a reference standard for consistent accurate concentrations, which are important for correlating exposure concentrations to environmental detections. 6PPD-q standards, including two standards that are isotopically labeled ($^{13}C_{12}$-6PPD-q and $^{13}C_{6}$-6PPD-q), are now available from multiple commercial vendors.

An interferent with the $^{13}C_{12}$-6PPD-q analog has been observed with some stormwater (Eurofins 2023[GZHAA9N4] Eurofins. 2023. "Research Summary for the Single-Laboratory Validation Study of a Draft EPA LC-MS-MS Isotope Dilution Method for 6PPD-Quinone." https://www.epa.gov/system/files/documents/2024-01/final-research-summary-6ppd-q-11-30-23.pdf.). Although matching isotopically labeled internal standards provide the best correction, other isotopically labeled internal standards have also been used: aniline-d_5, atrazine-d_5, benzophenone-d10, benzothiazole-d4, coumaphos-d10, caffeine-13C3, diphenylamine-d10, diphenylurea-d10, 5-methylbenzotriazole-d6, progesterone-d9, and pyrene-d10 (see Table 5-3).

5.3 Mapping and Modeling 6PPD-q and Potentially Vulnerable Ecosystems

The following text provides information on tools that can help focus sampling and mitigation efforts on 6PPD and 6PPD-q hot spots and potentially vulnerable ecological populations.

Although the causal link between 6PPD-q and URMS occurrences was first identified in the Pacific Northwest (McIntyre et al. 2021[MVL2LKBM] McIntyre, Jenifer K., Jasmine Prat, James Cameron, Jillian Wetzel, Emma Mudrock, Katherine T. Peter, Zhenyu Tian, et al. 2021. "Treading Water: Tire Wear Particle Leachate Recreates an Urban Runoff Mortality Syndrome in Coho but Not Chum Salmon." Environmental Science & Technology 55 (17): 11767–74.

https://doi.org/10.1021/acs.est.1c03569.Kendra and Willms 1990[BQ4XP54V] Kendra, Will, and Roger Willms. 1990. "Recurrent Coho Salmon Mortality at Maritime Heritage Fish Hatchery, Bellingham: A Synthesis of Data Collected from 1987–1989." Washington State Department of Ecology, Environmental Services Program, Surface Water Investigations Section.

https://apps.ecology.wa.gov/publications/documents/90e54.pdf.Scholz et al. 2011[S8ASEIXU] Scholz, Nathaniel L., Mark S. Myers, Sarah G. McCarthy, Jana S. Labenia, Jenifer K. McIntyre, Gina M. Ylitalo, Linda D. Rhodes, et al. 2011. "Recurrent Die-Offs of Adult Coho Salmon Returning to Spawn in Puget Sound Lowland Urban Streams." PLOS ONE 6 (12): e28013.

https://doi.org/10.1371/journal.pone.0028013.Spromberg and Scholz 2011[CT5HUEEI] Spromberg, Julann A, and Nathaniel L Scholz. 2011. "Estimating the Future Decline of Wild Coho Salmon Populations Resulting from Early Spawner Die-Offs in Urbanizing Watersheds of the Pacific Northwest, USA." Integrated Environmental Assessment and Management 7 (4): 648–56. https://doi.org/10.1002/ieam.219.), the potential global extent of effects of 6PPD-q on aquatic life is unknown. 6PPD and 6PPD-q have been found in various environmental media (for example Seiwert et al. 2022[QDRRVWMW] Seiwert, Bettina, Maolida Nihemaiti, Mareva Troussier, Steffen Weyrauch, and Thorsten Reemtsma. 2022. "Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater." Water Research 212:118122. https://doi.org/10.1016/j.watres.2022.118122.Monaghan et al. 2021[RKMTS6DI] Monaghan, Joseph, Angelina Jaeger, Alon R. Agua, Ryan S. Stanton, Michael Pirrung, Chris G. Gill, and Erik T. Krogh. 2021. "A Direct Mass Spectrometry Method for the Rapid Analysis of Ubiquitous Tire-Derived Toxin N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine Quinone (6-PPDQ)." Environmental Science & Technology Letters 8 (12): 1051–56.

https://doi.org/10.1021/acs.estlett.1c00794.Challis et al. 2021[T8TEWPCL] Challis, J. K., H. Popick, S. Prajapati, P. Harder, J. P. Giesy, K. McPhedran, and M. Brinkmann. 2021. "Occurrences of Tire Rubber–Derived Contaminants in Cold-Climate Urban Runoff." Environmental Science & Technology Letters 8 (11): 961–67.

https://doi.org/10.1021/acs.estlett.1c00682.Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. "Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers." Environmental Pollution 314 (December):120206. https://doi.org/10.1016/j.envpol.2022.120206.Greer et al.

2023[P6RF5UFR] Greer, Justin B., Ellie M. Dalsky, Rachael F. Lane, and John D. Hansen. 2023. “Establishing an In Vitro Model to Assess the Toxicity of 6PPD-Quinone and Other Tire Wear Transformation Products.” Environmental Science & Technology Letters, May. https://doi.org/10.1021/acs.estlett.3c00196.Rauert et al. 2022[9WERCXNS] Rauert, Cassandra, Nathan Charlton, Elvis D. Okoffo, Ryan S. Stanton, Alon R. Agua, Michael C. Pirrung, and Kevin V. Thomas. 2022. “Concentrations of Tire Additive Chemicals and Tire Road Wear Particles in an Australian Urban Tributary.” Environmental Science & Technology, January. https://doi.org/10.1021/acs.est.1c07451.Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. “New Evidence of Rubber-Derived Quinones in Water, Air, and Soil.” Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.Nedrich 2022[7LRY36T6] Nedrich, Sara. 2022. Preliminary Investigation of the Occurrence of 6PPD-Quinone in Michigan’s Surface Water. https://doi.org/10.13140/RG.2.2.34478.59204.), but the concentrations and distribution of 6PPD and 6PPD-q has not been well characterized to date. The spatial distribution of 6PPD-q is not uniform across landscapes and depends on multiple factors (see Section 4: Occurrence, Fate, Transport, and Exposure Pathways). Areas where URMS has been observed in streams near high-traffic areas in the Pacific Northwest (Ettinger et al. 2021[HA49KGTT] Ettinger, A. K., E. R. Buhle, B. E. Feist, E. Howe, J. A. Spromberg, N. L. Scholz, and P. S. Levin. 2021. “Prioritizing Conservation Actions in Urbanizing Landscapes.” Scientific Reports 11 (1): 818. https://doi.org/10.1038/s41598-020-79258-2.Feist et al. 2017[4PSDP2BG] Feist, Blake E., Eric R. Buhle, David H. Baldwin, Julann A. Spromberg, Steven E. Damm, Jay W. Davis, and Nathaniel L. Scholz. 2017. “Roads to Ruin: Conservation Threats to a Sentinel Species across an Urban Gradient.” Ecological Applications 27 (8): 2382–96. https://doi.org/https://doi.org/10.1002/eap.1615.Spromberg and Scholz 2011[CT5HUEEI] Spromberg, Julann A, and Nathaniel L Scholz. 2011. “Estimating the Future Decline of Wild Coho Salmon Populations Resulting from Early Spawner Die-Offs in Urbanizing Watersheds of the Pacific Northwest, USA.” Integrated Environmental Assessment and Management 7 (4): 648–56. https://doi.org/10.1002/ieam.219.) are assumed to correspond with high 6PPD-q concentrations. To better characterize potential risks and to strategically monitor URMS occurrences, scientists are developing spatially explicit sampling and assessment approaches (Chen et al. 2023[39YBXWMI] Chen, Xiaoli, Tao He, Xinlu Yang, Yijing Gan, Xian Qing, Jun Wang, and Yumei Huang. 2023. “Analysis, Environmental Occurrence, Fate and Potential Toxicity of Tire Wear Compounds 6PPD and 6PPD-Quinone.” Journal of Hazardous Materials 452 (June):131245. https://doi.org/10.1016/j.jhazmat.2023.131245.).

5.3.1 Data Layers and Tools

To date, there are no national databases or mapping tools dedicated to assessing 6PPD-q concentrations, effects to sensitive fish species, or associations between them. There are national data sets and mapping tools for landscape metrics that may help visualize stream crossing, traffic intensity, impervious surfaces, and other parameters that may be associated with 6PPD-q levels and delivery to streams. The occurrences of sensitive fish are available from national data sets via the Water Quality Portal, and lower density coverage is available via the USEPA National Aquatic Resource Surveys for lakes (National Lakes Assessment) and rivers/streams (National Rivers and Stream Assessment). Additional data processing is needed before mapping, and available data will not provide a census of every stream or waterbody. Furthermore, extirpation of sensitive fish species may have already occurred due to other causes (Smith and Sklarew 2013[EGWKDGVU] Smith, Albert K., and Dann Sklarew. 2013. “A Mid Atlantic Brook Trout (Salvelinus fontinalis) Stream Sustainability Statistic for Rating Non-Tidal Streams.” Sustainability of Water Quality and Ecology 1–2 (December):68–81. https://doi.org/10.1016/j.swaqe.2013.08.001.). Researchers have also developed coverages for projects not originally designed to address questions regarding 6PPD-q (for example, storm drain locations), which may nevertheless be useful for local and regional assessments.

Some local and regional data sets, mapping tools, and spatially explicit assessments are available, especially in the Pacific Northwest (Washington State Department of Ecology 2022[K2CG7KTE] Washington State Department of Ecology. 2022. “6PPD in Road Runoff Assessment and Mitigation Strategies.” 22-03–020. Olympia, Washington: Environmental Assessment and Water Quality Programs. https://apps.ecology.wa.gov/publications/documents/2203020.pdf.), and efforts have increased to better assess the scope of the problem both locally and nationally. Table 5-6 lists some of the resources that are currently available.

Table 5-6. Selected mapping tools and other resources that may be useful for visualizing water quality conditions in support of resource and stormwater management

Spatial Resource	Developer	Region

Coho Urban Runoff Mortality in Puget Sound	USFWS, NOAA, WSU	Puget Sound
EnviroAtlas	USEPA	United States
Freshwater Explorer	USEPA	United States
GridMET	Climatology Lab	CONUS
High Resolution Change Detection	WDFW	Washington State
How's My Waterway	USEPA	United States
National Aquatic Resource Surveys	USEPA	United States
NorWeST project	USDA	Washington State
Physical Solar Model V3	NREL	CONUS
Puget Sound Mapping Project	WDOC	Puget Sound
Puget Sound Stormwater Heatmap	TNC	Geosyntecs	Puget Sound
Puget Sound Stream Benthos	King County	Puget Sound
Puget Sound Watershed Characterization Project	WA Ecology	Puget Sound
Stormwater Discharge Mapping Tools National Aquatic Resource Surveys	USEPA	United States
Stream Flow	USGS	Washington State
StreamCAT	USEPA	United States
SWIFD	Salmonscape	NWIFC	WDFW	Washington State
Tire Contaminant in Salmonid Watersheds Story Map	WA Ecology	Washington State
Urban Canopy	City of Seattle	Puget Sound
Visualizing Ecosystem Land Management Assessments (VELMA)	USEPA	Flexible
WA's National Hydrography Dataset Program	WA Ecology	USGS	Washington State
Washington Geospatial Open Data	WaTech Solutions	Washington State
Washington Geospatial Open Data Portal	WA State Agencies	Washington State
Washington State Fish Passage	WDFW	Washington State
Water GeoViewer	USEPA	United States
Water Quality Atlas	WA Ecology	Washington State
Water Quality Portal	USEPA	USGS	United States
WSDOT Online Map Center	WSDOT	Washington State

Notes: NOAA=National Oceanic and Atmospheric Administration, NREL=National Renewable Energy Laboratory, NWIFC=Northwest Indian Fisheries Commission, SWIFD=Statewide Integrated Fish Distribution, TNC=The Nature Conservancy, USDA=U.S. Department of Agriculture, USEPA=U.S. Environmental Protection Agency, USFWS=U.S. Fish and Wildlife Service, USGS=U.S. Geological Survey, WA Ecology=Washington State Department of Ecology, WA State=State of Washington, WDFW=Washington Department of Fish and Wildlife, WDOC=Washington State Department of Commerce, WaTech Solutions=Washington (State) Technology Solutions, WSDOT=Washington State Department of Transportation, WSU=Washington State University

5.3.2 Spatial Data for Relevant Land Surface Features

The nearness to impervious surfaces, roads, and their proximity to streams are factors that have been linked to URMS and higher levels of 6PPD-q in the environment (Feist et al. 2017[4PSDP2BG] Feist, Blake E., Eric R. Buhle, David H. Baldwin, Julann A. Spromberg, Steven E. Damm, Jay W. Davis, and Nathaniel L. Scholz. 2017. “Roads to Ruin: Conservation Threats to a Sentinel Species across an Urban Gradient.” Ecological Applications 27 (8): 2382–96.

https://doi.org/https://doi.org/10.1002/eap.1615.Tian et al. 2022[BICQHLBC] Tian, Zhenyu, Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C. Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej. 2022. “6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard.” Environmental Science & Technology Letters, January, acs.estlett.1c00910. https://doi.org/10.1021/acs.estlett.1c00910.). Because 6PPD in TRWP is a source of 6PPD-q in the environment, these land surface features and traffic density have been used to identify locations with potential for elevated 6PPD-q concentrations in water. To date, quantitative models for predicting 6PPD-q concentrations have not been developed or validated nationally (Tian et al. 2022[BICQHLBC] Tian, Zhenyu, Melissa Gonzalez, Craig A. Rideout, Haoqi Nina Zhao, Ximin Hu, Jill Wetzel, Emma Mudrock, C. Andrew James, Jenifer K. McIntyre, and Edward P. Kolodziej. 2022. “6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard.” Environmental Science & Technology Letters, January, acs.estlett.1c00910. https://doi.org/10.1021/acs.estlett.1c00910.).

Good national coverages of impervious surfaces, roads, and their proximity to streams are readily available; however, traffic density data are not available for all roads or may not be available from open access data sets. USGS data sets on rainfall and other geographical factors that affect surface runoff and dilution have been conveniently curated by USEPA (StreamCat) and can be modeled (for example, Soil and Water Assessment Tool) (Arnold et al. 1998[2WHDKL8S] Arnold, J. G., R. Srinivasan, R. S. Muttiah, and J. R. Williams. 1998. “Large Area Hydrologic Modeling and Assessment Part I: Model Development1.” JAWRA Journal of the American Water Resources Association 34 (1): 73–89. https://doi.org/10.1111/j.1752-1688.1998.tb05961.x.). These data can be visualized with commercial mapping software or free open-source languages such as R and Python. These GIS software programs require some experience with GIS computing. No GIS experience is needed to visualize impervious surfaces, traffic, and road proximity to streams with the USEPA Freshwater Explorer mapping tool, which can be accessed from the USEPA Freshwater Explorer Landing page: https://www.epa.gov/water-research/freshwater-explorer from the add data widget.

As an example, Figure 5-1 uses data from the National Hydrography Dataset to create a map where streams (shown in red) cross major roads the U.S. highway system. Impervious surface has been linked with coho vulnerability (Feist et al. 2017[4PSDP2BG] Feist, Blake E., Eric R. Buhle, David H. Baldwin, Julann A. Spromberg, Steven E. Damm, Jay W. Davis, and Nathaniel L. Scholz. 2017. “Roads to Ruin: Conservation Threats to a Sentinel Species across an Urban Gradient.” Ecological Applications 27 (8): 2382–96. https://doi.org/https://doi.org/10.1002/eap.1615.). As also shown in the figure, streams in urban areas near Seattle, Washington, and Portland, Oregon, have greater amounts of imperviousness, road crossings, and traffic in their watersheds than other areas. No data set perfectly depicts all the small streams that often serve as spawning habitat, so absence of depiction of a stream on maps should not be construed as lack of habitat for sensitive species and local knowledge and reconnaissance are recommended.

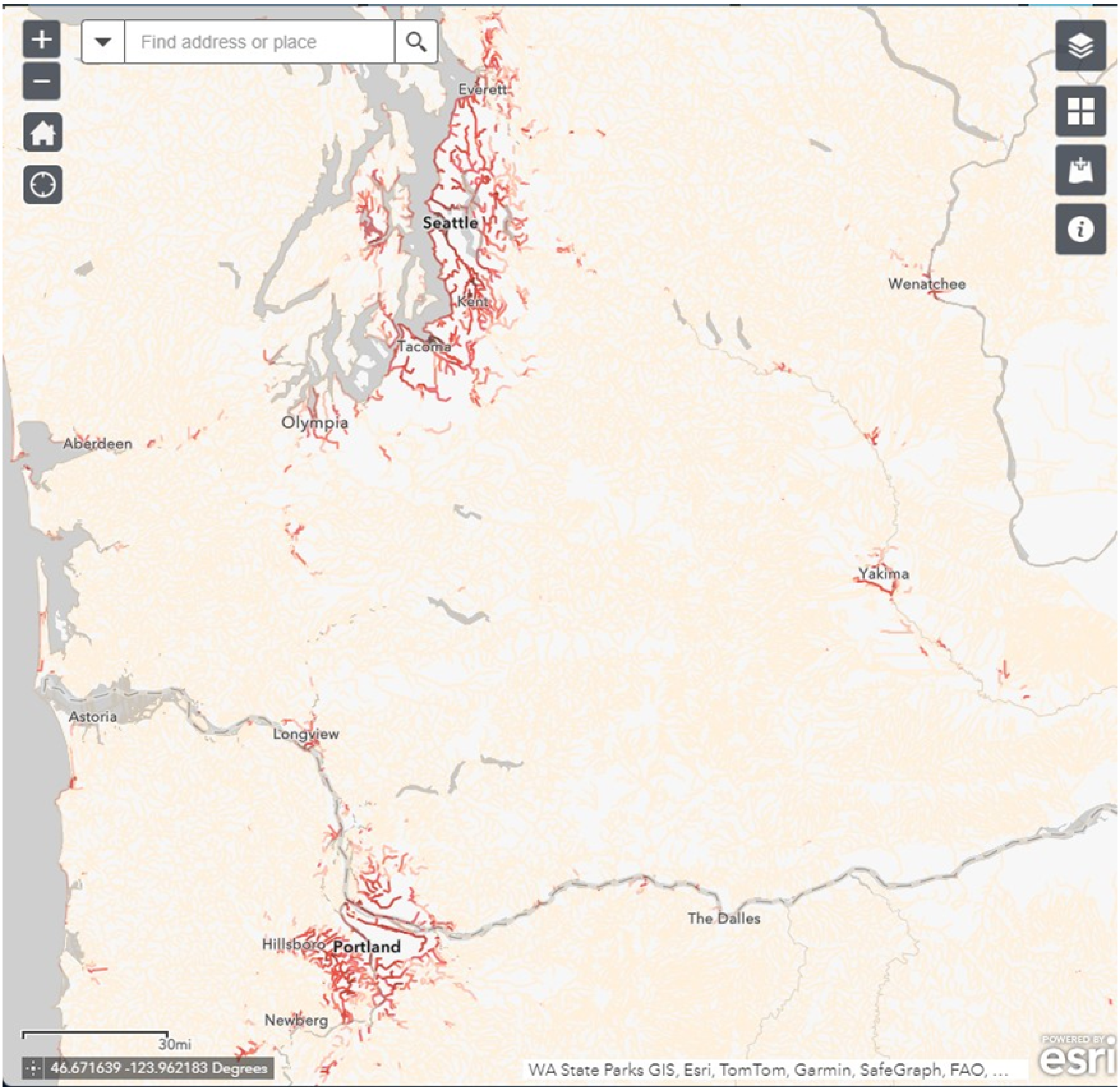


Figure 5-1. Depiction of distance of a stream from major roads in the northwestern United States using the National Hydrography Dataset

Source: USGS, National Hydrography Dataset

On a more local scale, more detail can be seen. The screenshot from the USEPA Freshwater Explorer (December 2023) in Figure 5-2 illustrates how spatial data can be used to depict information that may inform monitoring designs. The graphic shows streams color-coded for proximity to roads, with color warmth used to show stream proximity to roads (Figure 5-2). The inset box provides the data from a selected stream. In this example, the associated data box shows information for a segment of Beaverton Creek, Portland, Oregon (highlighted in turquoise), which has minor roads that cross it and is 147 m (about 482.28 feet) from a major road with 27,775 cars per day reported in a recent traffic count. (ESRI/Kalibrate TrafficMetrix. https://goto.arcgisonline.com/demographics5/USA_Traffic_Counts). Impervious cover is 52% and 63% for the watershed and the smaller catchment, respectively. Green areas in this satellite image are forests, and tan and gray areas are agricultural or urban areas.

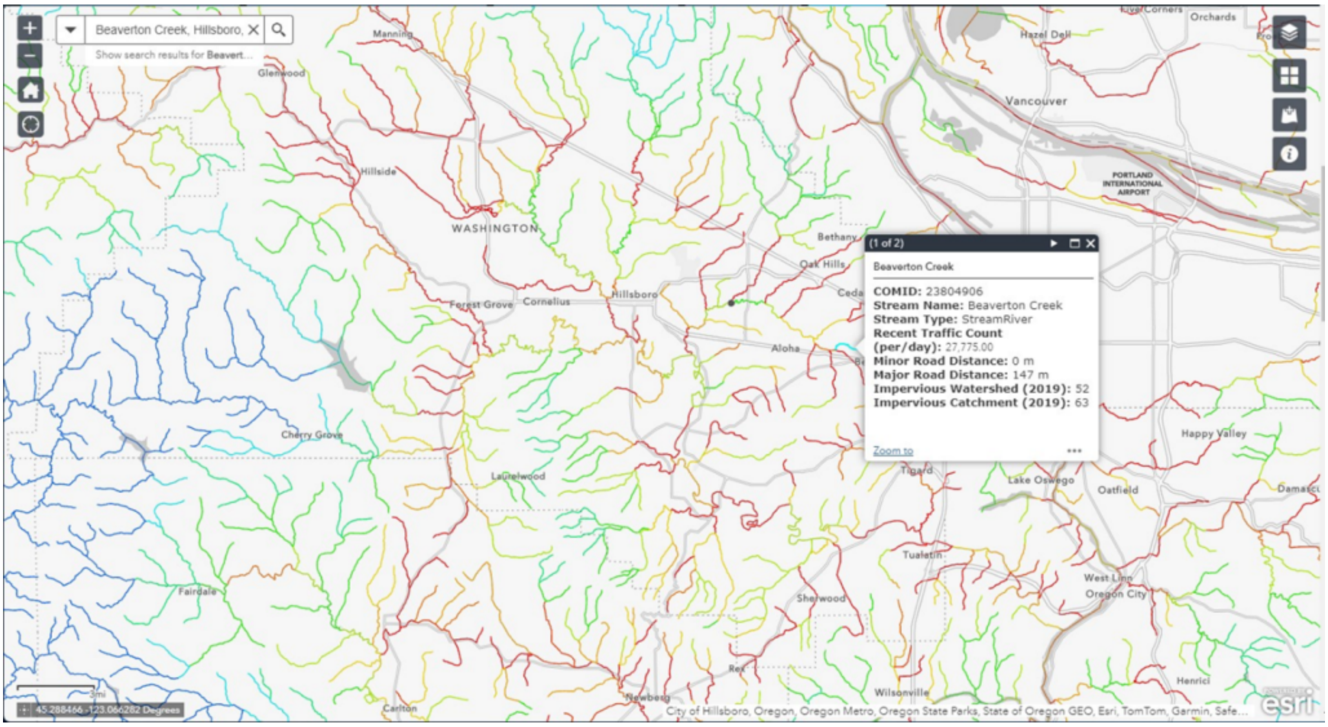


Figure 5-2. Streams are color-coded to indicate the proximity of stream to roads as part of a spatial data analysis that highlights the sources from which 6PPD-q enters streams.

Source: Screenshot from USEPA Freshwater Explorer, 20231005, Portland, Oregon

5.3.3 Fish Distribution

National data sets of the native range of fish species are available as well as occurrence data of fish species within and outside their native ranges. Distribution maps are shown for coho salmon (Figure 5-3), rainbow/steelhead trout (Figure 5-4), brook trout (Figure 5-5), and lake trout (Figure 5-6). The native ranges are shown in blue, and tan represents areas where one or more individuals were observed outside their native range. The boundaries of the geographic area drained by a river system or hydrologic unit used to make the maps are at the USGS 8-digit hydrologic unit level. For example, coho are native to the Pacific Northwest but have been introduced to the Great Lakes basin and the Northeast (see Figure 5-3) (USGS 2023[DT5PXSCQ] USGS. 2023. "Coho Salmon (Oncorhynchus kisutch) — Species Profile." USGS Nonindigenous Aquatic Species Database. 2023. https://nas.er.usgs.gov/queries/factsheet.aspx?SpeciesID=908.). Although rainbow, brook, and lake trout are much less sensitive to 6PPD-q than coho salmon, the distribution of these trout species across the United States is wider than the distribution of coho. A composite of native (blue) and introduced (tan) ranges of coho salmon and the three trout species noted above illustrates that fish sensitive to 6PPD-q are not limited to the Pacific coast (see Figure 1-3). Data for these maps were obtained from the USGS Nonindigenous Aquatic Species (NAS) database as of December 2023. Additional fish data (not shown here) are available from NOAA, USFW, USGS, and state fish and wildlife agencies.

Maps of the geographic distribution of native and non-native sensitive fish species.
(Click the image to enlarge)
Source: USGS Nonindigenous Aquatic Species (NAS) database.

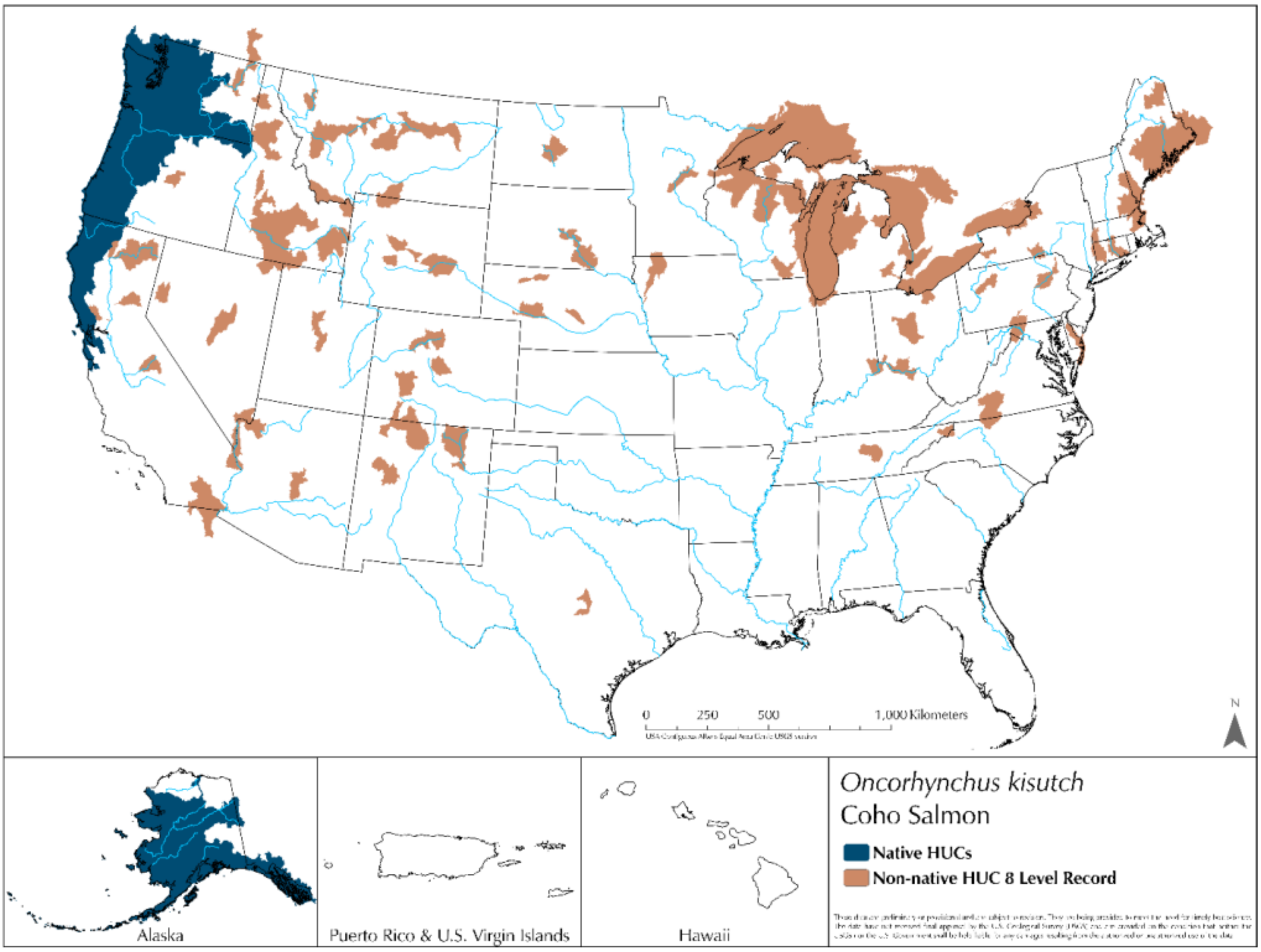


Figure 5-3 Coho salmon

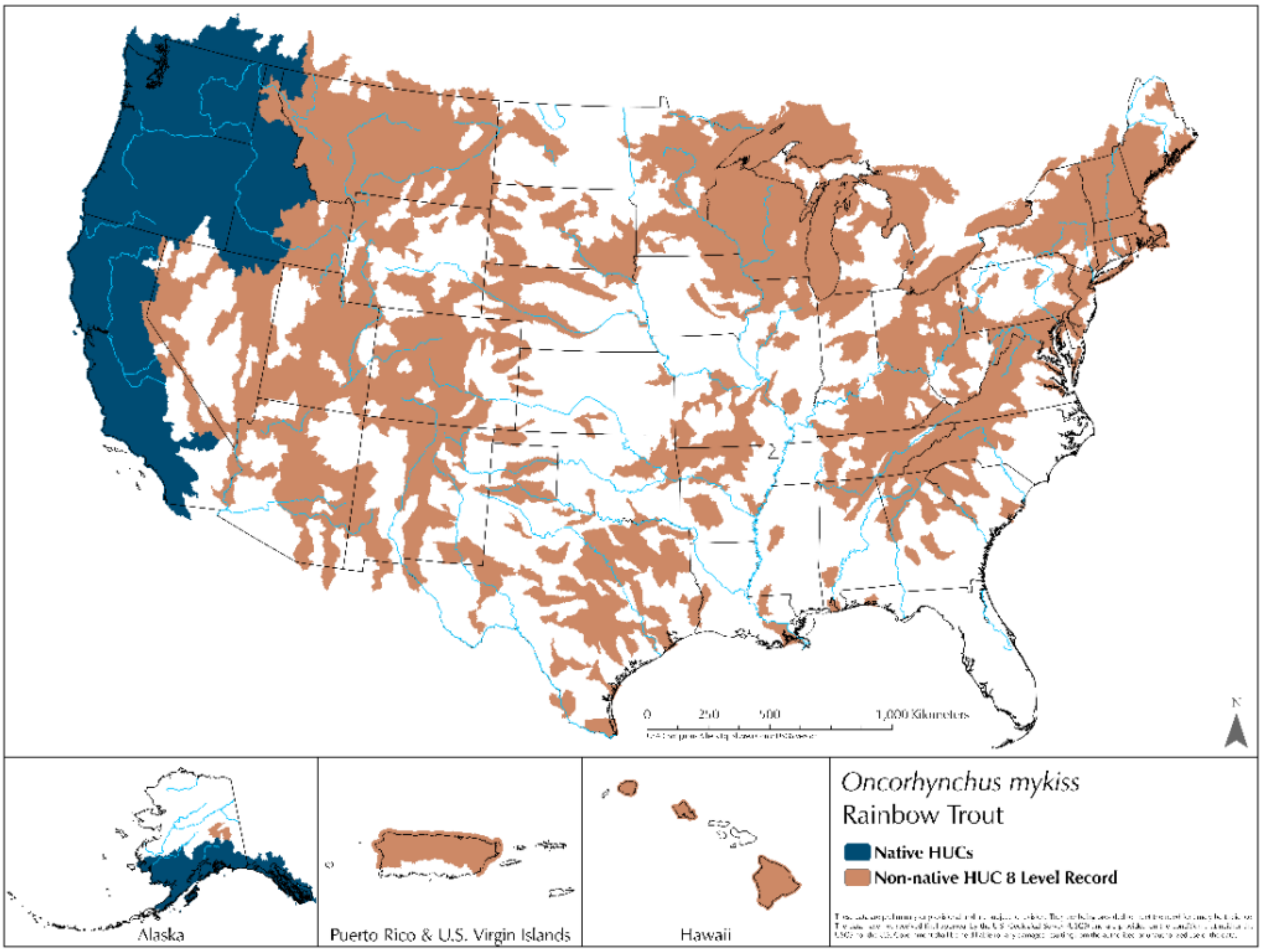


Figure 5-4 Rainbow trout / Steelhead

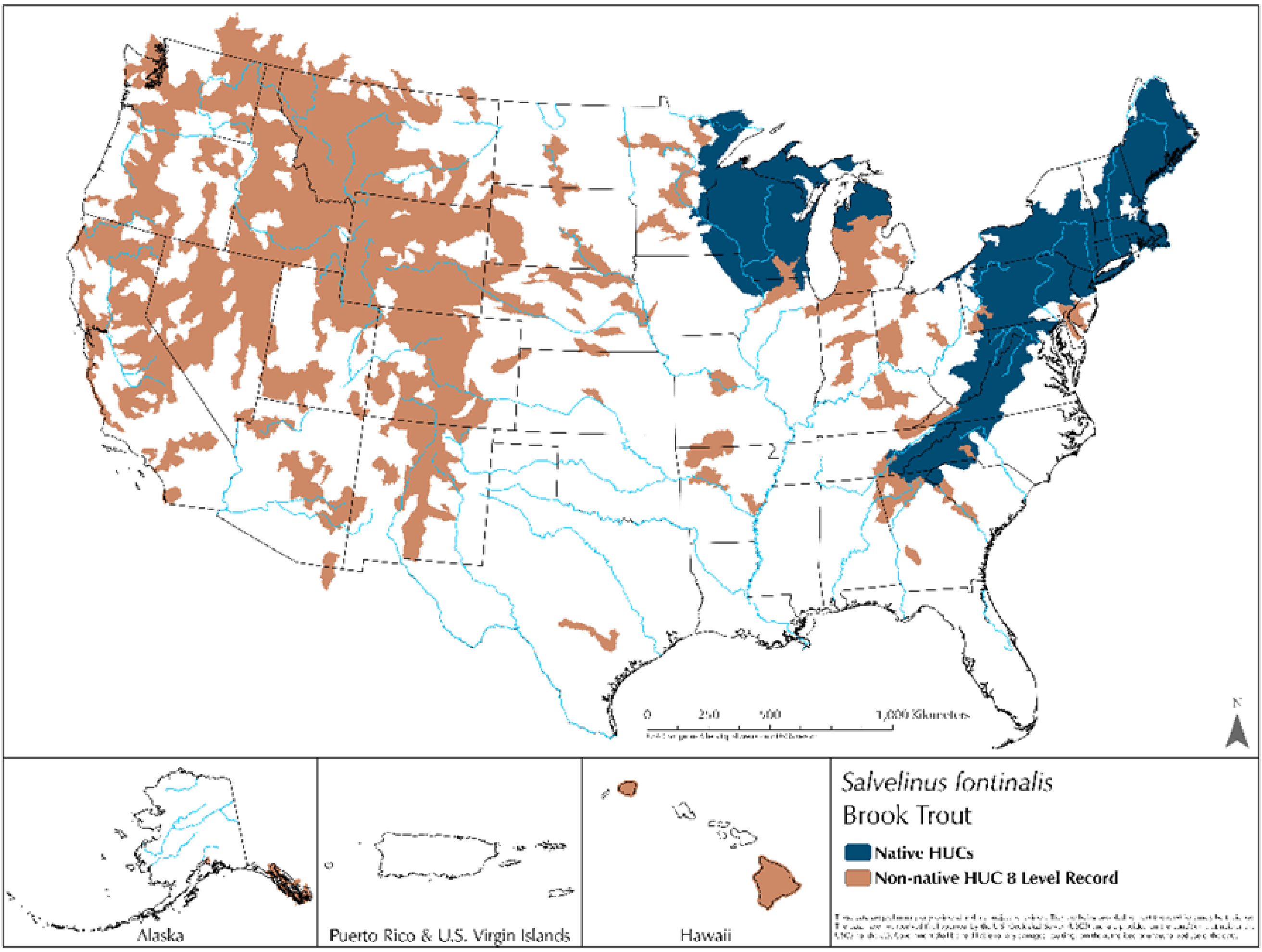


Figure 5-5 Brook trout

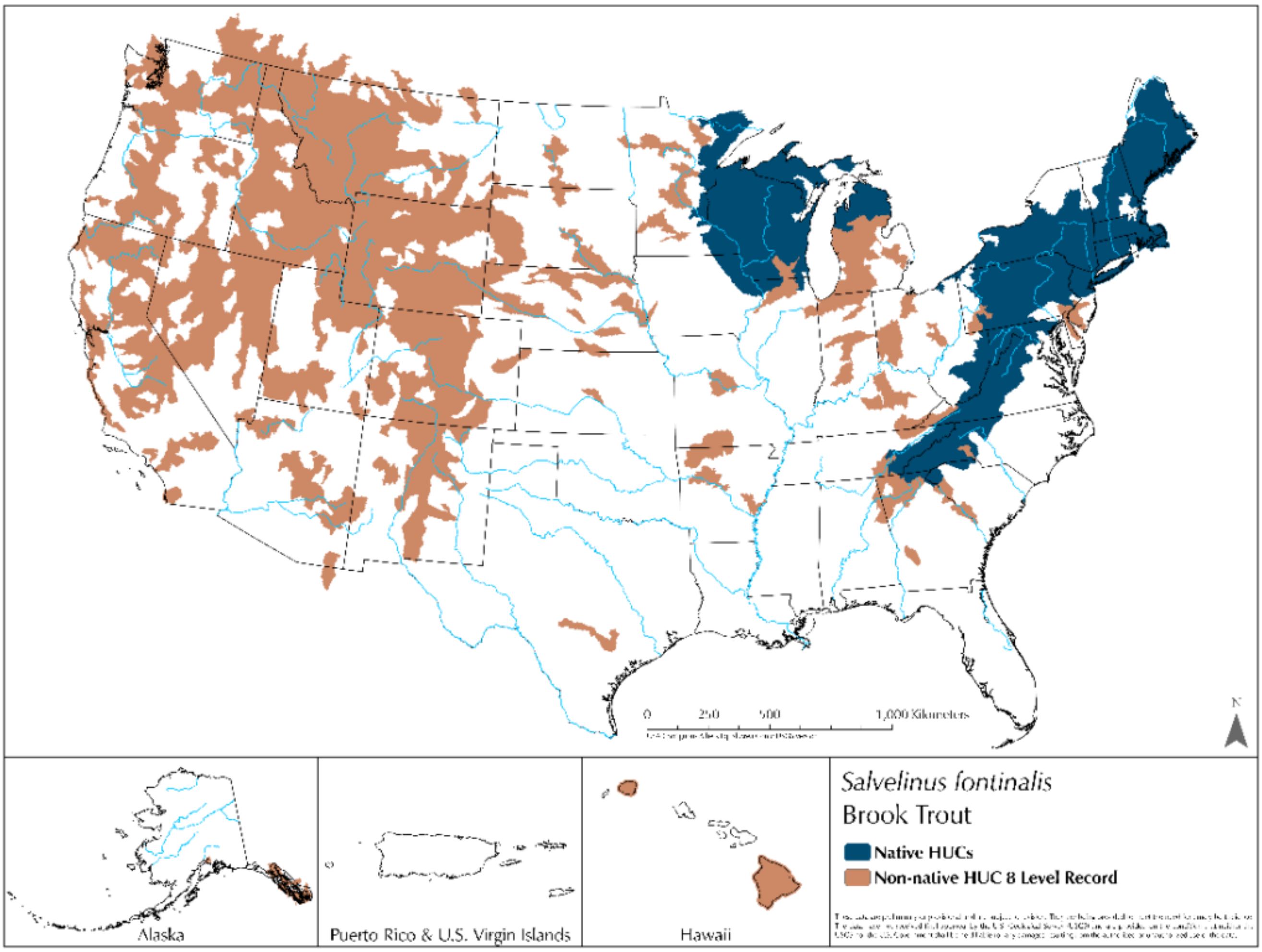


Figure 5-6 Lake trout

5.3.4 Scales of Occurrence, Exposure, and Risk

Desktop GIS can be applied at different scales to help identify toxic hotspots. These efforts are most effective when data infrastructure and resources are available to maintain the tools as new data layers are developed and new information becomes available.

As indicated in Section 5.3.1, there are currently no national databases or mapping tools dedicated to assessing the impact or prevalence of 6PPD or 6PPD-q in our nation's waterways. While local data are available for select areas, the issue of data scarcity is further exacerbated by the variability of coverages among data sets with relevant environmental inputs. The lack of pertinent and analytically compatible information may limit the areas in which traditional modeling techniques can be applied. Alternatively, adjusting modeling approaches to available data may be more pragmatic and more broadly applicable. This is of particular interest because environmental proxies such as nationwide data sets for streamflow, traffic, and fish populations are more readily available than measured 6PPD or 6PPD-q. These parameters to estimate 6PPD loadings may be used in data-driven modeling techniques to estimate the potential exposure and effects of 6PPD in areas with little monitoring and 6PPD-q data.

As an example, the model used to generate maps by Feist et al. (Feist et al. 2017[4PSDP2BG] Feist, Blake E., Eric R. Buhle, David H. Baldwin, Julann A. Spromberg, Steven E. Damm, Jay W. Davis, and Nathaniel L. Scholz. 2017. "Roads to Ruin: Conservation Threats to a Sentinel Species across an Urban Gradient." Ecological Applications 27 (8): 2382–96. https://doi.org/https://doi.org/10.1002/eap.1615.) was used to develop an interactive visualization of the Predicted Mean Annual Coho Urban Runoff Mortality Syndrome Rates Across the Puget Sound (USFWS, NOAA, and Washington State University 2019[ZBMYH66Y] USFWS, NOAA, and Washington State University. 2019. "Predicted Mean Annual Coho Runoff Mortality Syndrome Rates Across the Puget Sound." 2019. https://www.arcgis.com/apps/webappviewer/index.html?id=53ea11d4125146628026b80241716962.) (Figure 5-7). Users can visualize differences across the area and select drainage basins to see information such as the predicted mean percentage annual average coho spawner mortality and a brief characterization of the area. In both the published map and the interactive map (see Figure 5-7), red areas are predicted to have high mortality and yellow areas less mortality. The manuscript details the science, whereas information on the interactive map is more granular and adaptable to different assessment needs.

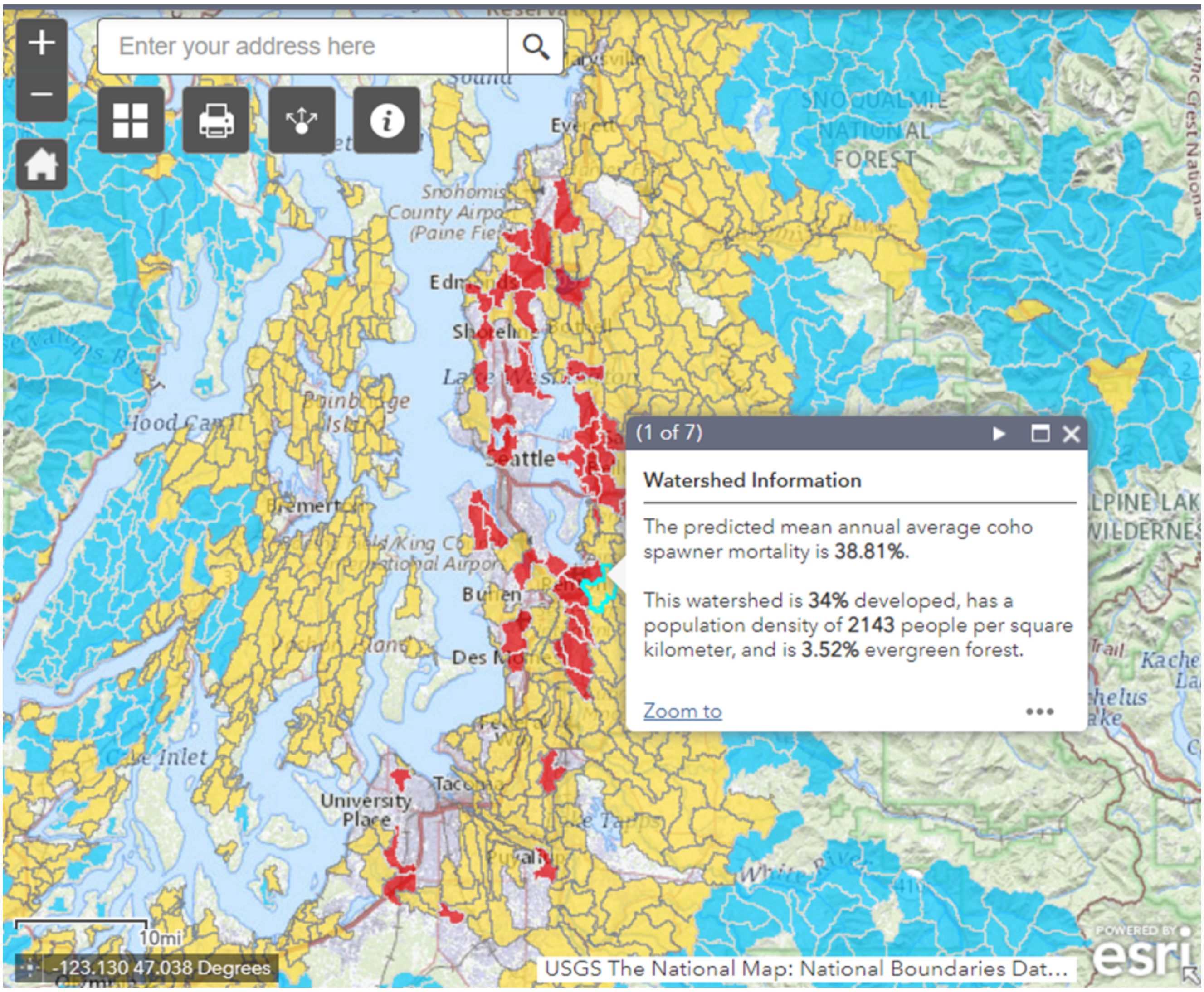


Figure 5-7. Mean annual spawner mortality urban runoff mortality syndrome.

Source: USFWS, NOAA, and Washington State University

(USFWS, NOAA, and Washington State University 2019[ZBMYH66Y] USFWS, NOAA, and Washington State University. 2019. “Predicted Mean Annual Coho Runoff Mortality Syndrome Rates Across the Puget Sound.” 2019. https://www.arcgis.com/apps/webappviewer/index.html?id=53ea11d4125146628026b80241716962.), https://fws.maps.arcgis.com/apps/MapSeries/index.html?appid=5dd4a36a2a5148a28376a0b81726a9a4

A variety of geographic data tools may be needed to address specific goals and scales of assessment. For example, a federal agency may be interested in a country-scale map and a state agency in a state-scale map. A tribe may want watershed-scale maps to design salmon or trout recovery programs. Initial goals may be related to mapping biological or environmental parameters or reconnaissance efforts. As data layers become more complete, spatially explicit data may become sufficient to build models to predict contaminant concentrations and estimate URMS in areas where sampling has not been done.

At smaller scales, it may also be possible to layer more detailed data for hotspot analyses. For example, a county-scale map may depict nonroad-based tire use areas such as playgrounds and fields using recycled tire or rubber or manufacturing facilities, tire recycling centers, landfills, and other facilities that could be sources of 6PPD/6PPD-q; this could help refine sampling locations. At finer scales depending on the local government, MS4s footprints and outfalls, combined sewer outfalls, and other stormwater discharge points may also be available and help refine hotspot mapping and source tracking.

An additional example of a statewide-scale tool is the tire contaminant in coho salmon watershed story map. This has an interactive web map to help guide sampling efforts across urban and traffic gradients and incorporates salmon and trout distributions (Figure 5-8).

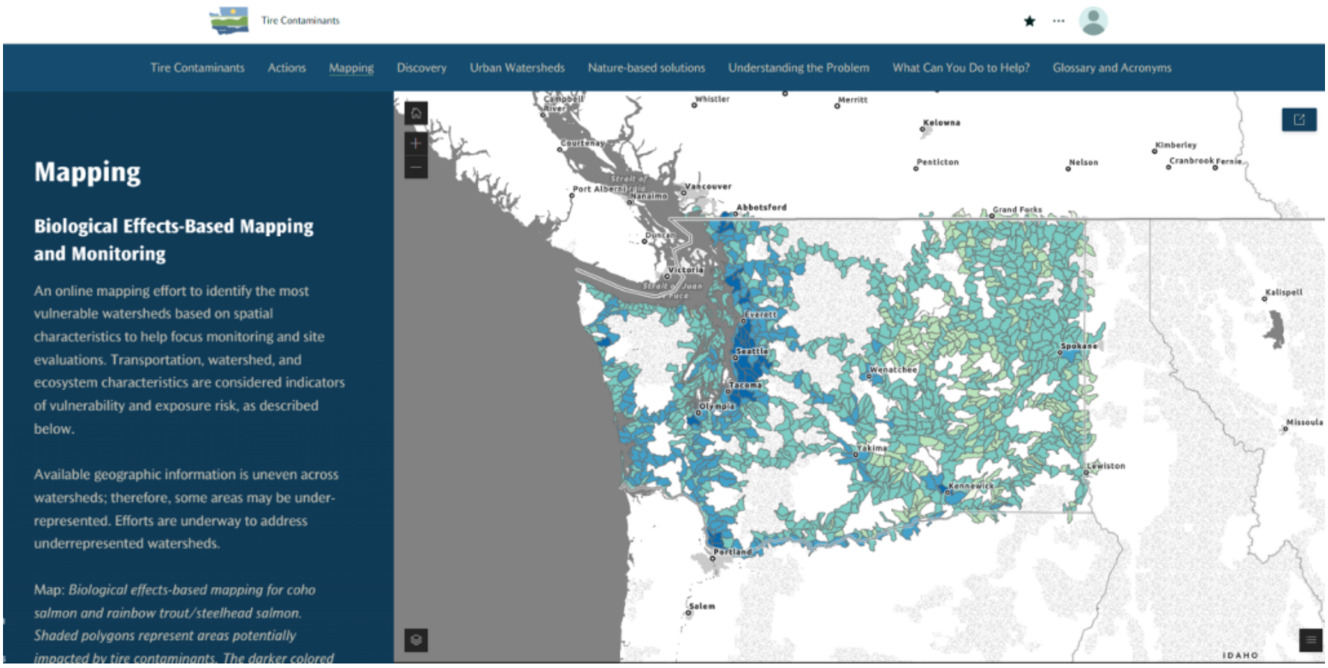


Figure 5-8. The Washington Department of Ecology Storymap helps visualize the potential occurrence of 6PPD-q along roadways near salmon-bearing waterbodies, which helps focus sampling efforts.

Source: Washington Department of Ecology website, Tire Contaminants (wa.gov)

5.3.5 Modeling to Support Regulation and Planning

5.3.5.1 Fate and Transport Modeling

5.3.5.1.1 Total Maximum Daily Load Modeling for Sinks, Sources, Occurrence, and Exposure

When a potentially harmful exposure or an adverse biological effect is observed, the CWA requires steps to reduce exposures and restore aquatic life use. Under Section 303(d) of the CWA, and in accordance with supporting regulations in 40 CFR Part 130.7, states are required to develop biennial lists of waters impaired or threatened by a pollutant. Under this regulation, “impaired” is used to refer to waters that fail to meet one or more applicable water quality standards. States are required to prepare a list of impaired waters that need a Total Maximum Daily Load (TMDL). TMDLs are calculated as the maximum pollutant quantity that a waterbody can receive. Water quality standards often define the water quality target in a TMDL. As part of developing TMDLs, allocation loads among the various point and nonpoint sources of the pollutant are also calculated. (For more information on CWA Section 303(d) Impaired Waters and TMDLs, visit: https://www.epa.gov/tmdl). The pollutants in this example are tire anti-degradants, and the adverse effect that requires remediation is fish survival and reproduction (see also Section 7.8: Clean Water Act).

Many strategies can be used to identify a water-quality target for a TMDL, but 6PPD-q is particularly challenging because of its acute toxicity and ubiquitous occurrence on and along transportation infrastructure (Washington State Department of Ecology 2023[M64YC38F] Washington State Department of Ecology. 2023. “6PPD Alternatives Assessment Hazard Criteria.” 23-04–036. https://apps.ecology.wa.gov/publications/documents/2304036.pdf.). Although USEPA has not yet recommended aquatic life criteria for 6PPD-q, states and tribes may independently adopt the recommended protective levels as their regulatory standards at their discretion. As a result, where 6PPD-q is the identified cause of a biological impairment, states and authorized tribes can develop and then obtain USEPA approval for restoration plans or TMDLs that include numeric targets developed by translating their narrative aquatic life criteria. If USEPA develops aquatic life criteria for 6PPD-q at some future date, then states and tribes may adopt the recommended protective levels as their regulatory standards, or they may propose alternative values based on their own scientifically defensible methods after review and approval by USEPA.

Typically, a TMDL follows a sequence of assessments, as shown in Figure 5-9 (USEPA 2002[F6FA44IC] USEPA. 2002. “Guidelines for Reviewing TMDLs under Existing Regulations Issued in 1992.” https://www.epa.gov/sites/default/files/2015-10/documents/2002_06_04_tmdl_guidance_final52002.pdf.). As described in Cormier and Suter (Cormier and Suter 2008[J4YBWALW] Cormier, Susan M., and Glenn W. Suter. 2008. “A Framework for Fully Integrating Environmental Assessment.” Environmental Management 42 (4): 543–56. https://doi.org/10.1007/s00267-008-9138-y.) and adapted from USEPA (USEPA 2002[F6FA44IC] USEPA. 2002. “Guidelines for Reviewing TMDLs under Existing Regulations Issued in 1992.” https://www.epa.gov/sites/default/files/2015-10/documents/2002_06_04_tmdl_guidance_final52002.pdf.), the “…corresponding components of the assessment and management framework are indicated in grey oblongs: condition assessment (listing process), causal assessment (problem/pollutant identification), risk assessment of effects from exposure (target analysis), source assessment, risk assessment of sources (linkage of sources and target), management assessment (allocation to sources), and outcome assessment (update next listing cycle)” (Cormier and Suter 2008[J4YBWALW] Cormier, Susan M., and Glenn W. Suter. 2008. “A Framework for Fully Integrating Environmental Assessment.” Environmental Management 42 (4): 543–56. https://doi.org/10.1007/s00267-008-9138-y.). Although adverse effects to coho could be the driver that initiates a TMDL, 6PPD-q may not be the cause of the adverse effects based on a causal assessment. When a causal assessment identifies 6PPD-q as a probable contributing cause, the state or authorized tribe could consider doing a more in-depth risk assessment to inform CWA program implementation efforts. If a TMDL is developed and controls are implemented to reduce loads, an outcome assessment could be used to evaluate the performance of the controls. Maps are useful for each type of assessment to scope the extent and patterns of adverse effects, to develop evidence for and against 6PPD-q as a cause, to model and allocate loadings, to design mitigation strategies and placement, and to map progress in achieving environmental goals.

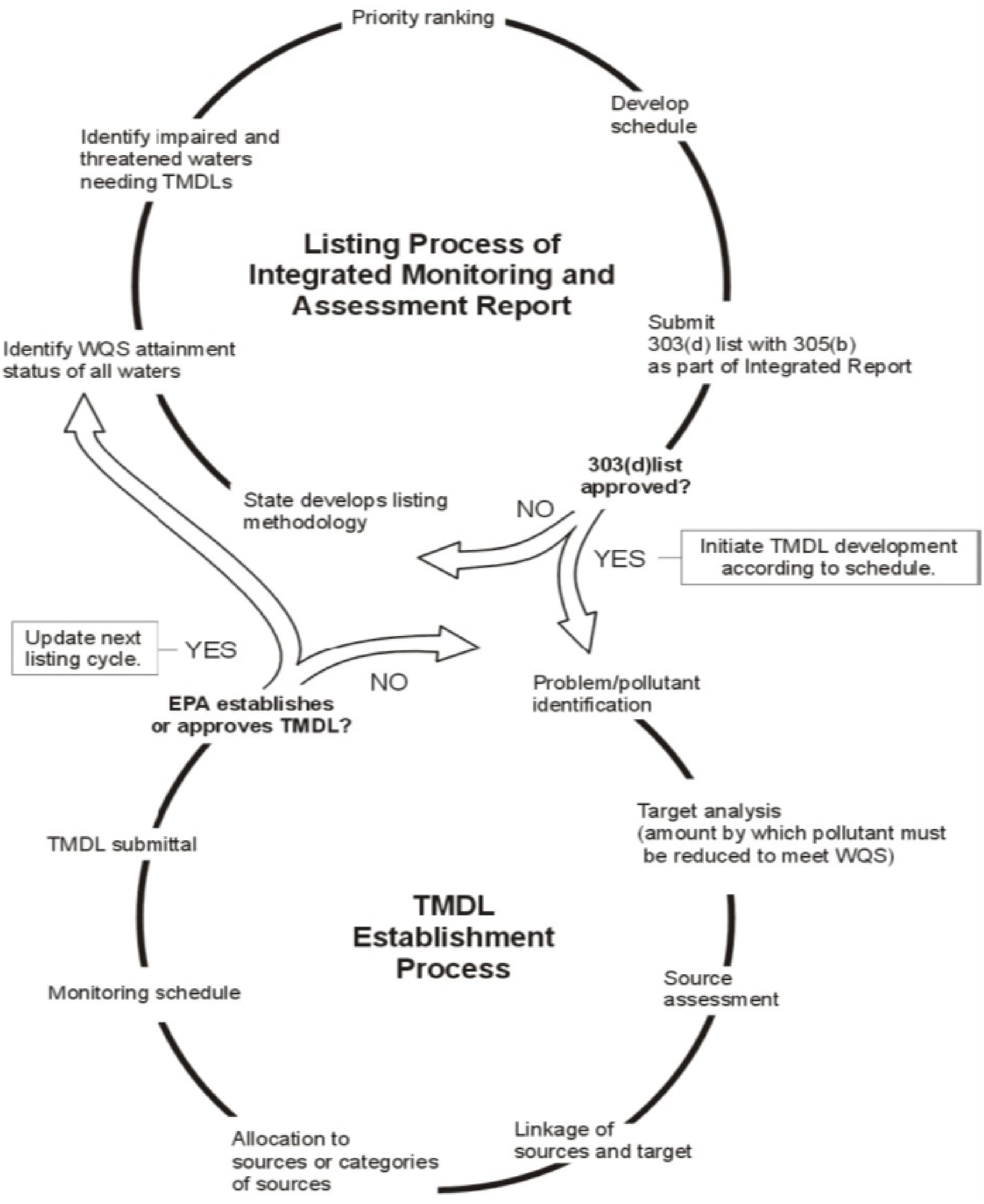


Figure 5-9. A diagram of the assessments and decisions involved in the listing of waters as impaired and the determination of total maximum daily loads. (WQS is water quality standards.)

Source: USEPA (USEPA 2002[F6FA44IC] USEPA. 2002. "Guidelines for Reviewing TMDLs under Existing Regulations Issued in 1992." https://www.epa.gov/sites/default/files/2015-10/documents/2002_06_04_tmdl_guidance_final52002.pdf.)

TMDL reductions can be implemented through stormwater permits administered under the NPDES. According to USEPA (USEPA 2015[52GNBRV5] USEPA. 2015. "Stormwater Discharges from Transportation Sources." Overviews and Factsheets. November 3, 2015. https://www.epa.gov/npdes/stormwater-discharges-transportation-sources.), "[s]imilar to traditional stormwater management authorities (cities and counties), transportation authorities are also responsible for managing the stormwater runoff that discharges to our nation's waters via regulated MS4s along streets, roads, and highways.…" For example, if the adverse effect requiring remedy might impair coho survival and reproduction, the probable cause might be 6PPD-q from a combination of nonpoint-source road runoff and from point-source discharges regulated by NPDES stormwater permits. The TMDL would identify a maximum amount of the pollutant (for example, 6PPD-q) that can enter the stream and an allocation of those loads to point and nonpoint sources. These allocations can guide management options for mitigating identified sources.

Maps of stormwater distribution systems and outfalls can play an important role in TMDL management. For example, VELMA was demonstrated as capable of identifying 6PPD-q hotspots at fine scales (5 m), with results potentially useful when prioritizing the green infrastructure treatment placement, type, and amounts (at the watershed scale) that could be used to reduce URMS (Halama et al. 2024[5UMEQW95] Halama, Jonathan, Robert B. McKane, Bradley L. Barnhart, Paul P. Pettus, Allen F. Brookes, Angela K. Adams, Catherine K. Gockel, et al. 2024. "Watershed Analysis of Urban Stormwater Contaminant 6PPD-Quinone Hotspots and Stream Concentrations Using a Process-Based Ecohydrological Model." Frontiers in Environmental Science 12 (March). https://doi.org/10.3389/fenvs.2024.1364673.Halama et al. 2022[6Z5EW4N9] Halama, Jonathan, Robert McKane, Vivian Phan, Allen Brookes, Kevin Djang, Edward Kolodziej, Katherine Peter, and Zhenyu Tian. 2022. "VELMA Model Green Infrastructure Applications for Reducing 6PPD-Quinone Concentrations in Puget Sound Urban Stream." Presented at the EMCON 2021, March 25. https://www.ezview.wa.gov/Portals/_2001/Documents/Documents/HalamaMcKaneGISummitSalishSeaTalk25Mar2022_SWG30Mar2022_UpdateJJH.pdf.). (For additional information on VELMA and its application to decision-making for environmental issues, visit: https://www.epa.gov/water-research/visualizing-ecosystem-land-management-assessments-velma-model).

The major transport and exposure of 6PPD-q to aquatic life is thought to be surface runoff and stormwater. Many other contaminants of concern are associated with transportation infrastructure and motor vehicles beyond 6PPD-q. Thus, the efforts to model stormwater and 6PPD-q have become entwined. Natural resource scientists and modelers recognized that existing runoff models developed for forestry practices and reducing sedimentation in rivers could be repurposed for stormwater modeling.

5.3.5.1.2 Groundwater Plume Modeling

Due to the limited amount of groundwater studies involving 6PPD and 6PPD-q, groundwater plume modeling has not been extensively examined.

5.3.5.2 Air Transport Modeling

TRWP transport by air is poorly understood and may represent an underestimated mechanism and source. TRWPs not only shed onto roadways but are dispersed in the air and deposited at distances from the roadways along a gradient that depends on the size and shape of the TRWP (see Figure 1-7 for a conceptual depiction of these phenomena). Numerous studies show particles greater than 10 µm at distances downwind of a roadway relevant for exposures to humans and biota. Airborne transport pathways should remain a concern until more research is available to verify its contribution to the environment.

Modeling of fine ($PM_{2.5}$) and coarse (PM_{10}) with estimates of TRWP allocations is a useful tool for predicting and comparing mass loading to the environment. Existing USEPA tools are useful resources for dispersion modeling methods using MOVES and AERMOD to estimate vehicle emissions and transport, including TRWP. State agencies often have higher-resolution information to support surrogates developed from state vehicle miles traveled data (see, for example, (Washington State Department of Ecology 2023[3NJSEXIP] Washington State Department of Ecology. 2023. "6PPD Alternatives Assessment Hazard Criteria." 23-04–036. https://apps.ecology.wa.gov/publications/SummaryPages/2304036.html.).

Transportation data sets, as discussed in Section 5.3.2 and Section 5.3.4, are another data source to consider when modeling impacted areas. Many traffic GIS data layers rely on the Federal Highway Administration's Highway Performance Monitoring System and the Freight Analysis Framework (FAF5), as well as local traffic monitoring systems managed by county and state agencies. High-resolution modeling efforts will help identify priority areas with greater tire emissions loads that can be cross-referenced with impervious surface within each watershed or basin.

5.3.5.2.1 Vapor

Significant knowledge gaps exist concerning contaminants associated with TRWP that may be present in the gas phase (

Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. “Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers.” Environmental Pollution 314 (December):120206. https://doi.org/10.1016/j.envpol.2022.120206.). Current data indicate that 6PPD and 6PPD-q are unlikely to volatilize at typical conditions in the natural environment (Section 3.4; Washington State Department of Ecology, 2022).

5.3.5.2.2 Deposition

The airborne fraction of TRWP reported in the literature ranges from 0.1% to 30% (Grigoratos and Martini 2014[RA3SMLZL] Grigoratos, Theodoros, and Giorgio Martini. 2014. “Non-Exhaust Traffic Related Emissions. Brake and Tyre Wear PM.” EUR 26648 EN. European Commission Joint Research Centre Institute of Energy and Transport.Grigoratos and Martini 2015[M7P4CR2U] Grigoratos, Theodoros, and Giorgio Martini. 2015. “Brake Wear Particle Emissions: A Review.” Environmental Science and Pollution Research 22 (4): 2491–2504. https://doi.org/10.1007/s11356-014-3696-8.Kole et al. 2017[NZZMY6WC] Kole, Pieter Jan, Ansje J. Löhr, Frank G. A. J. Van Belleghem, and Ad M. J. Ragas. 2017. “Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment.” International Journal of Environmental Research and Public Health 14 (10): 1265. https://doi.org/10.3390/ijerph14101265.). The fate of airborne TRWP strongly depends on particle size and shape. Larger TRWP (that is, TRWP with an average diameter greater than 10 μm) are likely to settle on or near the roadway (Kole et al. 2017[NZZMY6WC] Kole, Pieter Jan, Ansje J. Löhr, Frank G. A. J. Van Belleghem, and Ad M. J. Ragas. 2017. “Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment.” International Journal of Environmental Research and Public Health 14 (10): 1265. https://doi.org/10.3390/ijerph14101265.). By comparison, TRWP with an average diameter less than 10 μm) are likely to remain airborne for minutes to hours and can be transported from hundreds of meters to 50 km from the source depending on particle characteristics and local conditions (Kole et al. 2017[NZZMY6WC] Kole, Pieter Jan, Ansje J. Löhr, Frank G. A. J. Van Belleghem, and Ad M. J. Ragas. 2017. “Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment.” International Journal of Environmental Research and Public Health 14 (10): 1265. https://doi.org/10.3390/ijerph14101265.). Kole et al. (Kole et al. 2017[NZZMY6WC] Kole, Pieter Jan, Ansje J. Löhr, Frank G. A. J. Van Belleghem, and Ad M. J. Ragas. 2017. “Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment.” International Journal of Environmental Research and Public Health 14 (10): 1265. https://doi.org/10.3390/ijerph14101265.) further state that “[s]pecific transport data on the 0.1–1 μm fraction are lacking, but it is well known that $PM_{2.5}$ particles (i.e., particles less than 2.5 μm) can stay in the air for days or weeks and travel more than a thousand kilometers.”

As described in Section 4.4.2, concentrations of 6PPD and 6PPD-q are greater in road dust closer to roadways, and concentrations of 6PPD and 6PPD-q were higher in finer particles relative to coarser particles in road dust. More studies are needed to understand the distribution of 6PPD and 6PPD-q concentrations across particle sizes, including ultrafine ($PM_{0.1}$), fine ($PM_{2.5}$), and coarse (PM_{10}) fractions. More research is also needed to understand how the sizes and characteristics of air-transported particles impact the occurrence, concentration, and transport of 6PPD-q in the environment. Section 8.2 describes data gaps and research needs pertaining to Occurrence, Fate, Transport, and Exposure to 6PPD and 6PPD-q in more detail.

5.3.5.3 Modeling 6PPD-q Stormwater Transport to Surface Water

Contaminant hotspot maps help identify locations for source control and prioritize green stormwater infrastructure treatments (i.e., rain gardens, bioswales, pervious pavements) that can most effectively reduce contaminant loadings to threatened aquatic habitats. Models that help identify such hotspots can be a useful tool when planning this load reduction. (For more information on SCMs and BMPs/green stormwater infrastructure, see Section 6.3).

The USEPA’s VELMA tool provides high-resolution spatial and temporal analysis of 6PPD-q hotspots and is a tool for prioritizing the locations, amounts, and types of green infrastructure that can most effectively reduce 6PPD-q stream concentrations to levels protective of coho salmon and other aquatic species (Halama et al. 2024[5UMEQW95] Halama, Jonathan, Robert B. McKane, Bradley L. Barnhart, Paul P. Pettus, Allen F. Brookes, Angela K. Adams, Catherine K. Gockel, et al. 2024. “Watershed Analysis of Urban Stormwater Contaminant 6PPD-Quinone Hotspots and Stream Concentrations Using a Process-Based Ecohydrological Model.” Frontiers in Environmental Science 12 (March). https://doi.org/10.3389/fenvs.2024.1364673.). Figure 5-10 presents the modeling components used in VELMA to simulate 6PPD-q fate and transport in the Longfellow Creek watershed (Halama et al. 2024[5UMEQW95] Halama, Jonathan, Robert B. McKane, Bradley L. Barnhart, Paul P. Pettus, Allen F. Brookes, Angela K. Adams, Catherine K. Gockel, et al. 2024. “Watershed Analysis of Urban Stormwater Contaminant 6PPD-

Quinone Hotspots and Stream Concentrations Using a Process-Based Ecohydrological Model." Frontiers in Environmental Science 12 (March). https://doi.org/10.3389/fenvs.2024.1364673.).

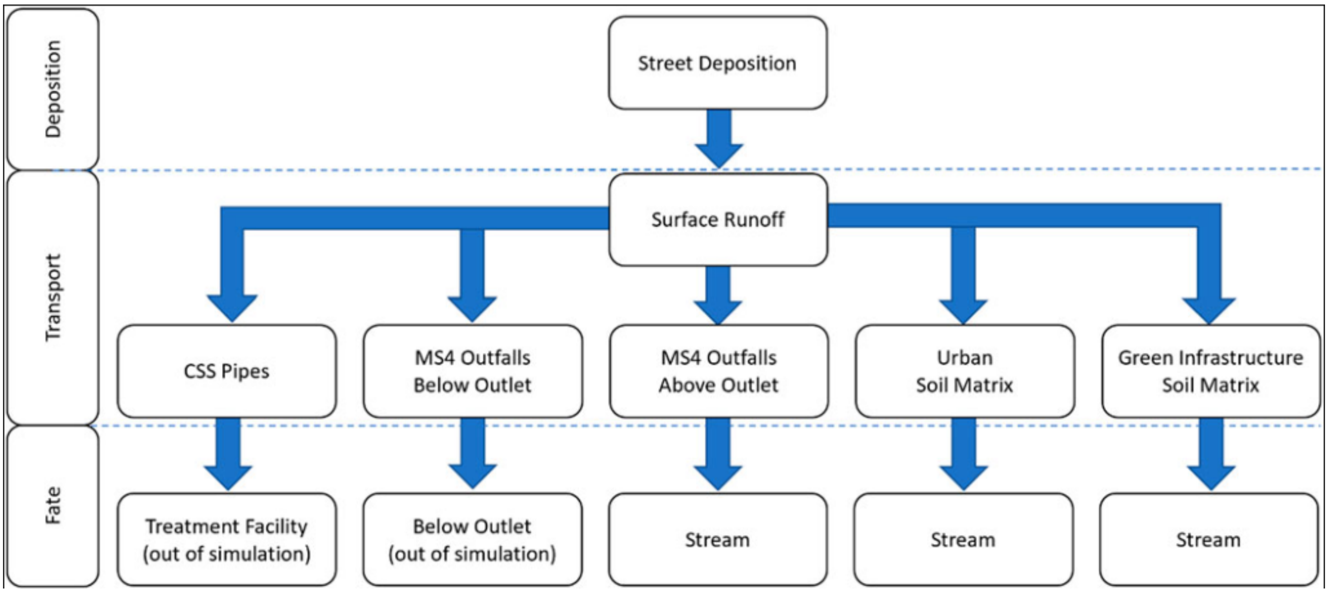


Figure 5-10. Example of how Visualizing Ecosystem Land Management Assessments (VELMA) modeling components can be used to simulate watershed-wide fate and transport of 6PPD-q.

Source: J. Halama et al. (Halama et al. 2024[5UMEQW95] Halama, Jonathan, Robert B. McKane, Bradley L. Barnhart, Paul P. Pettus, Allen F. Brookes, Angela K. Adams, Catherine K. Gockel, et al. 2024. "Watershed Analysis of Urban Stormwater Contaminant 6PPD-Quinone Hotspots and Stream Concentrations Using a Process-Based Ecohydrological Model." Frontiers in Environmental Science 12 (March). https://doi.org/10.3389/fenvs.2024.1364673.).

6 Mitigation Measures and Solutions

Other sections of this document have introduced what we know about 6PPD and 6PPD-q, including toxicity, fate, transport, and environmental sampling methods. This section provides possible mitigation strategies and potential solutions. These include the following:

- Assessing chemical alternatives to 6PPD in tires
- Mitigating the impacts of 6PPD-q in the environment through pollution prevention, air particulate mitigation, and stormwater source control measures
- Evaluating what is known and unknown about remediating 6PPD-q if it persists in the environment

6.1 Introduction

Near-term and long-term solutions are being evaluated to reduce and prevent harm to aquatic organisms and ecosystems from 6PPD and 6PPD-q. Additionally, many of the proposed solutions could address human health impacts, if 6PPD-q is found to negatively affect human populations. This section describes the status of identifying potential alternatives to 6PPD in tires, evaluating and implementing mitigation strategies such as SCMs and air particulate mitigation, and determining the need for remediation of media that have been impacted by 6PPD-q. This section also provides a description of policies, regulations, and laws that could be considered by decision-makers when assessing potential 6PPD planning activities.

Some of the research described throughout this section addresses TWPs or TRWPs instead of 6PPD-q explicitly. Because 6PPD-q was discovered very recently, TWP and TRWP research can be a helpful resource for assessing potential mitigation effectiveness. Additionally, the TWP and TRWP research studies included in this document were limited to studies where preventing or mitigating TRWP pollution is also likely to address 6PPD and 6PPD-q.

6.2 Tire Alternatives and Innovation

6PPD is a widely used anti-degradant found within all automotive tires and serves a critical role in tire safety and performance. 6PPD protects the components of the tire from degrading via ozone, oxygen, thermal degradation, and mechanical fatigue. Eliminating 6PPD in tires without an available alternative that offers comparable performance would compromise tire safety.

A process to identify potential alternatives to 6PPD in tires that do not have equivalent or worse hazard traits or other regrettable tradeoffs is known as an alternatives assessment. The National Research Council defines an alternatives assessment (AA) as the “process for identifying and comparing potential chemical and nonchemical alternatives that could replace chemicals of concern on the basis of their hazards, comparative exposure, performance, and economic viability” ([National Research Council 2014, p.13]). The careful consideration of replacement chemicals and other types of alternatives can help avoid regrettable substitutes.

Any potential less-toxic alternative for use in tires would need to be tested for multiple characteristics before being deployed. A chemical alternative to 6PPD would have to be compatible with other tire materials, including rubber, the manufacturing process, and the vulcanization process and provide protection from ozone and oxygen for the life of the tire.

Potential alternatives to 6PPD in tires would need to meet relevant regulatory requirements to ultimately be brought to market. Chemicals that will be entered into commerce in the United States are regulated by USEPA under the TSCA. Under TSCA, USEPA “…evaluates potential risks from new and existing chemicals and acts to address any unreasonable risks chemicals may have on human health and the environment” (USEPA 2023c). New tires are also regulated for safety and performance by the Department of Transportation National Highway Traffic Safety Administration under the Federal Motor Vehicle Safety Standards.

6.2.1 Potential 6PPD Alternatives

Multiple recent and ongoing efforts address the identification of potential alternatives to 6PPD in tires. The examples below are not an exhaustive list:

California’s Safer Consumer Products Program**:** California’s DTSC began regulating 6PPD in motor vehicles tires through the Safer Consumer Products Program on October 1, 2023. DTSC included a section on potential alternatives to 6PPD as part of its Priority Product Report and on its website, which also discusses reducing the formation of TRWP and the release of 6PPDq via other methods. These include coatings to prevent ozone from reaching tires, airless/nonpneumatic tires, and spring tires. The DTSC regulations require each tire manufacturer to conduct an alternatives analysis in order to continue selling tires in California. In their alternatives analyses, tire manufacturers are required to analyze and compare the hazards and adverse environmental impacts of potential alternatives to 6PPD. The reports are required to evaluate the benefits and tradeoffs of replacing 6PPD. This process leverages the technical expertise of the tire manufacturers and enables them to meet vehicle safety and consumer product safety requirements while providing a rigorous, transparent, and scientific framework for evaluating and comparing potential alternatives to 6PPD. The tire manufacturers' preliminary AAs were submitted on March 29, 2024; these reports can be viewed here. This submittal will be followed by a more in-depth analysis of several promising alternatives. Final alternatives analysis reports are due in mid-2025, but DTSC may grant requests for extensions of the submittal deadline to a later date. Many of the proposed alternatives are other PPD chemicals; although, some companies propose other types of chemicals, such as specialized graphene and lignin.

Washington's 6PPD Action Plan and Safer Products for Washington program: Washington State is developing a statewide action plan, funding research to fill in data gaps, conducting an AA to assess other potential tire anti-degradants, and developing specific data requirements and standards to assess the hazards of the alternatives. "Technical Memo: Assessment of Potential Hazards of 6PPD and Alternatives" (Washington State Department of Ecology 2021[2UEJGNJ2] Washington State Department of Ecology. 2021. "Technical Memo: Assessment of Potential Hazards of 6PPD and Alternatives." https://www.ezview.wa.gov/Portals/_1962/Documents/6ppd/6PPD%20Alternatives%20Technical%20Memo.pdf.) provides an overview of known toxicological hazards of chemicals that are or have been used as anti-degradants in tires. The Safer Products for Washington program, which aims to reduce toxic chemicals in consumer products, identified 6PPD as a priority chemical.

Collaborative Innovation Forum: Washington and California have both supported the "Collaborative Innovation Forum: Functional Substitutes to 6PPD in Tires" (Sustainable Chemistry Catalyst 2023[8F7X8M2J] Sustainable Chemistry Catalyst. 2023. "Collaborative Innovation Forum: Functional Substitutes to 6PPD in Tires. Meeting Report." https://static1.squarespace.com/static/633b3dd6649ed62926ed7271/t/63ee6cd15eb30a0fd4f0630d/1676569810601/6PPD-in-Tires-Innovation-Forum-Meeting-Report.pdf.), which is developing a road map for identifying safer alternatives to 6PPD.

University of California, Berkeley Study: A 2021 University of California, Berkeley study investigated alternative PPDs and several other options, including modification of 6PPD to prevent quinone formation, food preservatives, lignin-derived chemicals, and alternative rubber formulation, which would require less protection against ozone. The project did not evaluate the alternatives for their potential toxicity and viability for use in tires.

Flexsys and USDA: In April 2023, Flexsys, a major 6PPD manufacturer, and the U.S. Department of Agriculture (USDA) announced a Cooperative Research and Development Agreement to design and evaluate novel alternatives to 6PPD.

USEPA Small Business Innovation Research: USEPA is providing funding to support development and commercialization of rubber anti-degradant technologies for tires and other rubber products that are of lower concern for human health and the environment through the 2024 Small Business Innovation Research program.

USTMA and USGS: The USTMA announced in 2023 that it is partnering with the USGS on a research project to assess and refine methods of evaluating potential alternatives to 6PPD for use in tires. They are working to establish a new method for in vitro toxicity testing of alternatives to 6PPD through a Collaborative Research and Development Agreement.

The following case study describes another source control effort. It focuses on reducing copper in brake pads. This case study describes the partnerships formed for this effort and some of the challenges faced when addressing contamination through source control.

CASE STUDY: Source Control for Roadway Stormwater Pollutants

Stormwater pollutants from vehicles can be addressed through source control initiatives. Source control means reducing or removing the pollutant from its source, rather than treating or removing it once it is released. The following case study on copper brake pads demonstrates how states and industry can work with the USEPA to reduce stormwater pollutants.

Copper at elevated concentrations in stormwater runoff is highly toxic to fish and other aquatic organisms. Copper can interfere with a fish's sense of smell, thereby harming the ability of migratory species—especially salmon—to navigate to their spawning grounds and making them more vulnerable to predation. Other studies show that young salmon are especially vulnerable to the toxic effects of copper. Since the 1990s, states and municipalities have recognized that vehicle brake pads are a significant source of copper contamination in urban stormwater runoff. As they wear, brake pads release fine dust containing copper and other metals; this dust is deposited on roadways where stormwater can suspend and transport it to streams and other waterways.

To address the copper stormwater contamination problem, the states of California and Washington enacted legislation in 2010 to phase out the use of copper in vehicle brake pads and shoes by 2025. Washington adopted the “Better Brakes Law” (Chapter 70A.340 RCW) that phases out the sale of brake material containing copper exceeding 5% (by weight) by 2021 and requires a further reduction to no more than 0.5% (by weight) if low-copper alternatives are available. Similarly, in 2010 California adopted its Brake Pad Law (SB346) with the same deadline for reducing copper concentrations to no more than 5% (by weight) by 2021; California also set a 2025 deadline for limiting copper concentrations to no more than 0.5% (by weight).

Both statutes addressed the concern over finding suitable alternatives to copper brake pads by directing the state regulatory agencies to study alternatives and determine whether low-copper pads were available and whether extensions of the deadlines were needed. The statutes also addressed the problem of stranding inventories of copper brake pads exceeding limits by allowing manufacturers to sell their existing inventories of noncompliant materials after the deadlines.

Spurred by the laws in California and Washington, in January 2015 the Brake Manufacturers Council (BMC), Motor & Equipment Manufacturers Association (MEMA), USEPA, and the Environmental Council of the States signed a memorandum of agreement to reduce the use of copper and other materials in motor vehicle brake pads(“Memorandum of Understanding on Copper Mitigation in Watersheds and Waterways between U.S. Environmental Protection Agency and Motor & Equipment Manufacturers Association, Automotive Aftermarket Suppliers Association, Brake Manufacturers Council and Heavy Duty Manufacturers Association and Auto Care Association and Alliance of Automobile Manufacturers and Association of Global Automakers, Inc. and Truck and Engine Manufacturers Association and Environmental Council of the States” 2015[27XI297B] “Memorandum of Understanding on Copper Mitigation in Watersheds and Waterways between U.S. Environmental Protection Agency and Motor & Equipment Manufacturers Association, Automotive Aftermarket Suppliers Association, Brake Manufacturers Council and Heavy Duty Manufacturers Association and Auto Care Association and Alliance of Automobile Manufacturers and Association of Global Automakers, Inc. and Truck and Engine Manufacturers Association and Environmental Council of the States.” 2015. https://www.epa.gov/npdes/memorandum-understanding-copper-mitigation-watershed-and-waterways.). Specifically, the agreement calls for reducing copper in brake pads to less than 5% by weight in 2021 and no more than 0.5% by 2025. In addition to copper, this initiative reduces mercury, lead, cadmium, asbestiform fibers, and chromium-six salts in motor vehicle brake pads. The agreement also included guidance related to making and labeling friction-material packaging and products (Figure 6-1). The LeafMark™ certification marks shown in the figure are a visual representation of the allowable concentration of copper, selected other metals, and asbestiform fibers in brake pads for each environmental compliance level (A, B, or N). The LeafMark™ certification mark is owned by MEMA and BMC and is not in any way affiliated with USEPA.

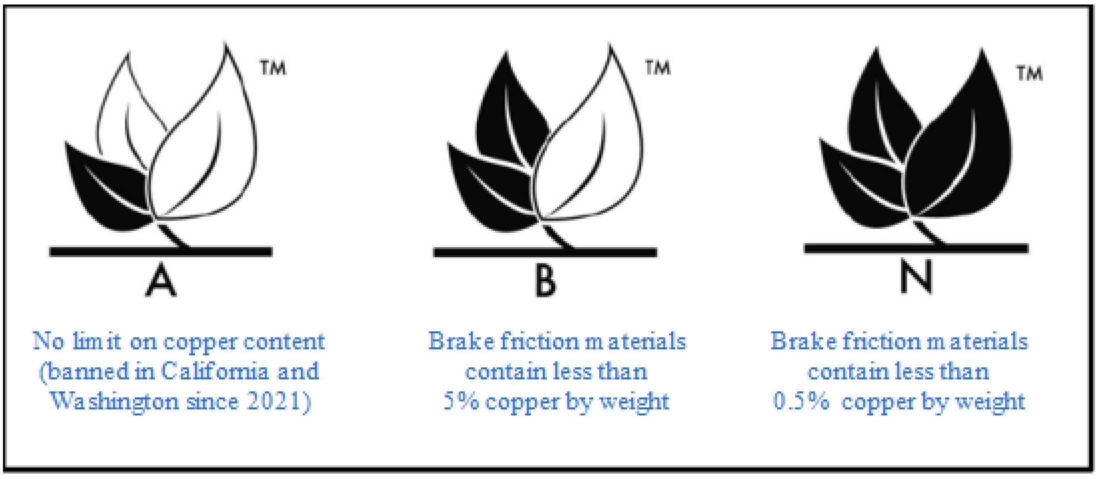


Figure 6-1. LeafMark™ label symbols for friction-material packaging.

Source: LeafMark™ used with permission from MEMA.

In a 2022 report to the legislature, the California regulatory agencies reported that more than 60% of brake pads on the market contained less than 0.5% copper (by weight). The report estimated this led to a 28% decrease in copper entering urban stormwater runoff.

6.2.2 Hazard Assessment

A technical memorandum released in November 2021 from WA Ecology under the direction of the Washington State Legislature evaluated the known hazards of several potential alternatives, including several other PPDs. Although some potential alternatives were identified with lower hazard than 6PPD, at the time of the report none of the alternatives had been tested for toxicity to coho salmon. In addition, the suitability of the alternatives from a performance perspective compared to 6PPD was questioned in comments by industry members.

6.2.3 Hazard Criteria

No state or federal regulations currently specify toxicity criteria for potential alternatives to 6PPD, and this lack of regulatory certainty may hinder the development of alternatives to 6PPD. In an effort to address this problem, WA Ecology has released the hazard criteria that they will be using to define "safer" for their AA. The hazard criteria guidance uses the Safer Products for Washington criteria, which includes several human health and environmental health criteria like carcinogenicity, reproductive or developmental toxicity, skin or respiratory sensitization, acute or chronic aquatic toxicity, and bioaccumulation. In addition to these criteria, WA Ecology's guidance includes additional aquatic toxicity criteria. First, to be considered a safer alternative to 6PPD, toxicity testing must be performed on coho salmon, rainbow trout, and two other trophic levels of test organisms such as a forage fish or macroinvertebrates. This testing must be done for alternative chemicals and their degradants after exposure to ozone. Since it is known that these chemicals will find their way into salmon-bearing streams, WA Ecology has also set an upper limit on the toxicity of these potential alternatives; the LC_{50}, must be greater than 0.1 mg/L (WA Ecology, n.d.[IHA5X6FP] WA Ecology. n.d. "6PPD - Washington State Department of Ecology." Accessed July 25, 2024. https://ecology.wa.gov/waste-toxics/reducing-toxic-chemicals/addressing-priority-toxic-chemicals/6ppd.).

6.3 Mitigation Practices

This section describes many efforts to understand how to mitigate the effects of 6PPD-q on the environment by preventing, treating, or managing 6PPD-q before it causes negative environmental impacts. Mitigation actions include pollution prevention efforts and control measures for stormwater and air quality mitigation.

6.3.1 Pollution Prevention

USEPA (1999) provides a universal reference on pollution prevention, including a description of a multi-component program that can be implemented to prevent pollutants from entering the environment or reaching sensitive receptors. Implemented actions could involve physically separating pollution sources from receiving waters and/or managing activities that are pollution sources. Some entities, such as WA Ecology, refer to this type of mitigation as source control. The Washington State Stormwater Management Manuals define source control measures as: "A structure or operation intended to prevent pollutants from coming into contact with stormwater through physical separation of areas or careful management of activities that are sources of pollutants."

The following information describes the current state of knowledge on the predicted potential pollution prevention measures that could be used to mitigate 6PPD-q in stormwater. This information is provided for general information and is not intended to replace site-specific evaluation of the appropriateness and feasibility of these or any other potential pollution prevention measures.

6.3.1.1 Driver Behavior

Driver behavior has a direct impact on the generation rate of TRWP. Frequent or abrupt acceleration and braking, as well as sharp high-speed turns can all increase tire wear rate (Zhang et al. 2024[V4RZKMVQ] Zhang, Qijun, Tiange Fang, Zhengyu Men, Ning Wei, Jianfei Peng, Tianqiang Du, Xinfeng Zhang, Yao Ma, Lin Wu, and Hongjun Mao. 2024. "Direct Measurement of Brake and Tire Wear Particles Based on Real-World Driving Conditions." Science of the Total Environment 906:167764. https://doi.org/10.1016/j.scitotenv.2023.167764.). Proper tire inflation also plays a role in the wear rate of passenger vehicle and heavy truck and bus tires. Research by Verschoor and de Valk (Verschoor and De Valk 2018[Z9893S5Z] Verschoor, A.J., and E. De Valk. 2018. “Potential Measures against Microplastic Emissions to Water.” Rijksinstituut voor Volksgezondheid en Milieu. https://rivm.openrepository.com/rivm/handle/10029/622058, DOI:10.21945/RIVM-2017-0193.) indicate that TRWP emissions could potentially be reduced by 14% through the use of tire pressure monitors. Improper vehicle suspension alignment can also increase tire wear rates. Education regarding driver practices and vehicle maintenance can reduce the generation rate of TRWPs (AcuTread 2017[TTV33B74] AcuTread. 2017. “Tire Wear | AcuTread Tire Service | Retreading Manufacturers.” AcuTread (blog). February 28, 2017. https://acutread.com/resources/post/factors-influence-tire-wear/.), which may reduce 6PPD-q in the environment.

The “Puget Sound Starts Here” campaign (September–October 2023) was an effort in WA State to cultivate more awareness over how proper tire care can reduce 6PPD-q in stormwater. The campaign used the Terry the Tire mascot as an attention grabber, with message recall, videos, and social media posts all used to show how easy it is to check and inflate your tires. Figure 6-2 presents an example of how Terry the Tire was used in this campaign.

Figure 6-2. Example of how Terry the Tire is used in the “Puget Sound Starts Here” campaign.

6.3.1.2 *Driving Alternatives*

According to U.S. Department of Energy statistics from 2020, 75% of people in the United States drive a personal vehicle to work, 9% carpool in a personal vehicle, 7% work from home, 5% take public transit, 3% walk, and 1% bike to work (Center for Sustainable Systems, University of Michigan 2023[ZD76DM9U] Center for Sustainable Systems, University of Michigan. 2023. “Personal Transportation Factsheet.” Center for Sustainable Systems. July 2023. https://css.umich.edu/publications/factsheets/mobility/personal-transportation-factsheet.). Increasing transportation options and reducing barriers to accessing those options reduces TRWP pollution in the environment through the reduced use of personal vehicles. Additional alternatives to driving personal vehicles include increased telework options and increasing the number of walkable and accessible communities.

6.3.1.3 *Vehicle Design*

Vehicle characteristics that have an impact on tire wear include mass, load and load distribution, type and condition of suspension, available torque, and drive wheel location (Robbins and Tran 2015[R78QJLSP] Robbins, Mary M., and Nam Tran. 2015. “Literature Review: The Impact of Pavement Roughness on Vehicle Operating Costs.” NCAT Report 15-02. Auburn University, Auburn, Alabama: National Center for Asphalt Technology.). (See also USTMA for additional information.)

The average electric vehicle is heavier due to the weight of the batteries and has higher torque than its gas-powered counterpart (Liu et al. 2021[XDW2JS3N] Liu, Ye, Haibo Chen, Jianbing Gao, Ying Li, Kaushali Dave, Junyan Chen, Matteo Federici, and Guido Perricone. 2021. “Comparative Analysis of Non-Exhaust Airborne Particles from Electric and Internal Combustion Engine Vehicles.” Journal of Hazardous Materials 420:126626. https://doi.org/10.1016/j.jhazmat.2021.126626.). Though electric vehicles are seen as a promising alternative for climate change and some air pollution mitigation, it is unclear whether electric vehicles will result in increased or decreased tire wear (OECD 2021[85YRE5NG] OECD. 2021. “Mitigation Technologies and Best Practices.” In Policies to Reduce Microplastics Pollution in Water. OECD. https://doi.org/10.1787/156bdfa5-en.; Liu et al. 2021[XDW2JS3N] Liu, Ye, Haibo Chen, Jianbing Gao, Ying Li, Kaushali Dave, Junyan Chen, Matteo Federici, and Guido Perricone. 2021. “Comparative Analysis of Non-Exhaust Airborne Particles from Electric and Internal Combustion Engine Vehicles.” Journal of Hazardous Materials 420:126626. https://doi.org/10.1016/j.jhazmat.2021.126626.). How electric vehicle technologies affect tire wear is a complex and often vehicle-specific issue. It is unknown whether there are current efforts underway to reduce tire wear through modification of vehicle load distribution, type and condition of suspension, or drive wheel location.

Several companies are developing devices to capture TRWP as they are generated. These include The Tyre Collective, GelbKo, and Nexen’s Pureback tire. Currently, none of these broader types of collection techniques are commercially available, and the extent to which they would reduce 6PPD and 6PPD-q release to the environment remains to be seen.

6.3.1.4 *Road Surfaces*

Road surface composition could affect tire wear, and the roughness and frictional characteristics of a paved surface might play an important role in tire wear. An improvement in roughness was found in asphalt rubber–asphaltic concrete friction courses over Portland cement concrete, resulting in reduced tire wear (Allen, Alexandrova, and Kaloush 2006[P4VNFFZD] Allen, Jonathan O., Olga Alexandrova, and Kamil E. Kaloush. 2006. “Tire Wear Emissions for Asphalt Rubber and Portland Cement Concrete Pavement Surfaces.” Arizona State University. https://azdot.gov/sites/default/files/2019/05/tire-wear-emissions-for-asphalt-rubber-portland-cement-concrete-April2006.pdf.). Nedrich (Nedrich 2022[7LRY36T6] Nedrich, Sara. 2022. Preliminary Investigation of the Occurrence of 6PPD-Quinone in Michigan’s Surface Water. https://doi.org/10.13140/RG.2.2.34478.59204.) compared 6PPD-q concentrations in surface water and puddle samples from rubber-modified asphalt (RMA) and traditional asphalt. The results from surface water samples taken from RMA road runoff locations were nondetect for 6PPD-q. The results from puddle samples on top of RMA and traditional asphalt contained similar concentrations. These results indicate that RMA might not be a direct source of 6PPD-q, although more research is needed to confirm. In another study, researchers found that RMA can serve as sorbents for 6PPD-q (Lokesh et al. 2023[LBXMIT5W] Lokesh, Srinidhi, Siththarththan Arunthavabalan, Elie Hajj, Edgard Hitti, and Yu Yang. 2023. “Investigation of 6PPD-Quinone in Rubberized Asphalt Concrete Mixtures.” ACS Environmental Au, July. https://doi.org/10.1021/acsenvironau.3c00023.).

Porous pavement has been found to improve water quality from arterial road runoff ([http://zotpress items=”{4911552:CF43N7NF}” style=”chicago-author-date”]; Holzer and Lindbo 2018[YE2TKX83] Holzer, Katie, and Torrey Lindbo. 2018. “Pervious Pavement Pollutant Study.” Presented at the Lower Willamette River Toxics Reduction Meeting, January 31. https://gaftp.epa.gov/region10/columbiariver/WWTRP/Meeting-2018-01-31/gresham-pervious-pavement-pollutant-study.pdf.), to remove the majority of TRWP mass, and to remove a significant portion of 6PPD-q from stormwater (Mitchell and Jayakaran 2024[TKDFS24E] Mitchell, Chelsea J., and Anand D. Jayakaran. 2024. “Mitigating Tire Wear Particles and Tire Additive Chemicals in Stormwater with Permeable Pavements.” Science of the Total Environment 908 (January):168236. https://doi.org/10.1016/j.scitotenv.2023.168236.).

6.3.1.5 Traffic Management

The design of the road itself impacts driving characteristics and tire wear. Reducing torque and friction, which are actions that contribute to tire wear, is the goal of traffic management as a mitigation effort. Actions to achieve this might include minimizing the need for high speeds, sharp turns, and reducing the frequency of acceleration and deceleration. Roundabouts and syncing up stop lights to increase traffic flow could also reduce TRWPs, so long as harsh braking and acceleration are avoided (Liu et al. 2021[XDW2JS3N] Liu, Ye, Haibo Chen, Jianbing Gao, Ying Li, Kaushali Dave, Junyan Chen, Matteo Federici, and Guido Perricone. 2021. “Comparative Analysis of Non-Exhaust Airborne Particles from Electric and Internal Combustion Engine Vehicles.” Journal of Hazardous Materials 420:126626. https://doi.org/10.1016/j.jhazmat.2021.126626.; Tonegawa and Sasaki 2021[9NME6IST] Tonegawa, Yoshio, and Sousuke Sasaki. 2021. “Development of Tire-Wear Particle Emission Measurements for Passenger Vehicles.” Emission Control Science and Technology 7 (1): 56–62.

https://doi.org/10.1007/s40825-020-00181-z.; Feißel et al. 2024[L8SQWPUC] Feißel, Toni, Miles Kunze, David Hesse, Valentin Ivanov, Klaus Augsburg, and Sebastian Gramstat. 2024. "On-Road Vehicle Measurement of Tire Wear Particle Emissions and Approach for Emission Prediction." Tire Science and Technology 52 (1): 2–14. https://doi.org/10.2346/tire.22.21024.).

6.3.1.6 *Street Sweeping and Other Road Maintenance Activities*

The effectiveness of street sweeping for controlling TRWPs and potentially 6PPD-q is uncertain. Based on a literature review, a WA Ecology report suggested that street sweeping has a high potential effectiveness in capturing TRWP (Navickis-Brasch et al. 2022[MT6MFFH8] Navickis-Brasch, Aimee, Mark Maurer, Taylor Hoffman-Ballard, Susan Bator, and Jerry Diamond. 2022. "Stormwater Treatment of Tire Contaminants Best Management Practices Effectiveness." https://fortress.wa.gov/ecy/ezshare/wq/Permits/Flare/2019SWMMWW/Content/Resources/DocsForDownload/2022_SWTreatmentOfTireContaminants-BMPEffectiveness.pdf.). The effectiveness of street sweeping depends on its efficiency in collecting various particle sizes, the frequency of street sweeping and timing relative to rain events, the type of street sweeping equipment used, and other impervious surfaces downwind of the road (Evergreen StormH20 2023). Studies to assess the effectiveness of street sweeping are underway, including a paired watershed study from the Stormwater Action Monitoring Program in Washington State.

Reducing road roughness (fewer bumps, potholes, etc.) through regular maintenance can result in reduced tire wear (Robbins and Tran 2015[R78QJLSP] Robbins, Mary M., and Nam Tran. 2015. "Literature Review: The Impact of Pavement Roughness on Vehicle Operating Costs." NCAT Report 15-02. Auburn University, Auburn, Alabama: National Center for Asphalt Technology.). At the time this document was prepared, no studies that correlate a reduction in road roughness to less 6PPD-q in surface water were found, but a reduction in tire wear could result in less 6PPD-q reaching surface water.

6.3.2 Air Particulate Mitigation

TRWPs are suspended within the boundary layer of the tire (Kuraishi, Takizawa, and Tezduyar 2019[MJP3IDF9] Kuraishi, Takashi, Kenji Takizawa, and Tayfun E. Tezduyar. 2019. "Tire Aerodynamics with Actual Tire Geometry, Road Contact and Tire Deformation." Computational Mechanics 63 (6): 1165–85. https://doi.org/10.1007/s00466-018-1642-1.). A portion of these TRWPs are deposited onto the road, and a portion becomes airborne. The extent of transport of these airborne particles at or away from the road depends on many factors including the size of particles emitted, the number and type of vehicles on the road, the activity of vehicles on the road, local meteorology, and local terrain conditions (Baldauf et al. 2009[CHVB6EB8] Baldauf, Richard W., N. Watkins, D. Heist, C. Bailey, P. Rowley, and R. Shores. 2009. "Near-Road Air Quality Monitoring: Factors Affecting Network Design and Interpretation of Data." Air Quality, Atmosphere & Health 2 (1): 1–9. https://doi.org/10.1007/s11869-009-0028-0.; Wang et al. 2010[U9T8Q8YR] Wang, F., D.S. Chen, S.Y. Cheng, J.B. Li, M.J. Li, and Z.H. Ren. 2010. "Identification of Regional Atmospheric PM10 Transport Pathways Using HYSPLIT, MM5-CMAQ and Synoptic Pressure Pattern Analysis." Environmental Modelling & Software 25 (8): 927–34. https://doi.org/10.1016/j.envsoft.2010.02.004.). A recent study in Boston, Massachusetts, estimated that 12% of $PM_{2.5}$ consisted of TRWP at sites from the roadside to 100 m away (Matthaios et al. 2022[IN77R968] Matthaios, Vasileios N., Joy Lawrence, Marco A.G. Martins, Stephen T. Ferguson, Jack M. Wolfson, Roy M. Harrison, and Petros Koutrakis. 2022. "Quantifying Factors Affecting Contributions of Roadway Exhaust and Non-Exhaust Emissions to Ambient PM10–2.5 and PM2.5–0.2 Particles." Science of the Total Environment 835:155368. https://doi.org/10.1016/j.scitotenv.2022.155368.).

Studies have measured 6PPD-q in urban ambient air samples not located near roadways (Cao et al. 2022[VBAMJHA7] Cao, Guodong, Wei Wang, Jing Zhang, Pengfei Wu, Xingchen Zhao, Zhu Yang, Di Hu, and Zongwei Cai. 2022. "New Evidence of Rubber-Derived Quinones in Water, Air, and Soil." Environmental Science & Technology 56 (7): 4142–50. https://doi.org/10.1021/acs.est.1c07376.; Johannessen et al. 2022[RYBDCBV4] Johannessen, Cassandra, Amandeep Saini, Xianming Zhang, and Tom Harner. 2022. "Air Monitoring of Tire-Derived Chemicals in Global Megacities Using Passive Samplers." Environmental Pollution 314 (December):120206. https://doi.org/10.1016/j.envpol.2022.120206.; Zhang et al. 2022[G77DTKD6] Zhang, Yanhao, Caihong Xu, Wenfen Zhang, Zenghua Qi, Yuanyuan Song, Lin Zhu, Chuan Dong, Jianmin Chen, and Zongwei Cai. 2022. "p-Phenylenediamine Antioxidants in PM2.5: The Underestimated Urban Air Pollutants." Environmental Science & Technology 56 (11): 6914–21. https://doi.org/https://doi.org/10.1021/acs.est.1c04500.; Wang et al. 2022[TMV9VLRS] Wang, Wei, Guodong Cao, Jing Zhang, Pengfei Wu, Yanyan Chen, Zhifeng Chen, Zenghua Qi, Ruijin Li, Chuan Dong, and Zongwei Cai. 2022. "Beyond Substituted p-Phenylenediamine Antioxidants: Prevalence of Their Quinone Derivatives in PM2.5." Environmental Science & Technology, July, acs.est.2c02463. https://doi.org/10.1021/acs.est.2c02463.;

Wu, Venier, and Hites 2020[F7XN9GAC] Wu, Yan, Marta Venier, and Ronald A. Hites. 2020. “Broad Exposure of the North American Environment to Phenolic and Amino Antioxidants and to Ultraviolet Filters.” Environmental Science & Technology 54 (15): 9345–55. https://doi.org/10.1021/acs.est.0c04114.; Zhang et al. 2022[GHLGNCHV] Zhang, Ying-Jie, Ting-Ting Xu, Dong-Min Ye, Ze-Zhao Lin, Fei Wang, and Ying Guo. 2022. “Widespread N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine Quinone in Size-Fractioned Atmospheric Particles and Dust of Different Indoor Environments.” Environmental Science & Technology Letters 9 (5): 420–25. https://doi.org/https://doi.org/10.1021/acs.estlett.2c00193.; Wang et al. 2022[77EKBKUV] Wang, Wei, Guodong Cao, Jing Zhang, Zhifeng Chen, Chuan Dong, Jianmin Chen, and Zongwei Cai. 2022. “p-Phenylenediamine-Derived Quinones as New Contributors to the Oxidative Potential of Fine Particulate Matter.” Environmental Science & Technology Letters, August, acs.estlett.2c00484. https://doi.org/10.1021/acs.estlett.2c00484.) and along transects away from the road (Olubusoye et al. 2023[R8HSVPUG] Olubusoye, Boluwatife S., James V. Cizdziel, Matthew Bee, Matthew T. Moore, Marco Pineda, Viviane Yargeau, and Erin R. Bennett. 2023. “Toxic Tire Wear Compounds (6PPD-Q and 4-ADPA) Detected in Airborne Particulate Matter Along a Highway in Mississippi, USA.” Bulletin of Environmental Contamination and Toxicology 111 (6): 68. https://doi.org/10.1007/s00128-023-03820-7.). Because TRWPs containing 6PPD-q have been identified in airborne particulate matter samples collected away from the road, a holistic 6PPD-q mitigation strategy would need to target both air particulates and stormwater runoff.

Roadside vegetation and solid structures (for example, noise walls, fences) can be used to mitigate air pollution near the road. Some of this reduction is through dilution, and some is the result of the forms and characteristics of vegetation that can capture and remove airborne particles. Solid structures located adjacent to roadways, such as noise barriers or K-rail barriers, can inhibit air flow away from the roadway and increase the deposition of larger TRWPs, thus decreasing transport of TRWPs that may contain 6PPD-q (Baldauf et al. 2008[5F9IGYHU] Baldauf, R., E. Thoma, A. Khlystov, V. Isakov, G. Bowker, T. Long, and R. Snow. 2008. “Impacts of Noise Barriers on Near-Road Air Quality.” Atmospheric Environment 42 (32): 7502–7. https://doi.org/10.1016/j.atmosenv.2008.05.051.; Gallagher et al. 2015[I3SXYRM3] Gallagher, John, Richard Baldauf, Christina H. Fuller, Prashant Kumar, Laurence W. Gill, and Aonghus McNabola. 2015. “Passive Methods for Improving Air Quality in the Built Environment: A Review of Porous and Solid Barriers.” Atmospheric Environment 120:61–70. https://doi.org/10.1016/j.atmosenv.2015.08.075.; Baldauf et al. 2016[JF4ZB7DP] Baldauf, Richard W., Vlad Isakov, Parikshit Deshmukh, Akula Venkatram, Bo Yang, and K. Max Zhang. 2016. “Influence of Solid Noise Barriers on Near-Road and on-Road Air Quality.” Atmospheric Environment 129:265–76. https://doi.org/10.1016/j.atmosenv.2016.01.025.). Studies on K-rail barriers are limited, and to have this effect they must be next to the travel lane. Particles across a range of sizes, from larger coarse particulate matter to small nano-size particles, can also be removed by impaction and diffusion onto vegetation surfaces. These particles typically remain on the vegetation until removal by precipitation or as debris from falling leaves or needles. Certain vegetation characteristics can have positive effects, reducing the number of particles by 50% or more; however other vegetation characteristics (that is, highly porous, gaps between trees, high canopy trees) can lead to increased air pollution concentrations near the road (Baldauf 2017[JR7YD4FW] Baldauf, Richard W. 2017. “Roadside Vegetation Design Characteristics That Can Improve Local, near-Road Air Quality.” Transportation Research Part D: Transport and Environment 52:354–61. https://doi.org/10.1016/j.trd.2017.03.013.; Abhijith et al. 2017[CIIV2BTG] Abhijith, K.V., Prashant Kumar, John Gallagher, Aonghus McNabola, Richard Baldauf, Francesco Pilla, Brian Broderick, Silvana Di Sabatino, and Beatrice Pulvirenti. 2017. “Air Pollution Abatement Performances of Green Infrastructure in Open Road and Built-up Street Canyon Environments—A Review.” Atmospheric Environment 162:71–86. https://doi.org/10.1016/j.atmosenv.2017.05.014.; Tiwari et al. 2019[A2URNURS] Tiwari, Arvind, Prashant Kumar, Richard Baldauf, K. Max Zhang, Francesco Pilla, Silvana Di Sabatino, Erika Brattich, and Beatrice Pulvirenti. 2019. “Considerations for Evaluating Green Infrastructure Impacts in Microscale and Macroscale Air Pollution Dispersion Models.” Science of the Total Environment 672:410–26. https://doi.org/10.1016/j.scitotenv.2019.03.350.; Deshmukh et al. 2019[AZD7J8VP] Deshmukh, Parikshit, Vlad Isakov, Akula Venkatram, Bo Yang, K. Max Zhang, Russell Logan, and Richard Baldauf. 2019. “The Effects of Roadside Vegetation Characteristics on Local, near-Road Air Quality.” Air Quality, Atmosphere, & Health 12 (March):259–70. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7339705/.). “Recommendations for Constructing Roadside Vegetation Barriers to Improve Near-Road Air Quality” describes the characteristics of vegetation needed to achieve air pollution control and the characteristics to avoid (Baldauf 2016[I5U5RA8E] Baldauf, Richard W. 2016. “Recommendations for Constructing Roadside Vegetation Barriers to Improve Near-Road Air Quality.” 321772. https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&dirEntryId=321772&simpleSearch=1&searchAll=Recommendations+for+constructing+roadside+vegetation+barriers+to+improve+near+road+air+quality.). Placing properly designed vegetation and solid structures along the roadside may help capture airborne 6PPD-q–containing tire particles at the roadside that can be treated using the stormwater runoff mitigation strategies described in the next section. This could prevent transport of 6PPD-q over large distances that will require treatment at the watershed level rather than focused on the roadside (Deshmukh et al. 2019[AZD7J8VP] Deshmukh, Parikshit, Vlad Isakov, Akula Venkatram, Bo Yang, K. Max Zhang, Russell Logan, and Richard Baldauf. 2019. “The Effects of Roadside Vegetation Characteristics on Local, near-Road Air Quality.” Air Quality, Atmosphere, & Health 12 (March):259–70. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7339705/.).

Beyond mitigating for 6PPD-q, implementing air particulate mitigation strategies could lead to co-benefits or multiple environmental and social benefits. Communities near roadways are disproportionally lower-income, nonwhite, and often experience disproportionate environmental harms (Rowangould 2013[9KKD6N4U] Rowangould, G.M. 2013. “A Census of the US Near-Roadway Population: Public Health and Environmental Justice Considerations.” Transportation Research, Part D: Transport and Environment 2013 (25): 59–67. https://doi.org/10.1016/j.trd.2013.08.003.; Antonczak et al. 2023[IETZJYHC] Antonczak, Brittany, Tammy M. Thompson, Mindi W. DePaola, and Gregory Rowangould. 2023. “2020 Near-Roadway Population Census, Traffic Exposure and Equity in the United States.” Transportation Research Part D: Transport and Environment 125 (December):103965. https://doi.org/10.1016/j.trd.2023.103965.). Air particulate mitigation could reduce airborne 6PPD-q and address existing environmental justice concerns (Tian, Xue, and Barzyk 2013[JKKV3HH3] Tian, Nancy, Jianping Xue, and Timothy M Barzyk. 2013. “Evaluating Socioeconomic and Racial Differences in Traffic-Related Metrics in the United States Using a GIS Approach.” Journal of Exposure Science & Environmental Epidemiology 23 (2): 215–22. https://doi.org/10.1038/jes.2012.83.) . These mitigation strategies could also reduce noise pollution and additional toxics in the environment (USEPA 2017[DPMSMEZ9] USEPA. 2017. “Living Close to Roadways: Health Concerns and Mitigation Strategies.” Overviews and Factsheets. January 10, 2017. https://www.epa.gov/sciencematters/living-close-roadways-health-concerns-and-mitigation-strategies.). Installing roadside vegetation could also reduce the urban heat island effect, which is a climate change mitigation and adaptation measure (USEPA 2024[2P8GQ97U] USEPA. 2024. “Heat Islands and Equity.” July 16, 2024. https://www.epa.gov/heatislands/heat-islands-and-equity.).

CASE STUDIES: Roadside Green Infrastructure Characteristics that Benefit Air Quality, USEPA

The following three field studies provided by USEPA demonstrate how roadside green infrastructure can improve air quality. The strategies used in these studies to mitigate particulate matter could also be beneficial for 6PPD-q mitigation when combined with stormwater treatment methods, though this remains untested. These studies are ongoing and unpublished.

The first study was conducted at Kemeny Park in Detroit, Michigan. Roadside vegetation was planted along the boundary between Kemeny Park and a major highway (I-75) in Detroit. Particulate matter and other air pollutant measurements were collected before the planting and measurements are currently being collected as the vegetation grows. Lessons learned are that planting new vegetation for air quality benefits can be difficult and planting mature vegetation provides greater air quality benefits although mature vegetation also has a lower survivability rate and requires some spacing to allow growth. Air quality benefits can be achieved after 3–5 years of growth. To achieve air quality benefits right away, hedges and bushes, or a solid structure like a fence, are needed to get initial air quality benefits while trees and larger vegetation grow.

The second case study took place at Brookfield Elementary School in Oakland, California. Roadside vegetation was planted along the boundary of a school playground behind a noise barrier along a major highway (I-880) in Oakland. Particulate matter and other air pollutant measurements were collected before planting and data collection continues as the vegetation grows. Lessons learned include the following: planting next to an existing noise barrier provides immediate air quality benefits from the solid wall, and these benefits increase as the vegetation grows. The case study highlights the need to adequately assess soil quality and provide stormwater management infrastructure simultaneously given the often harsh conditions present near large highways.

A third field study was conducted in the San Francisco Bay area. The study compared air quality downwind of a large highway and assessed how particulate matter and other air pollution varied behind different vegetation characteristics. Lessons learned include the following: vegetation must have low porosity, and vegetation must have coverage from the ground to the top of the canopy to achieve air quality benefits. Gaps in the vegetation, along with high-porosity bushes and trees, can actually lead to increased downwind air pollution levels (Deshmukh et al. 2019[AZD7J8VP] Deshmukh, Parikshit, Vlad Isakov, Akula Venkatram, Bo Yang, K. Max Zhang, Russell Logan, and Richard Baldauf. 2019. “The Effects of Roadside Vegetation Characteristics on Local, near-Road Air Quality.” Air Quality, Atmosphere, & Health 12 (March):259–70.

https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7339705/.).

The following case studies describe how vegetation, which is a green infrastructure feature, improves air quality. Field studies like these could be applied and tested to inform 6PPD-q mitigation.

6.3.3 Stormwater Runoff Mitigation: Stormwater Control Measures

Stormwater runoff can be defined as rain or snow melt that flows over the land surface rather than infiltrating into the subsurface. When flowing over impervious surfaces like paved streets, parking lots, and rooftops, runoff picks up numerous pollutants, including 6PPD-q. If left untreated, runoff can transport those pollutants into streams and other waterways, degrading water quality. Stormwater control measures, known as SCMs, are helpful tools to slow the flow of runoff and remove pollutants. SCMs function by capturing runoff and releasing it through natural processes (such as infiltration into the ground, evaporation, or evapotranspiration) and/or treating runoff as it flows through soils or vegetation prior to exiting stormwater facilities. Some entities refer to SCMs as BMPs. This document will use the term SCM for consistency, except when referring to a source document that uses the term BMP. Note that different entities use a variety of terminology for SCMs that filter and absorb stormwater, such as green infrastructure, green stormwater infrastructure, low-impact development, or nature-based solutions.

Multiple scientific publications point to bioretention, which refers to an SCM that infiltrates stormwater runoff into soil media, as an SCM that can reduce toxicity in stormwater, thus preventing acute mortality to coho salmon (Spromberg et al. 2016[GI97QYN4] Spromberg, Julann A., David H. Baldwin, Steven E. Damm, Jenifer K. McIntyre, Michael Huff, Catherine A. Sloan, Bernadita F. Anulacion, Jay W. Davis, and Nathaniel L. Scholz. 2016. “Coho Salmon Spawner Mortality in Western US Urban Watersheds: Bioinfiltration Prevents Lethal Storm Water Impacts.” Journal of Applied Ecology 53 (2): 398–407. https://doi.org/https://doi.org/10.1111/1365-2664.12534.; McIntyre et al. 2021[MVL2LKBM] McIntyre, Jenifer K., Jasmine Prat, James Cameron, Jillian Wetzel, Emma Mudrock, Katherine T. Peter, Zhenyu Tian, et al. 2021. “Treading Water: Tire Wear Particle Leachate Recreates an Urban Runoff Mortality Syndrome in Coho but Not Chum Salmon.” Environmental Science & Technology 55 (17): 11767–74. https://doi.org/10.1021/acs.est.1c03569.; Rodgers et al. 2023[LZXSW5WM] Rodgers, Timothy F. M., Yanru Wang, Cassandra Humes, Matthew Jeronimo, Cassandra Johannessen, Sylvie Spraakman, Amanda Giang, and Rachel C. Scholes. 2023. “Bioretention Cells Provide a 10-Fold Reduction in 6PPD-Quinone Mass Loadings to Receiving Waters: Evidence from a Field Experiment and Modeling.” Environmental Science & Technology Letters, June. https://doi.org/10.1021/acs.estlett.3c00203.). Rodgers et al. (Rodgers et al. 2023[LZXSW5WM] Rodgers, Timothy F. M., Yanru Wang, Cassandra Humes, Matthew Jeronimo, Cassandra Johannessen, Sylvie Spraakman, Amanda Giang, and Rachel C. Scholes. 2023. “Bioretention Cells Provide a 10-Fold Reduction in 6PPD-Quinone Mass Loadings to Receiving Waters: Evidence from a Field Experiment and Modeling.” Environmental Science & Technology Letters, June. https://doi.org/10.1021/acs.estlett.3c00203.), concluded from a field experiment and modeling that bioretention cells provided a 10fold reduction in 6PPD-q mass loadings to receiving waters. Scientific and practical questions around bioretention remain, from design details to optimize performance to how to site bioretention SCMs. While bioretention may be a solution in some areas, other SCMs may be needed where bioretention is not feasible. This section documents ongoing projects to further investigate bioretention and projects investigating other SCMs for potential effectiveness in mitigating toxicity from 6PPD-q in stormwater.

6.3.3.1 Potential SCM Effectiveness: WA Ecology BMP Effectiveness Report

WA Ecology partnered with Osborn and Evergreen StormH2O to develop a literature review to assess different mitigation strategies and predict potential SCM effectiveness for 6PPD-q (Navickis-Brasch et al. 2022[MT6MFFH8] Navickis-Brasch, Aimee, Mark Maurer, Taylor Hoffman-Ballard, Susan Bator, and Jerry Diamond. 2022. “Stormwater Treatment of Tire Contaminants Best Management Practices Effectiveness.” https://fortress.wa.gov/ecy/ezshare/wq/Permits/Flare/2019SWMMWW/Content/Resources/DocsForDownload/2022_SWTreatmentOfTireContaminants-BMPEffectiveness.pdf.; Washington State Department of Ecology 2022[K2CG7KTE] Washington State Department of Ecology. 2022. “6PPD in Road Runoff Assessment and Mitigation Strategies.” 22-03–020. Olympia, Washington: Environmental Assessment and Water Quality Programs. https://apps.ecology.wa.gov/publications/documents/2203020.pdf.). The report evaluated currently published BMPs for presumed effectiveness at capturing and treating TRWPs, 6PPD, and 6PPD-q based on a literature review and the best judgment of subject matter experts (Table 6-1).

Table 6-1: Examples of BMPs and their predicted effectiveness, as hypothesized in the WA Ecology BMP Effectiveness Report

Ranking of Potential Effectiveness	**Example BMP**	**Category Definitions for Ranking Potential Effectiveness**
Flow and Treatment BMPs		
High	Bioretention, Infiltration Basins, Media Filter Drain, Dispersion	Dispersion, Infiltration, and some Biofiltration BMPs (that use bioretention soil media or compost) where the underlying soils meet soil suitability criteria, or BMPs that provide the treatment process sorption.
Medium	Sand Filter, Detention Ponds, Permeable Pavements	BMPs that provide sedimentation (removal dependent on size/detention time) or filtration (removal dependent on size of particles). May need a polishing layer/treatment train including sorption (for example, sand filter with zero valent iron layers).
Low	Perforated Stub-Out Connection, Vegetated Roofs, Tree Retention and Tree Planting	BMPs that do not provide infiltration, sorption, filtration, or sedimentation
Source Control BMPs		
High	BMPs for Streets and Highways, BMPs for Maintenance of Roadside Ditches	BMP separates a source (i.e., roadway, parking, etc.) from stormwater.
Medium	Education and Outreach Programs Related to 6PPD or 6PPD-q, Construction Wheel Wash	BMP partially separates 6PPD and 6PPD-q from stormwater (including education and outreach efforts); prevents 6PPD and 6PPD-q from entering stormwater from a minor source (i.e., traffic at a construction site).
Low	BMPs for Temporary Fruit Storage, BMPs for Railroad Yards	Unlikely to provide any measurable separation between 6PPD and stormwater.
Source: Stormwater Treatment of Tire Contaminants | Best Management Practices Effectiveness (Navickis-Brasch et al. 2022)		

Notes: BMPs=best management practices

6.3.3.2 Ongoing Research into SCMs for Mitigating Toxicity Related to 6PPD-q

Several research efforts are underway that test the effectiveness of SCMs at retaining and treating 6PPD-q. Some of these studies build off WA Ecology's effectiveness literature review (Navickis-Brasch et al. 2022[MT6MFFH8] Navickis-Brasch, Aimee, Mark Maurer, Taylor Hoffman-Ballard, Susan Bator, and Jerry Diamond. 2022. "Stormwater Treatment of Tire Contaminants Best Management Practices Effectiveness." https://fortress.wa.gov/ecy/ezshare/wq/Permits/Flare/2019SWMMWW/Content/Resources/DocsForDownload/2022_SWTreatmentOfTireContaminants-BMPEffectiveness.pdf.) and are seeking to verify and optimize the effectiveness of SCMs noted as having moderate to high potential effectiveness (Navickis-Brasch et al. 2022[MT6MFFH8] Navickis-Brasch, Aimee, Mark Maurer, Taylor Hoffman-Ballard, Susan Bator, and Jerry Diamond. 2022. "Stormwater Treatment of Tire Contaminants Best Management Practices Effectiveness." https://fortress.wa.gov/ecy/ezshare/wq/Permits/Flare/2019SWMMWW/Content/Resources/DocsForDownload/2022_SWTreatmentOfTireContaminants-BMPEffectiveness.pdf.). Other studies are investigating the effectiveness of new stormwater SCMs with different specifications or configurations. Ultimately, SCM effectiveness research helps describe several mitigation tools that could be applied depending on the location. Several examples of ongoing studies are described below, but this is not intended to be an exhaustive list.

6.3.3.2.1 6PPD SCM Effectiveness Research—WA Ecology

WA Ecology has contracted several BMP effectiveness studies supported by Washington State Legislative funds:

- The University of Washington–Tacoma has completed its study of various engineered and natural materials to gauge their effects on 6PPD-q in stormwater samples.

- King County is performing column tests with stormwater samples to help determine which mixtures of high-performance bioretention soil mixes (HPBSM), as defined in the WA Ecology Stormwater publications (Howie and Lubliner 2024[ZMESPTJ8] Howie, Douglas, and Brandi Lubliner. 2024. “Guidance on Using New High Performance Bioretention Soil Mixes.” Olympia, Washington: Washington State Department of Ecology, Water Quality Program. https://apps.ecology.wa.gov/publications/documents/2110023.pdf.) and Stormwater Manual (Washington State Department of Ecology 2018[8VMVK98Y] Washington State Department of Ecology. 2018. “Technical Guidance Manual for Evaluating Emerging Stormwater Treatment Technologies.” Washington State Department of Ecology. https://apps.ecology.wa.gov/publications/documents/1810038.pdf.), might be most effective at reducing 6PPD-q.

- Herrera Environmental Consultants, in collaboration with King County Environmental Lab (KCEL), is testing TAPE, or Technology Assessment Protocol-Ecology, treatment technologies via influent and effluent of stormwater samples while also developing field sampling protocols and comparing 6PPD-q analysis results across two laboratories (see case study below for more information).

- KCEL is working on a project to characterize stormwater in a mixed highway and residential area. The wide range of contaminants measured in this study includes 6PPD-q.

- Washington State University, in partnership with Evergreen StormH2O, is working to create a street-sweeping manual that will help stormwater permittees across Washington State create new or improve existing street-sweeping programs.

- Pierce County Public Works is examining the effectiveness of decant facilities and granular activated carbon at addressing 6PPD-q.

CASE STUDY: 6PPD-q in Highway Runoff, BMP Effectiveness, and Field Protocol Development

Supported by WA Ecology, Herrera Environmental Consultants (Herrera) is conducting 6PPD-q sampling at the I-5 Ship Canal Testing Facility and the Oregon Department of Transportation Stormwater Technology Testing Center to improve understanding of 6PPD-q in stormwater. Herrera is partnering with KCEL, which is conducting the laboratory analyses of more than 400 6PPD-q samples. This sampling occurs throughout “storm events,” or when it rains for at least one hour following a somewhat dry period. Contaminants like 6PPD-q can accumulate on roads when there is little rain and can then be flushed into stormwater during storm events and discharged into salmon-bearing streams. The proposed sampling will do the following:

- Help assess whether existing field-sampling protocols for 6PPD-q need to be refined, for example, with respect to the use of carboys, bottle types, and pump tubing material. To ensure that protocols are reliable in different conditions, Herrera will test these field protocols over three storm events.
- Characterize 6PPD-q in untreated highway runoff in Seattle and Portland. Stormwater characterization helps stormwater managers understand the full chemical profile of contaminants in runoff throughout a storm event, including assessing whether there is variability in when 6PPD-q concentrations are highest during the storm. This information is essential for managing and regulating 6PPD-q.
- Evaluate the ability of emerging stormwater treatment technologies (TAPE) to reduce 6PPD-q concentrations. Depending on the device, TAPE devices have been proven to reduce the concentrations of phosphorus, oil,

suspended solids, heavy metals, and other contaminants in stormwater. This study will test some of these implemented devices for their effectiveness with 6PPD-q treatment.

- Assess whether there are differences between the reported values of 6PPD-q between two different laboratories: KCEL and Manchester Environmental Lab. Laboratory methods are still being developed, so it is crucial to understand what might contribute to differences in how laboratories analyze samples.

All in all, this project is expected to improve understanding of 6PPD-q levels in runoff, assess whether existing and already implemented stormwater technologies can filter this emergent contaminant, and help improve field sampling protocols to ensure that samples intended for 6PPD-q testing remain viable and reliable.

The Snoqualmie Indian Tribe is assessing the effectiveness of floating treatment wetlands, native vegetation, and grassy swales. They are also characterizing a high-use parking lot.

6.3.3.2.2 Stormwater Action Monitoring Program—WA Ecology

The Stormwater Action Monitoring Program, which is permittee-driven, permittee-funded, and facilitated by WA Ecology, has five 6PPD projects funded by the 2022–2023 and 2023–2025 provisos granted to WA Ecology's Water Quality Program. These projects are in progress, and deliverables can be found on the Stormwater Action Monitoring—Effectiveness Studies webpage.

- Washington State University's "Longevity of Bioretention Depths for Preventing Acute Toxicity from Urban Stormwater Runoff," seeks to determine the efficacy of bioretention media over time.

- The City of Redmond seeks to study the benefits of street sweeping by evaluating receiving water conditions. This long-term project has, as of 2022, added parameters for 6PPD-q to its scope of study.

- Seattle Public Utilities, in collaboration with Herrera Environmental Consultants, is exploring the potential for reducing 6PPD-q by examining and characterizing street-sweeping loads from arterial roads in the City of Seattle, with study components including examining possible correlations between 6PPD-q and other stormwater contaminants as well as the characterization of particle size distribution, seasonality, and land-use differences.

- King County, in partnership with Whatcom County, is seeking to test HPBSM at a full-scale stormwater facility, building upon King County's HPBSM column bench study (Howie and Lubliner 2024) to test and monitor how HPBSM performs in the field.

- The City of Tacoma, in partnership with the University of Washington– Tacoma, Herrera Environmental Consultants, and Aspect Consulting are monitoring stormwater outfalls for CEC, including 6PPD-q, at 15 sites in the Puget Sound region.

6.3.3.2.3 Floating Treatment Wetland / Biomedia Modules to Reduce Stormwater Contaminants with a Focus on 6PPD-q—University of Washington

Funded by King County, this research project has used floating treatment wetlands as a vehicle for placing a tested biomedia mix into the affected waterbody at the point of stormwater entry (Seebacher, Pierce, and Turner 2023[AZ6MCQ8J] Seebacher, Lizbeth Ann, Brianna Pierce, and Rob Turner. 2023. "Floating Treatment Wetland and Biomedia Module for Stormwater Treatment and 6ppd Quinone Removal." https://doi.org/10.2139/ssrn.4471002.). Using a floating treatment wetlands / biomedia module planted with wetland species and a biomedia mix within and underneath, a mesocosm experiment resulted in 79% 6PPD-q reduction (255 ng/L to 53.5 ng/L) and 100% survival of juvenile coho after a 24hour exposure period with no symptoms of 6PPD-q toxicity. Foldvik et al. 2022[LQWXZHJA] Foldvik, Anders, Fedor Kryuchkov, Roar Sandodden, and Silvio Uhlig. 2022. "Acute Toxicity Testing of the Tire Rubber–Derived Chemical 6PPD-Quinone on Atlantic Salmon (Salmo Salar) and Brown Trout (Salmo Trutta)." Environmental Toxicology and Chemistry 41 (12): 3041–45.

https://doi.org/10.1002/etc.5487.This potential SCM would be considered a treatment facility and could be used at sites where other SCMs are not feasible or in addition to other SCMs to increase 6PPD-q removal. For more information, please see the floating wetland treatment webpage.

6.3.3.2.4 Other Relevant Stormwater Research

Addressing Stormwater Runoff with a Self-Contained Portable Treatment System (2023 Department of Transportation Small Business Innovation Research grants): Awardees will work to develop a mechanism to remove pollutants, including emerging contaminants such as 6PPD-q, from highway construction and urban stormwater runoff sources.

Development of On-Bridge Stormwater Treatment Practices (National Cooperative Highway Research Program): This project will develop on-bridge stormwater treatment applications for retrofitting bridges. 6PPD-q is among the analytes.

CASE STUDY: Mobile Biofiltration Unit—Nisqually Indian Tribe and Cedar Grove Compost

A pilot project by the Nisqually Tribe and partners has been testing a mobile biofiltration unit that is meant to filter harmful materials from stormwater at Ohop Creek in Washington. It collects stormwater from more than 13,000 square feet of roadway and filters it through layers of compost-based filtration media to remove toxic compounds. It also has an external polishing layer to remove phosphorous before the water is discharged to the wetlands near the creek. They first operated the unit in Summer 2022, and preliminary results from three rain events showed high effectiveness, reducing the 6PPD q levels low enough to not be acutely toxic to coho (greater than 90% reduction in 6PPD q concentrations). They are looking to conduct more sampling in the future with the goal of getting the system approved for use in projects across Washington.

Opportunities for Stormwater Retrofit (Washington Department of Transportation (WSDOT):

Projects include an emphasis on green infrastructure retrofits. One example is the Urban Stormwater Partnership—I-5 Ship-Canal Bridge Pilot in Seattle, which leverages partnerships to establish a multijurisdictional stormwater facility that treats high volumes of 6PPD-q and other pollutants, incorporates community-identified needs, and provides opportunities to research the effectiveness of 6PPD-q treatment.

Stormwater Management to Address Highway Runoff Toxicity Due to 6PPD-q from Tire Rubber ***(Transportation Pooled Fund Study):*** Project aims to equip departments of transportation with a targeted approach for effectively managing 6PPD-q in highway runoff and to provide regulatory agencies with a better understanding of department of transportation management options.

6.4 Remediation

Alternative chemicals and mitigation are the first line of preventive defenses against 6PPD-q in the environment. Remediation follows as a secondary tier of treatment strategies and as a long-term solution to treat 6PPD-q that is not captured by SCMs. The fate and transport of 6PPD-q in the environment is not well understood. Although 6PPD-q appears to have a short half-life in stormwater and in the aquatic environment (see Section 3: Properties of 6PPD and 6PPD-q), the propensity of 6PPD-q to sorb to organic matter in soil and sediments remains to be determined (see also Section 4.2: Soil and Section 4.3: Sediment).

The first step in determining if cleanup is necessary is identification of cleanup levels. These cleanup levels vary depending on the affected media, the constituent's toxicity to human and other receptors, and the likely exposure pathway of the receptor. See Section 7 (Policies, Regulations, and Laws) for how these cleanup levels are determined by regulatory agencies. The purpose of this section is to provide an overview of what data and information are needed to identify future remedial strategies if and when it becomes apparent that cleanup is necessary.

6.4.1 Inputs Needed in the Remedy Selection Process

A widely used framework for identifying a preferred remedy is the USEPA Remedial Investigation/Feasibility Study (RI/FS) process (Figure 6-3); most states have similar processes, albeit often with different terminology for certain steps or documents. Although 6PPD and 6PPD-q in the environment are not within the scope of the CERCLA, also known as Superfund, the programs developed under the CERCLA regulatory framework can be instructive. Tables 6-2 through 6-6 describe the steps of the RI/FS process and the current status of applying the remedial process to 6PPD-q given the limited data currently available regarding fate and transport and toxicity for the compound.

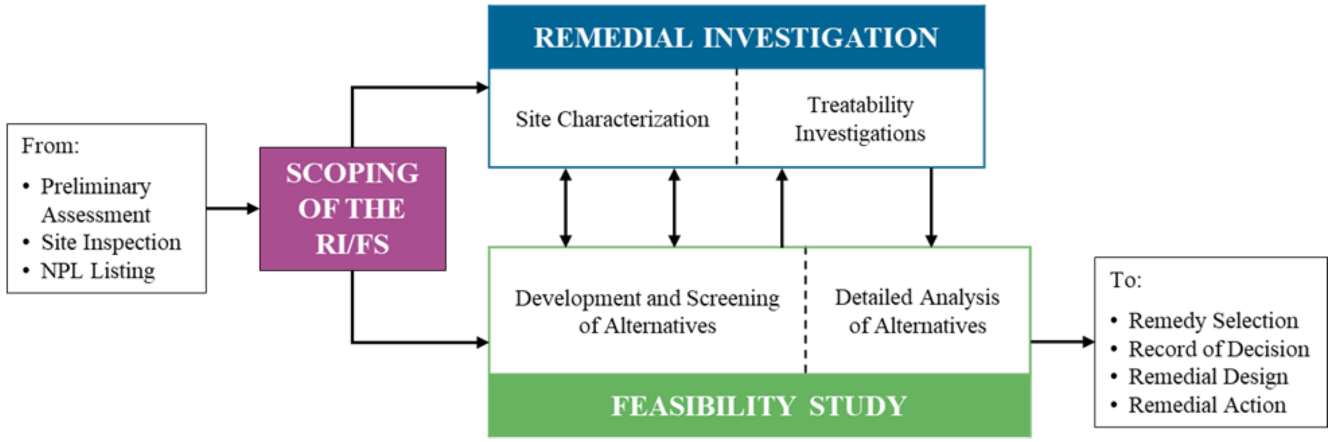


Figure 6-3. Simplified overview of the phased RI/FS process

Source: Adapted from USEPA (1988)

Table 6-2: Remedial Investigation Phase: Scoping

Step	Current Status and Notes
Collect and analyze existing data	Only limited data are currently available in many areas (see also: Section 4: Occurrence, Fate, Transport, and Exposure Pathways).
Identify initial project/operable unit, likely response scenarios, and remedial action objectives	Project area may be identified, based on limited data; likely response scenarios may be difficult to identify; and remedial action objectives may be difficult to identify, given the data gaps currently associated with human and ecological toxicity and persistence of 6PPD/6PPD-q in the environment.
State/federal ARAR identification	State or federal ARAR include media-specific and land use–related cleanup criteria (for example, MCLs, Eco-SSLs, or similar), which have yet to be developed for 6PPD/6PPD-q for human or ecological receptors.
Establish data quality objectives (DQOs)	DQOs may be difficult to establish, given the numerous data gaps (for example, toxicity, mobility, persistence, etc.)
Prepare project plans	See site characterization (Table 6-3) and treatability investigation (Table 6-4) below.

Notes: ARAR=applicable or relevant and appropriate requirements, Eco-SSLs=ecological soil screening levels, MCL=maximum contaminant levels

Table 6-3: Remedial Investigation Phase: Site Characterization

Step	Current Status and Notes
Conduct field investigation	Laboratory analysis of water, soil, sediment, and particulate samples is currently possible; however, sampling methods are not yet standardized for 6PPD-q.
Define nature and extent of contamination	Currently possible.
Identify federal and state chemical- and location-specific ARAR	State or federal ARAR include media-specific and land use–related cleanup criteria (for example, MCLs, Eco-SSLs, or similar criteria), which have yet to be developed for 6PPD/6PPD-q for human or ecological receptors.
Conduct baseline risk assessment	A baseline risk assessment may be difficult to perform due to the data gaps in toxicity, mobility, persistence, etc.

Notes: ARAR=applicable or relevant and appropriate requirements, Eco-SSLs=ecological soil screening levels, MCL=maximum contaminant levels

Table 6-4: Remedial Investigation Phase: Treatability Investigations

Step	Current Status and Notes
Perform bench or pilot treatability studies as necessary	Treatability studies will need to be conducted for all remediation technologies under consideration to evaluate their efficacy and cost-effectiveness relative to TRWPs, 6PPD, and/or 6PPD-q; current and future research related to SCMs may be informative (see also ITRC's Microplastics Guidance, Table 6-3(ITRC 2023); Remedy Selection for Contaminated Sediments (ITRC 2014[YN4LSVHV] ITRC. 2014. "Contaminated Sediments Remediation: Remedy Selection for Contaminated Sediments." August 2014. https://clu-in.org/download/contaminantfocus/sediments/Sediment-ITRC-CS-2.pdf.); Sediment Cap Chemical Isolation Guidance

Note: TRWPs=tire- and road-wear particles

Table 6-5: Feasibility Study Phase: Development and Screening of Alternatives

Step	Current Status and Notes
Identify potential treatment technologies containment/disposal requirements for residuals or untreated waste	Identify potential treatment and disposal technologies and complete an initial screen of technology types and process options to eliminate those that are clearly ineffective or unworkable at a site.
Screen technologies	Further evaluate process options based on effectiveness, implementability, and relative cost to select a representative process for each technology type.
Assemble technologies into cleanup alternatives	Multiple technologies may need to be assembled (for example, as a treatment train) to achieve applicable cleanup criteria.
Screen alternatives to reduce the number subject to detailed analysis	A typical range of alternatives evaluated at this step in the process is 5 to 10.
Identify action-specific ARARs	State or federal ARARs may include laws or regulations pertaining to the management of waste, land disposal restrictions, or other cleanup-related activities.

Notes: ARAR=applicable or relevant and appropriate requirements

Table 6-6: Feasibility Study Phase: Detailed Analysis of Alternatives

Step	Current Status and Notes

Analyze alternatives against the nine criteria used for Superfund projects or other, similar, sets of criteria applicable to non-Superfund remediation projects. The nine criteria below are part of the National Contingency Plan (40 CFR 300.430(e)(9)): <u>Threshold Criteria</u> 1. Overall protection of human health and the environment 2. Compliance with ARARs <u>Primary Balancing Criteria</u> 3. Long-term effectiveness and permanence 4. Reduction of toxicity, mobility, or volume 5. Short-term effectiveness 6. Implementability 7. Cost <u>Modifying Criteria</u> 8. State acceptance 9. Community acceptance	Evaluation of cleanup alternatives against the evaluation criteria (whether the nine criteria applicable to the CERCLA process or other federal or state criteria) depends on data and information that is generally not yet available but are areas of active or future research and development, as described above for the preceding steps. For example, the development of federal and state ARARs, specifically media- and location-specific cleanup levels, is necessarily dependent upon the outcomes of current and future research examining toxicity (in humans and other organisms) and fate and transport of TRWPs, 6PPD, and 6PPD-q in the environment. In addition, significant research, including bench-scale and pilot-scale studies, is needed to identify and develop treatment technologies or systems that are effective for these constituents. Evaluation of the community acceptance criterion may include community outreach efforts, including to communities with environmental justice concerns.
Analyze alternatives against other sets of criteria, for example, state sustainability criteria.	Evaluation of cleanup alternatives against state sustainability criteria is contingent in part on information specific to the technologies being evaluated (for example, quantity of greenhouse gases that will be emitted while implementing any given alternative).

Notes: ARAR=applicable or relevant and appropriate requirements, CERCLA=Comprehensive Environmental Response, Compensation, and Liability Act, CFR=Code of Federal Regulations, TWP=tire-wear particles

6.4.2 Cleanup Technologies: Recent Research

Current research efforts are generally focused on SCMs, but some of the technologies currently under development may eventually translate into remediation technologies. For example, a filtration medium deployed as part of a stormwater management and treatment program may be packed into a treatment vessel for groundwater remediation or can be used to treat wastewater generated during sediment dewatering. The SCM section describes current SCM technologies under research, including bioretention and infiltration basins.

6.4.3 Cleanup Technologies Development and Evaluation: Additional Resources

Existing ITRC guidance documents may provide additional information and remedy evaluation frameworks. Several are listed below:

- Microplastics (2023)—This report may provide a framework for evaluating approaches that may be effective for sample collection and analysis and capturing TRWP, given that TRWP are a type of microplastic (ITRC 2023).
- Stormwater Best Management Practices Performance Evaluation (2018)—This guidance provides details on post-construction stormwater SCM performance evaluation. The guidance is based on SCM life cycle processes from selection to long-term maintenance (ITRC 2018[MUH6ZPQV] ITRC. 2018. “Stormwater Best Management Practices Performance Evaluation.” 2018. https://stormwater-1.itrcweb.org/.).
- Remedy Selection for Contaminated Sediments (2014)—This guidance document is intended to assist decision-makers in identifying which contaminated sediment remedial technology is most favorable for a site based upon an evaluation of site-specific physical, sediment, contaminant, and land and waterway use characteristics. Any such evaluation must consider the demonstrated effectiveness of the technology relative to TRWP, 6PPD, and/or 6PPD-q (ITRC 2014[YN4LSVHV] ITRC. 2014. “Contaminated Sediments Remediation: Remedy Selection for Contaminated Sediments.” August 2014. https://clu-in.org/download/contaminantfocus/sediments/Sediment-ITRC-CS-2.pdf.).

- Other ITRC guidance documents may provide helpful tools such as frameworks for monitored natural attenuation that may be adapted to monitoring 6PPD-q in surface water, for the optimization of groundwater pump-and-treat systems or evaluation of in situ groundwater treatment technologies, and other steps in the evaluation of remediation processes. These documents are available on the ITRC website.

7 Policies, Regulations, and Laws

ITRC has prepared an overview of the current understanding of 6PPD-quinone (6PPD-q) sources, exposure, fate, transport, toxicity, alternatives, mitigation strategies, on-going research, and data needs. This section describes federal-level regulations, policies, and laws that might be considered by decision-makers from a variety of jurisdictions when addressing 6PPD and 6PPD-q. This section also provides several examples of how regulations, policies, and laws have been leveraged to take action on 6PPD.

The discussion below uses many federal-level laws to narrow the discussion of legal programs that might affect the potential future regulation of 6PPD, 6PPD-q, and tires. This section is not meant to definitively speak to any given entity's jurisdiction over an issue or decision. It also does not provide policy recommendations.

7.1 Tribal Treaty Rights

The following case study describes how tribal treaty rights come into play in Washington State. Federal, state, and local governments should understand how tribal treaty rights and legal precedents affect 6PPD affairs in their region.

CASE STUDY: Tribal Treaty Rights: Supreme Law of the Land

Treaties between the United States government and Tribal Nations are considered the "supreme law of the land" and should be interpreted as having the same legal status as federal statutes (US Department of the Interior 2021). Therefore, Treaty Rights expressly stated in Treaties must be recognized by state governments, and the federal government must uphold its Treaty obligations through federal actions.

For Tribal Nations in Washington State, the right to fish is an inherent right that has been affirmed through Treaty Rights and reaffirmed through court case decisions. By causing mortality in salmon, 6PPD and 6PPD-quinone directly threaten Tribal Treaty Rights. Salmon are significant to Tribal Nations for cultural practices, food sovereignty, community health, traditional knowledge, their way of life, and their identity as Salmon People (Columbia River Inter-Tribal Fish Commission, 2021). The Boldt Decision (also known as United States v. Washington, 1974) established that the Tribes are entitled to 50% of the fishing catch in their usual and accustomed fishing grounds (U&As) within WA State; additionally, the decision requires that the Tribes and WA State co-manage fisheries together (UW Gallagher Law Library, 2023). Because of this co-management status, the Tribes are important decision-makers in WA State. Over 50 additional court filings between 1974 – 2021 have expanded upon the Boldt Decision and have continued to reaffirm Tribal Treaty Rights.

Washington State's Centennial Accord is an example of how WA State holds government-to-government relation between Tribes and Washington State (WA State Governor's Office of Indian Affairs). In addition to the protocols defined in the Centennial Accord, there are several best practices that state governments can take when engaging and consulting Tribal Nations to honor Tribal Treaty Rights. Foremost, it is essential to recognize that each Tribal Nation holds unique customs, cultures, and governance systems. Characterizing the opinions and decisions of one or some Tribal Nations as that of all Tribes can lead to harmful consequences. Creating systems that support the co-production of knowledge can lead to the representation of multiple knowledge systems, which enrich decision making processes (University of Colorado Boulder). It is also essential to honor Tribal Data Sovereignty, which is the right of Tribal Nations to collect and own their own data and to consent to the use of that data by other parties (American Indian Health Commission for Washington State). Washington State agencies utilize the 30-60-90 day rule, where significant agency actions that will require attendance from Tribal partners are notified 90 days prior to the event, and then also re-notified 60 and 30 days before the event. Many state agencies also employ a Tribal Liaison, who often is a member of a Tribal Nation themselves. As a best practice, staff should work closely with their Tribal Liaison to determine the level of consultation and engagement appropriate for state actions.

For more information about the significance of 6PPD to Tribal Treaty Rights, see Section 1.3.3. Tribal Nations.

7.2 Toxic Substances Control Act (TSCA)

CASE STUDY: Example Activity Related to TSCA Authority

On November 2, 2023, USEPA approved a petition under section 21 of the TSCA that was filed on behalf of the Puyallup, Port Gamble S'Klallam, and Yurok Tribes. The petition asked the agency to create rules that forbade the production, use, distribution, and processing of 6PPD. In granting the petition, USEPA stated that "…while the agency will promptly commence an appropriate proceeding under TSCA Section 6(a), the agency cannot commit to a specific rulemaking timeframe or outcome." (USEPA 2023[4X7Q2I9W] USEPA. 2023. "Chemicals under the Toxic Substances Control Act (TSCA)." Collections and Lists. August 16, 2023. https://www.epa.gov/chemicals-under-tsca.) Further, USEPA indicated that it…

"…plans to take action to address the risk to the environment presented by 6PPD, and the degradant 6PPD-q through an advance notice of proposed rulemaking under TSCA section 6. EPA also plans to propose a rule under section 8(d) of TSCA to require manufacturers (including importers) of 6PPD to report certain lists and copies of unpublished health and safety studies to EPA."

The TSCA, as amended by the Frank R. Lautenberg Chemical Safety for the 21st Century Act, requires USEPA to evaluate potential risks from new and existing chemicals and acts to address any unreasonable risks chemicals may have on human health and the environment.

7.3 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

CERCLA established prohibitions and requirements concerning closed and abandoned hazardous waste sites, provided for liability of persons responsible for releases of hazardous waste at these sites, and established a trust fund to provide for cleanup when no responsible party could be identified. (USEPA 2022[DURCCUKN] USEPA. 2022. "Superfund: CERCLA Overview." U.S. Environmental Protection Agency. https://www.epa.gov/superfund/superfund-cercla-overview.). At this time, neither 6PPD-q, TWP, nor waste tire material have been identified as "hazardous waste," and are therefore not regulated under CERCLA.

7.4 Resource Conservation and Recovery Act (RCRA)

The RCRA establishes the framework for the proper management of hazardous and nonhazardous solid waste. States play a lead role in implementing these regulations. In absence of an approved state program, the federal requirements must be met by waste facilities (USEPA 2015[K9FCXZZ2] USEPA. 2015. "Resource Conservation and Recovery Act (RCRA) Overview." Other Policies and Guidance. August 18, 2015. https://www.epa.gov/rcra/resource-conservation-and-recovery-act-rcra-overview.).

Currently, data gaps exist as to the level to which 6PPD-q is a leachate of concern in landfills. Jurisdictions may also be working to address illegal dumping of tires, generally for policy reasons that predate the discovery of 6PPD-q. RCRA and other solid waste programs may affect the handling and disposal of filtration media and systems used as treatment for 6PPD, 6PPD-q, and TRWP.

Waste management of street sweeper decant solids and liquids, and tracking of TRWP waste post-secondary uses or disposal options may be regulated through RCRA programs or state and local initiatives. These systems are generally different locality-by-locality, even though tire disposal and reuse processing networks operate regionally or nationally.

Under RCRA Subtitle D, state environmental agencies oversee the beneficial use of industrial nonhazardous secondary materials, including waste tires. USEPA provides a Methodology for Evaluating Beneficial Uses of Industrial Non-Hazardous Secondary Materials and the Beneficial Use Compendium.

7.5 Endangered Species Act (ESA)

Under Section 7(a)(1) of the ESA, federal agencies are directed to implement programs for the conservation of threatened and endangered species. Under Section 7(a)(2) federal agencies must consult with NOAA Fisheries "when any project or action they take might affect an ESA threatened and endangered species or designated critical habitat (NOAA Fisheries 2024[IPJKS2XB] NOAA Fisheries. 2024. "Endangered Species Action Consultations | NOAA Fisheries." NOAA. January 22, 2024. https://www.fisheries.noaa.gov/topic/consultations.). In addition federal agencies must consult with United States Fish and Wildlife Service (USFWS 1998[FL8Z44ZV] USFWS. 1998. "ESA Section 7 Consultation." Fish. March 1, 1998. https://www.fws.gov/service/esa-section-7-consultation.) "when any project or action they authorize, fund, or carry out may affect a listed species or designated critical habitat" (USFWS 1998[FL8Z44ZV] USFWS. 1998. "ESA Section 7 Consultation." Fish.

March 1, 1998. https://www.fws.gov/service/esa-section-7-consultation.). The relevant agency or agencies for consultation will depend on the location of the activity and potentially affected species. Projects/actions that commonly require consultation include large construction activities and permitting programs.

7.6 Magnuson-Stevens Fishery Conservation and Management Act (MSA)

The Magnuson-Stevens Fishery Conservation and Management Act (MSA) is the primary law governing marine fisheries management in U.S. federal waters (NOAA Fisheries 2023[59W6MRDF] NOAA Fisheries. 2023. "Magnuson-Stevens Fishery Conservation and Management Act | NOAA Fisheries." NOAA. June 15, 2023. https://www.fisheries.noaa.gov/resource/document/magnuson-stevens-fishery-conservation-and-management-act.). One of its objectives is "…protecting habitat that fish need to spawn, breed, feed, and grow to maturity" (NOAA Fisheries 2023[59W6MRDF] NOAA Fisheries. 2023. "Magnuson-Stevens Fishery Conservation and Management Act | NOAA Fisheries." NOAA. June 15, 2023. https://www.fisheries.noaa.gov/resource/document/magnuson-stevens-fishery-conservation-and-management-act.). In 1996, Congress revised the MSA and "…established new requirements for fishery management councils to identify and describe Essential Fish Habitat, and to protect, conserve, and enhance EFH [essential fish habitat] for the benefit of fisheries" (NOAA Fisheries 2023[59W6MRDF] NOAA Fisheries. 2023. "Magnuson-Stevens Fishery Conservation and Management Act | NOAA Fisheries." NOAA. June 15, 2023. https://www.fisheries.noaa.gov/resource/document/magnuson-stevens-fishery-conservation-and-management-act.). A 2002 update to EFH regulations allowed fishery management councils to designate Habitat Areas of Particular Concern, specific areas within EFH that have extremely important ecological functions and/or are especially vulnerable to degradation "…[The Sustainable Fisheries Act also] established a federal EFH consultation process that advises federal agencies to avoid, minimize, mitigate, or otherwise offset adverse effects on EFH" (NOAA Fisheries 2023[WT3GYCT8] NOAA Fisheries. 2023. "Laws & Policies: Magnuson-Stevens Act | NOAA Fisheries." NOAA. December 6, 2023. https://www.fisheries.noaa.gov/topic/laws-policies.). Identification of 6PPD-q hot spots is ongoing at NOAA (NOAA Fisheries 2024[BMKXPEDP] NOAA Fisheries. 2024. "Coho Salmon (Protected) | NOAA Fisheries." NOAA. January 17, 2024. https://www.fisheries.noaa.gov/species/coho-salmon-protected.).

7.7 Safe Drinking Water Act (SDWA)

The Safe Drinking Water Act (SDWA) is the federal law that protects public drinking water supplies throughout the nation. Under the SDWA, states conduct assessments of their sources of drinking water (USEPA 2004[EPLXS8IM] USEPA. 2004. "Understanding the Safe Drinking Water Act," June.). Source Water Assessment Programs require that "…[e]very state must conduct an assessment of its sources of drinking water (rivers, lakes, reservoirs, springs, and groundwater wells) to identify significant potential sources of contamination and to determine how susceptible the sources are to these threats" (USEPA 2004[EPLXS8IM] USEPA. 2004. "Understanding the Safe Drinking Water Act," June.). 6PPD and 6PPD-q are not identified as contaminants under or regulated by the SDWA.

7.8 Clean Water Act (CWA)

The CWA establishes the basic structure for regulating discharges of pollutants into the waters of the United States and regulating quality standards for surface waters.

7.8.1 National Pollutant Discharge Elimination System (NPDES)

The CWA created the NPDES to address water pollution by regulating point sources that discharge pollutants to waters of the United States. Operators of these sources may need an NPDES permit before they can release stormwater to a receiving water body. Most states have been authorized to implement the NPDES permitting from USEPA, though USEPA continues to be the permitting authority for some stormwater discharges in a few states, most territories, most federal facilities, and most Indian Nation lands. NPDES individual permits are written to reflect site-specific conditions of a single discharger (or, sometimes to multiple co-permittees) while NPDES general permits are written to cover multiple dischargers with similar operations and types of discharges. Stormwater discharges can be covered under several types of permits: MS4 permits, industrial stormwater permits, and construction stormwater permits. Stormwater and wastewater may also be covered under combined sewer overflow permits.

7.8.1.1 Municipal Separate Storm Sewer Systems

CASE STUDY: Washington State Action on 6PPD Using Municipal Separate Storm Sewer Systems (MS4) Authority

WA Ecology is in the process of reissuing the Phase I and Phase II Municipal Stormwater General Permits by Summer 2024. During the draft reissuance process, several changes were proposed that could improve water quality by addressing 6PPD, 6PPD-q, and a range of other contaminants. Proposed changes include requiring more new development and redevelopment, increasing retrofits for existing development, adding street sweeping requirements, and requiring a Stormwater Management Action Plan. WA Ecology will also update the Stormwater Management Manuals with up-to-date guidance on 6PPD and 6PPD-q management.

According to USEPA (USEPA 2015[RS4CLFUU] USEPA. 2015. “Stormwater Discharges from Municipal Sources—Developing an MS4 Program.” Overviews and Factsheets. November 2, 2015. https://www.epa.gov/npdes/stormwater-discharges-municipal-sources.), “[p]olluted stormwater runoff is commonly transported through MS4, and then often discharged, untreated, into local water bodies.” MS4 permits often cover stormwater discharges draining from larger municipal landscapes or transportation networks. Certain MS4 operators are required to obtain NPDES permits and develop stormwater management programs which describe the stormwater control practices that will be implemented consistent with permit requirements to minimize the discharge of pollutants from the sewer system. Each stormwater management program describes how the MS4 will reduce discharges of pollutants and address areas including construction site runoff control, pollution prevention/good housekeeping, and post-construction runoff control. (USEPA 2015[RS4CLFUU] USEPA. 2015. “Stormwater Discharges from Municipal Sources—Developing an MS4 Program.” Overviews and Factsheets. November 2, 2015. https://www.epa.gov/npdes/stormwater-discharges-municipal-sources.). If an MS4 is subject to a TMDL, it may also contain water quality-based effluent limits related to the relevant pollutant(s). Some stormwater discharges from roadways are covered under the NPDES MS4 regulations. Transportation stormwater management differs from traditional MS4 stormwater programs in several ways. USEPA’s 2018 Transportation Stormwater Permit Compendium contains excerpted permit language from transportation-specific MS4 permits and other resources.

7.8.1.2 Industrial Stormwater Permits

Industrial stormwater permits can contain conditions including on-site SCMs like good housekeeping and maintenance, or treatment of stormwater prior to discharge. They can include sector-specific conditions.

7.8.1.3 Construction Stormwater Permits

Construction stormwater permits can contain conditions related to pollution prevention practices, materials management, and inspections. These permits apply to new construction or redevelopment parcels but also to activities such as required bridge maintenance and safety. They can include sector-specific conditions.

7.8.1.4 Combined Sewer Overflow Permits

Some older communities in the U.S. handle stormwater through combined sewer systems. Combined sewer overflow permits are subject to the NPDES permitting program.

7.8.1.5 Residual Designation Authority

USEPA and authorized states also have a residual designation authority to require NPDES permits for other stormwater discharges or category of discharges that are not covered by more traditional permits on a case-by-case basis.

7.8.2 Other Relevant CWA Programs

CASE STUDY: Washington State and Aquatic Life Toxics Criteria

Washington State is the first state in the United States to adopt a numeric water quality criterion for 6PPD-q; this criterion for acute (short-term) exposures applies to all fresh surface waters in the state (Washington Administrative Code 173-201A). WA Ecology established this criterion under CWA Section 303(c). Not enough information is available to develop criteria for chronic (long-term) exposures or for marine surface waters in the state. Washington’s acute criterion aims to limit the amount of 6PPD-q in fresh waters to protect the most sensitive species in Washington, coho salmon, during their most sensitive life stage. Under the CWA, USEPA must approve water quality criteria before they can be used for CWA regulatory programs, such as permitting. USEPA also generally engages in ESA Section 7(a)(2) interagency consultation with the USFWS and the National Marine Fisheries Service to determine whether its proposed approval of a state's water quality criterion may affect ESA-listed species.

Other relevant programs under the CWA authority include water quality standards and impaired waters and TMDLs (see also Section 5.3.5.1.1 TMDL Modeling for Sinks, Sources, Occurrence, and Exposure). USEPA also develops resources that can support states, territories, and tribes in implementing their own CWA regulatory programs, such as nationally recommended CWA 304(a) criteria and CWA analytical methods. Washington State adopted an aquatic life criterion for 6PPD-q under Chapter 173-201A of the Washington Administrative Code, Water Quality Standards for Surface Waters of the state of Washington, in August 2024 (see also CASE STUDY: Washington State and Aquatic Life Toxics Criteria). USEPA developed acute 6PPD-q and 6PPD aquatic life screening values for freshwater based on the best available data on the toxicity of 6PPD-q and 6PPD to aquatic organisms in U.S. freshwaters. These values are available for optional use to support implementation of CWA programs. USEPA also developed a draft CWA analytical method for detection of 6PPD-q in surface water and stormwater (Draft EPA Method 1634).

8 Information Gaps and Research Needs

Since the discovery of 6PPD-q in 2020 (Tian et al. 2021[X8BRFG3P] Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. “A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon.” Science 371 (6525): 185–89. https://doi.org/10.1126/science.abd6951.), researchers around the world have prioritized learning more about environmental occurrences, sampling protocols, mitigation strategies, and toxicity to aquatic species, but there is still a lot to learn. This section highlights knowledge gaps and research needs that, if addressed, could further characterize and mitigate the risks associated with 6PPD-q or its parent compound, 6PPD.

8.1 Effects Characterization and Toxicity

Section 2 provides an overview of the emerging research on the toxicity of 6PPD-q and 6PPD, the ecological and human-health effects associated with exposure to these contaminants, biomonitoring results, and populations of concern. That research is still in its infancy and many knowledge gaps remain related to the toxicological concerns for human and ecological receptors. Table 8-1 provides a tabulated list of these knowledge gaps and why they are needed areas of research.

Table 8-1. Research Needs and Knowledge Gaps—Effects Characterization and Toxicity

Research Need /Knowledge Gap	Justification
ECOLOGICAL TOXICITY	
• Understand the toxicity mechanism of 6PPD-q, including responses from same species with different life histories (e.g., migratory vs non-migratory, dwelling completely in fresh water vs. living in both fresh water and marine ecosystems).	• Predicting 6PPD-q toxicity to a given species is difficult because research has shown that closely related salmonids have varying responses to exposure. • Further research into the mode of toxicity will help explain species sensitivity. • Sensitive species predictions can help inform the selection of a replacement chemical to avoid regrettable substitutions.
• Investigate toxicity in other species and trophic levels, including microbial communities, algae, aquatic plants, and terrestrial organisms (for example, amphibians, reptiles, birds).	• Broaden the understanding of potential ecological impacts of these chemicals. • Inform water quality criteria and other media-specific criteria. • Knowledge of 6PPD-q ecological impacts will help inform mitigation strategies and regulatory solutions.

• Investigate sublethal and/or chronic impacts to both acutely affected and tolerant species. • Assess whether sublethal and/or chronic impacts alter survivorship.	• Understanding whether 6PPD-q has long-term effects on species populations can inform impacts to ecosystems. • Inform ongoing salmon and ecosystem recovery assessments. • Inform fisheries planning and yearly catch limits. • Inform ESA consultations.
HUMAN TOXICITY	
• Test 6PPD-q toxicity for mammalian and human-health endpoints.	• Toxicity values are needed to derive human-health–based guideline values and points of departure to inform risk.
• Conduct tests on short- and long-term exposures to 6PPD-q through different exposure routes (for example, inhalation, ingestion) that assess the health of multiple organs and organ systems.	• Provide information on potential human exposure. • Provide information on potential human toxicity.
HUMAN BIOMONITORING	
• Conduct biomonitoring on 6PPD and 6PPD-q in people in the United States (for example, urine, serum, organs).	• Compare with findings in international studies. • Correlate occurrence data with traffic patterns and urban planning to inform mitigation strategies. • Provide information relevant to human risk assessment.
SOCIAL AND CULTURAL IMPACTS	
• Investigate disproportionate impacts from 6PPD-q to different groups of people, including overburdened communities. • Characterize exposure factors in overburdened communities that may lead to increased exposure.	• Evaluate health and cultural impacts for tribal communities due to decline of coho populations, particularly in the Pacific Northwest (DTSC 2022[2M3Z8Z4F] DTSC. 2022. “Product-Chemical Profile for Motor Vehicle Tires Containing N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine (6PPD) from the California Department of Toxic Substances Control (DTSC).” https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf.). • Understand socioeconomic impacts to subsistence and commercial fishers. • Assess impacts on communities near heavily trafficked roads. • Consider potential cumulative impacts, especially in overburdened communities and those conducting subsistence activities.

8.2 Occurrence, Fate, Transport, and Exposure to 6PPD and 6PPD-q

6PPD and 6PPD-q are emerging contaminants and subjects of ongoing research. Widespread sampling has yet to begin; therefore, our understanding of TRWP, 6PPD, and 6PPD-q and their movement through the environment is limited. Section 3 reviews the modeled and measured physicochemical properties of 6PPD and 6PPD-q. Section 4 reviews the fate, transport, occurrence of tire particles containing 6PPD and 6PPD-q in the environment, potential sources of the chemicals, and how people may come into contact with 6PPD-q and 6PPD. Section 5 reviews a variety of methods for assessing and measuring 6PPD and 6PPD-q among variable environmental matrices and landscapes. Table 8-2 provides a tabulated list of knowledge gaps related to these subject areas.

Table 8-2. Research Needs and Knowledge Gaps—Physicochemical Properties, Fate and Transport, Occurrence, and Sources

Research Need /Knowledge Gap	Justification
PHYSICOCHEMICAL PROPERTIES	
• Determine the persistence and half-life of 6PPD and 6PPD-q in the environment and understand how it varies with different environmental conditions. • Verify fugacity modeling that predicts where 6PPD-q will partition in the environment, with sampling of media. • Identify other transformation and degradation products of 6PPD and 6PPD-q.	• Verification of the characteristics of 6PPD and 6PPD-q is needed to guide planning and mitigation strategies and support human and environmental health impact analysis.
• Validate estimated or predicted properties with observations and measurements from natural systems.	• Environmental data (for example, occurrence data) can support laboratory observations to increase confidence in our understanding of the physicochemical properties of 6PPD and 6PPD-q.
• Investigate bioaccumulation of 6PPD and 6PPD-q in organisms and concentrations of the chemicals in edible tissues, including organism (plant and animal) uptake and exposure through the food web.	• Understanding uptake of 6PPD and 6PPD-q in different species and its absorption, metabolism, and excretion in organisms will help inform exposure assessments. • Determine whether bioaccumulation modeling predictions for the chemicals are valid. • Inform water quality criteria. • Inform health-based guideline values (for example, fish consumption advisories).
FATE AND TRANSPORT	
• Identify all transport pathways for TRWP, whole tire, tire debris, 6PPD, and 6PPD-q. • Investigate leaching rates of 6PPD and 6PPD-q from TRWP and whole tires.	• Inform our understanding of exposure routes and managing sources of 6PPD-q to aid preventive measures.
• Determine air dispersion potential of 6PPD and 6PPD-q and variability based on environmental conditions and land use. • Determine size fractions of TRWP containing 6PPD and 6PPD-q and analyze how these change under different tire, road, or other environmental conditions.	• Identify factors (chemical, physical, biological) that influence the fate, transport, distribution, and persistence of 6PPD and 6PPD-q in the environment
• Determine conditions (for example, temperature, concentration of ozone in air, presence of other oxidants) that impact the reaction of 6PPD into 6PPD-q. • Characterize factors that influence the formation of 6PPD-q in tires and TRWP in the environment, as well as the factors that cause its degradation.	• Assist with understanding conditions where more or less 6PPD-q is produced. • Information can be applied in mitigation strategies.
OCCURRENCE	

• Investigate the levels of 6PPD and 6PPD-q in environmental media in the United States.	• Compare with environmental monitoring results internationally in environmental media (for example, marine and freshwater, sediment, soil). • Inform exposure in humans and biota.
• Characterize the occurrence and persistence of 6PPD-q in data-poor media, such as in indoor dust, pore water in sediment, snow, food (for example, crops, seafood), and drinking water.	• Characterize sources of 6PPD-q and routes of human exposure. • Support setting media-specific contaminant level goals. • Data needed to quantify human exposure and risk.
OTHER PRODUCTS, PPDS, AND SOURCES	
• Identify additional product sources of 6PPD and 6PPD-q. These may include newly manufactured products, as well as products or uses of end-of-life tires. • Characterize ecological and human exposure from 6PPD used in other rubber products (sneaker soles, garden hoses, climbing shoes, and windshield wipers) and, potentially electronics, (see Liang et al. 2022[SZPLJY9T] Liang, Bowen, Jiehua Li, Bibai Du, Zibin Pan, Liang-Ying Liu, and Lixi Zeng. 2022. "E-Waste Recycling Emits Large Quantities of Emerging Aromatic Amines and Organophosphites: A Poorly Recognized Source for Another Two Classes of Synthetic Antioxidants." Environmental Science & Technology Letters, June, acs.estlett.2c00366. https://doi.org/10.1021/acs.estlett.2c00366.). • Products made from recycled tires can contain 6PPD and 6PPD-q. Recycled tires are used mainly in outdoor products (tire reefs, erosion control along embankments, crumb-rubber infill for artificial turf, playground surfaces, tire mulch, and tire aggregate used in civil engineering projects) and some indoor uses (indoor mats, flooring, ramps).	• Understanding whether other products that use 6PPD, products made from recycled tires, or other uses of recycled tires may act as sources—and the relative importance of those sources—can help to inform ecological and human exposures. • May identify the need to find safer alternatives to 6PPD for use in other rubber products. • Inform how and where recycled tires and products made from recycled products can be used to minimize exposures.
• Determine what products contain other PPDs, their capacity to form quinones, their toxicity, and their occurrence in different environmental media or products.	• A range of PPDs and transformation products originating from tires, industrial uses, and other consumer goods, are known to exist and occur, but little is known about their toxicity or transport.
• Determine the potential for particular facilities, such as those that produce rubber, manufacture tires, or retread tires, to emit or release tire-related particulates, 6PPD, or 6PPD-q.	• Classify all potential sources to inform planning and risk assessments
• Determine the impacts of combined sewer systems and application of biosolids on 6PPD and 6PPD-q fate and transport.	• Combined sewer systems direct stormwater into WWTP. 6PPD-q transport may vary depending on the capacity of the system during events, especially during overflow events. 6PPD is predicted, and 6PPD-q has been observed (Dennis, Braun, and Gan 2024[RNAS6357] Dennis, Nicole M., Audrey J. Braun, and Jay Gan. 2024. "A High-Throughput Analytical Method for Complex Contaminant Mixtures in Biosolids." Environmental Pollution 345:123517. https://doi.org/10.1016/j.envpol.2024.123517.), to sorb to biosolids from WWTP, which can then be applied to urban landscapes, agricultural lands, or cultivated forests. • Inform mitigation strategies to reduce 6PPD and 6PPD-q in the environment.

• Determine whether decant facilities that process the waste collected by street sweeping potentially act as another source of 6PPD or 6PPD-q	• Inform solutions planning that includes street sweeping as a recommended form of mitigation
HUMAN EXPOSURE	
• Identify different exposure routes to humans and their relative importance. Potential exposure routes include ambient air, drinking water, diet and subsistence activities, recreational activities in water, use of recycled or manufactured rubber products, and worker exposure at tire and tire recycling facilities.	• Data are needed to quantify human exposure and risk. • Data are needed to estimate levels of exposure in different sectors of the population. • Inform mitigation needs.

Notes: PPDs=para-phenylenediamines, TRWP=tire- and road-wear particles, WWTP=wastewater treatment plants

8.3 How Effective Are the Proposed Solutions?

Significant uncertainty surrounds the effectiveness of the various solutions discussed in this document (Table 8-3). Section 6 provides possible mitigation strategies and potential solutions, including assessing chemical alternatives to 6PPD in tires; mitigating the impacts of 6PPD-q in the environment through pollution prevention, air particulate mitigation, and stormwater source control measures; and assessing remediation of 6PPD-q if it persists in the environment.

Table 8-3. Research Needs and Knowledge Gaps—Mitigation Strategies and Alternatives

Research Need /Knowledge Gap	Justification
STORMWATER BEST MANAGEMENT PRACTICES	
• Identify the effectiveness of SCMs such as street sweeping, catchment/management, biochar-enhanced SCMs, and permeable pavement at preventing 6PPD-q exposure. • Assess the effectiveness of SCMs across various land uses, factoring in location and space availability. • Evaluate the potential impact of fate and transport of TRWP in air on 6PPD-q concentrations in stormwater and how this may influence SCMs. • Identify the fate of 6PPD and 6PPD-q in infiltration-based SCMs and their impact on groundwater.	• Informs measures that intercept, prevent, and manage pathways to exposures from 6PPD-q in waterways. • Develop SCMs that provide the greatest mitigation. • Increase understanding of effective mitigation strategies.
• Characterize the capacity of roadside barriers and vegetation to modify the fate and transport of 6PPD and 6PPD-q.	• Informs BMPs and their effectiveness in reducing 6PPD and 6PPD-q in the environment.
• Determine how street sweeping affects the transport and loading of TRWP, 6PPD, or 6PPD-q.	• Increase understanding of the contribution of street-sweeping activities to TRWP, 6PPD, or 6PPD-q loading. • Informs BMP selection.
• Determine which policies may reduce 6PPD-q exposures (for example, road design, stormwater permitting).	• Informs which proposed solutions are effective and provides direction for implementation.
• Characterize the amount of 6PPD and 6PPD-q in sediment and the potential for TRWP to act as ongoing sources of these chemicals in sediment.	• Informs whether sediment-disturbing processes (for example, dredging, dam removal) might generate pulses of the chemicals. • Informs exposure assessment for sediment-dwelling organisms.
ALTERNATIVES	

• Identify safer alternatives to 6PPD (either within the PPD chemical family or non-PPD alternatives) that provide required antiozonant, antioxidant, and anti-fatigue protection to tires. • Investigate toxicity and transformation products for identified alternatives. • Identify potential environmental trade-offs associated with alternatives.	• Informs long-term replacement of 6PPD in tires and removal of 6PPD-q from TRWP and subsequent exposures.

Notes: BMPs=best management practices, SCM=stormwater control measure, TRWP=tire- and road-wear particles,

8.4 Current Research

Many institutions, including, but not limited to, federal agencies (NOAA, USDA, USEPA, and USGS), state agencies, tribes, academia, and citizen science groups, are funding and conducting research to address information gaps on 6PPD and 6PPD-q. Resources for learning more are listed below:

- USEPA’s website on 6PPD-q highlights ongoing research, as well as funding opportunities associated with 6PPQq.

- The USGS has been leading research on monitoring surface water and studying toxicity in different fishes. USGS’s Western Fisheries Research Center has a cooperative research and development agreement with the USTMA to screen the toxicity of several potential alternatives using cell lines.

- The NOAA Northwest Fisheries Science Center first characterized URMS, and researchers are actively engaged in understanding 6PPD-q’s aquatic toxicity, bioaccumulation, and fate.

- The USDA has been researching the properties of 6PPD to inform the development of safer and bio-based alternatives to 6PPD. The Agricultural Research Service has a cooperative research and development agreement with Flexsys, a manufacturer of 6PPD.

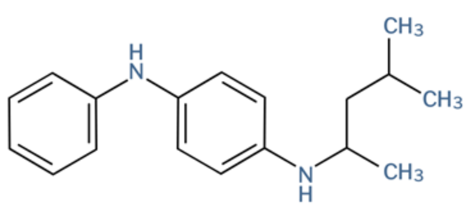
What We Know: 6PPD and 6PPD-quinone

In the short time since 6PPD-quinone (6PPD-q) was isolated and characterized, scientists have been working to understand its prevalence and behaviors in the environment. This focus sheet provides environmental officials with a brief overview of the current understanding of 6PPD-q sources, exposure, fate, transport, toxicity, and mitigation strategies. In-depth ITRC guidance will be released in summer 2024.

In 2020, researchers in Washington State discovered and identified 6PPD-quinone (6PPD-q) as the stormwater chemical responsible for urban runoff mortality syndrome observed in coho salmon (*Oncorhynchus kisutch*) around Puget Sound over the last 25 years.[1,2] Research has demonstrated that 6PPD-q is also acutely lethal to brook trout[3] and rainbow trout/steelhead.[3–5] 6PPD is the primary anti-degradant in tires and has been in use since the 1960s. 6PPD-q is one of the products formed by the reaction of 6PPD and ozone (Figure 1). 6PPD-q may be present in many places impacted by tire use. 6PPD and 6PPD-q have been detected in stormwater and surface waters on many continents[1,6–10] and have been found in airborne particulates,[11–14] sediment,[15] soil,[11] rubber products other than tires,[16] and human urine.[17]

6PPD

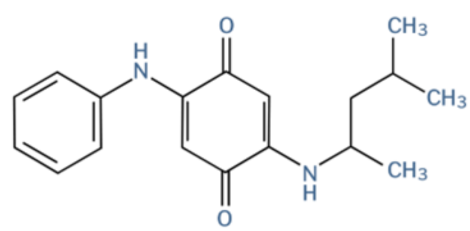
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-



CASRN 793-24-8

6PPD-quinone

2-anilino-5-[(4-methylpentan-2-yl)amino] cyclohexa-2,5-diene-1,4-dione



CASRN 2754428-18-5

Figure 1. Chemical structures for 6PPD and 6PPD-quinone.

How Is 6PPD-q Entering Surface Waters?

Tire wear particles (TWPs) containing 6PPD-q are transported via stormwater to surface water (Figure 2). Many urban stormwater systems are designed to control flooding, not capture and treat contaminants. In separate storm sewer systems, rainwater is transported to natural receiving waters through a network of ditches and pipes without natural or engineered green spaces to remove pollutants prior to entering surface waters. Additionally, some areas with installed stormwater best management practices (BMPs) are failing to contain stormwater due to increased urbanization and storm events that are larger than the infrastructure was designed for, leading to direct conveyance of 6PPD-q to vulnerable aquatic ecosystems.

What We Know: 6PPD and 6PPD-quinone

Multiple aspects of the lifecycle of 6PPD-q are under investigation. This includes the factors that influence the formation of 6PPD-q in tires and tire wear particles (TWPs) in the environment, 6PPD-q's leaching rates from TWPs, and its persistence and bioaccumulation potential. Programs that divert scrap tires from landfills recycle the tires into crumb rubber materials used on sports fields, rubber-modified asphalt, tire-derived aggregate used in civil engineering projects, and more. The levels of 6PPD-q released from recycled tire products is also actively being researched.

Conceptual Transport and Exposure Model

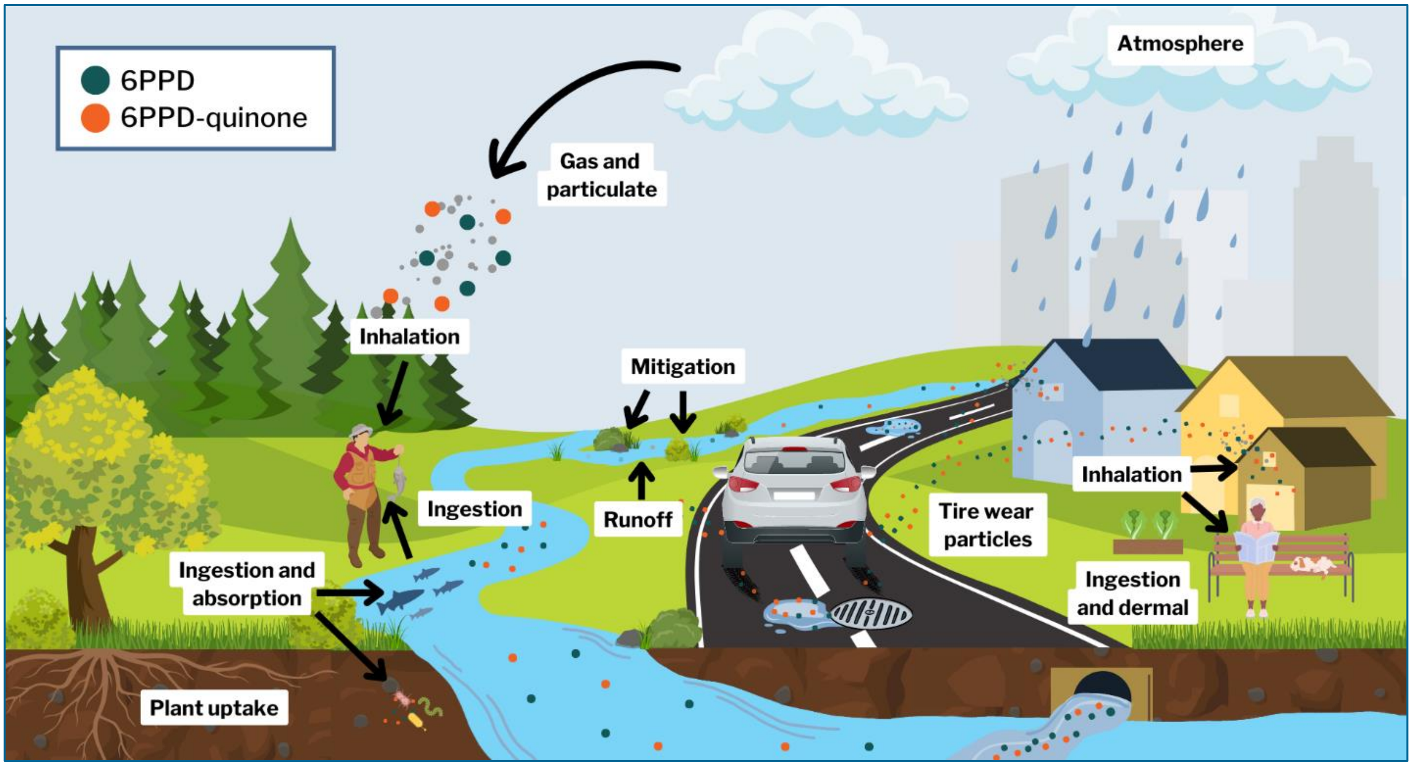


Figure 2. 6PPD in tires is converted to 6PPD-quinone (6PPD-q) when exposed to ozone. 6PPD-q is contained in tire wear particles that can be transported in the air and potentially inhaled by people. The particles can also be deposited on surfaces, soils, and plants, including foods, leading to potential plant uptake and human dermal exposure and ingestion. Tire wear particles can also stay near the roadway and be transported to surface waters through stormwater drains and runoff. 6PPD-q in surface waters can be ingested and absorbed by fishes. Exposed organisms can be ingested by humans and other species. 6PPD-q can potentially be mitigated by green stormwater infrastructure. Research is ongoing to further define 6PPD-q's environmental behaviors, exposures, and the potential development of adverse health outcomes. Figure credit: Hannah Vinyard, Washington State Department of Ecology.

Ecological Toxicity

Both 6PPD and 6PPD-q surpass the threshold for *very high* acute aquatic toxicity using the Globally Harmonised System of Classification and Labeling of Chemicals.[18] This section focuses on 6PPD-q, which ranks as one of the most potent acute aquatic toxicants when compared to chemicals with existing Clean Water Act[2] Aquatic Life Ambient Water Quality Criteria. Most of the ecological toxicity data generated thus far focuses on the acute freshwater aquatic toxicity of 6PPD-q. Two studies on the toxicity of 6PPD-q to marine organisms have been conducted,[19,20] but no studies have been done on the toxicity of 6PPD-q to the estuarine and marine stages of salmonids, which represents a significant data gap. Sublethal effects and chronic toxicity of

6PPD-q are being investigated. There is limited research regarding its toxicity to terrestrial species (e.g., *Caenorhabditis elegans*[21–23]).

Acute Toxicity. Research to date has demonstrated acute toxicity to 6PPD-q in only a few species within the salmonid family, which includes salmon, char, and trout (Table 1). Coho salmon are the most sensitive species documented, with a median LC_{50} concentration (50% mortality in lab tests) of 0.08 µg/L and death occurring within hours.[1,2,4,24] Toxicity to 6PPD-q does not follow a phylogenetic relationship. Species within the *Oncorhynchus* genus show radically different acute toxicities, from an LC_{50} as low as 0.040 µg/L in coho hatchlings[24] to no mortality observed in sockeye at 50 µg/L.[25] Some salmonids in the *Salvelinus* genus (white-spotted char[26] and brook trout[3]) are acutely sensitive at relatively low concentrations (see Table 1), while others are not.[3] *Oncorhynchus mykiss*, which encompasses rainbow trout (freshwater only) and steelhead (ocean-going), show mortality at higher doses and a slower onset of symptoms in response to 6PPD-q.[3] The LC_{50} for Chinook salmon is well above environmentally relevant concentrations[25]; however, Chinook had a low level of mortality when exposed to undiluted roadway runoff.[27] Salmonids that do not experience acute toxicity to 6PPD-q include sockeye salmon,[25] Arctic char,[3] Atlantic salmon, and brown trout,[28] as well as two varieties of Asiatic salmon: southern Dolly Varden and cherry salmon.[26]

Table 1. Reported 6PPD-quinone LC_{50} concentrations (50% observed mortality) of salmonids.

Species	LC_{50} (µg/L)	Test duration (h)	Toxicity Key
Coho salmon (*Oncorhynchus kisutch*)	0.04,[24] 0.08,[25] 0.095[2]	24	Higher
White-spotted char (*Salvelinus leucomaenis pluvius*)	0.51[26]	24	
Brook trout (*Salvelinus fontinalis*)	0.59[3]	24	
Rainbow trout/steelhead (*Oncorhynchus mykiss*)	0.64,[29] 1.0,[3] 2.26[5]	96	
Chinook salmon (*Oncorhynchus tshawytscha*)	67.3[24], 82.1[25]	24	
Sockeye salmon (*Oncorhynchus nerka*)	Not acutely toxic at 50[25]	24	Lower
Atlantic salmon (*Salmo salar*)	Not acutely toxic at 12.2[28]	48	
Brown trout (*Salmo trutta*)	Not acutely toxic at 12.2[28]	48	
Arctic char (*Salvelinus alpinus*)	Not acutely toxic at 12.7[3]	24	
Southern Dolly Varden (*Salvelinus curilus*)	Not acutely toxic at 3.8[26]	48	
Cherry salmon (*Oncorhynchus masou masou*)	Not acutely toxic at 3.5[26]	48	

Note: Example species in the table are listed from very high to low across a toxicity gradient based on the LC_{50} value, with the following ratings: coho = very high; white-spotted char and brook trout = high; rainbow trout / steelhead = medium high; Chinook salmon = medium low; and sockeye salmon, Atlantic salmon, brown trout, Arctic char, southern Dolly Varden, and cherry salmon = low. Chinook salmon were assigned medium-low toxicity out of an abundance of caution. They have an LC_{50} above environmentally relevant concentrations and potentially above some of the salmonids listed below it in the table. Nevertheless, Chinook showed low levels of mortality in undiluted roadway runoff, which could be a result of 6PPD-q or another contaminant. Until further research clarifies whether any life stage of Chinook experiences acute mortality in response to 6PPD-q at potentially environmentally relevant exposures, they were assigned medium-low toxicity.

Chum salmon (*Oncorhynchus keta*) do not show toxicity to roadway runoff[27] or tire leachate[30] but have not been tested with 6PPD-q. Outside the salmonid family, environmentally relevant concentrations of 6PPD-q (up to 2.8 µg/L) are not fatal to several fishes (white sturgeon,[3] zebrafish, and medaka[31]) and aquatic invertebrates (*Daphnia* and the crustacean (*Hyalella azteca*).[31] Toxicity studies on 6PPD-q in marine invertebrates, *Brachionus koreanus*[19] and *Parhyale hawaiensis,*[20] indicated no acute toxicity.

Acute symptoms mimic respiratory distress and include gasping at the water's surface, fin splaying, and loss of equilibrium[32]; onset of symptoms can occur within 90 minutes.[1] Examples of the effects are shown in the [Puget Soundkeeper — Longfellow Creek coho salmon video]. Scientists are still working to determine how 6PPD-q causes mortality in fish. Researchers have demonstrated exposure to roadway runoff causes fluid to leak out of the blood vessels in the gills and brain of coho, demonstrating that the blood–brain barrier is compromised in coho.[33] Mahoney and colleagues provide evidence that energy production at the cellular level may be disrupted.[34] The researchers further suggest that the potential inability of sensitive species to metabolize 6PPD-q into a less toxic form may contribute to its selective toxicity.[34]

Sublethal toxicity. It is still unknown whether 6PPD-q causes sublethal toxicity in wild fish populations. Sublethal effects could impact growth and reproduction and make fishes susceptible to other stressors, such as pathogens, higher temperatures, or other poor water quality parameters. Additional studies are needed to determine the concentrations of 6PPD-q that could result in adverse effects to salmonids, particularly because some populations are protected under the Endangered Species Act.

Limited work has been done studying sublethal effects in zebrafish, where 6PPD-q influenced embryo movement and heart rate.[35] In addition, environmentally relevant concentrations of 6PPD-q have been shown to alter the central nervous system of zebrafish, changing their exploratory behavior, wake/sleep cycle, and heart rate.[36] Beyond fish, chronic toxicity of 6PPD-q has been studied in *C. elegans,* a soil-dwelling round worm. The worms have neurobehavioral changes and show symptoms of oxidative stress at concentrations starting as low as 0.1 µg/L.[21,22] At 1 µg/L the worms have diminished reproductive capacity.[23] How these results translate to salmonids that are more susceptible to acute toxicity and how these sublethal effects relate to survival of aquatic species require further research.

Human Health

This section provides the most salient (e.g., not comprehensive) toxicological information on 6PPD and 6PPD-q. The health effects of 6PPD are better characterized than 6PPD-q. The health hazards of other 6PPD transformation products remain another notable data gap.[37]

6PPD. 6PPD is a well-documented skin sensitizer, resulting in allergic contact dermatitis in sensitized individuals.[38] 6PPD is also listed as a category 1B reproductive toxicant by the European Chemicals Agency (ECHA).[39] Exposed rats experienced prolonged and difficult birth, including some pregnant rats to the point of death.[39] The no adverse effect level for reproduction is 7 mg/kg body weight per day for females.[39] 6PPD increased fat accumulation in liver in mice that were given oral doses of 10 mg/kg body weight per day for 6 weeks.[40] Similarly, ECHA identified the liver and blood cells as targets of toxicity in a 28-day oral exposure rat study. Effects on the liver were reversible at 20 mg/kg body weight per day, and both sexes showed fat deposition in the liver and anemia at 100 mg/kg body weight per day.[39]

6PPD-quinone. 6PPD-q is predicted to cause oxidative stress.[41] 6PPD-q increased lipid accumulation in the livers of mice that were given oral doses of 10 mg/kg body weight per day for 6 weeks.[40] In addition, 6PPD-q increased liver triglycerides at all doses tested (10, 30, and 100 mg/kg body weight per day).[40]

Human Exposure. 6PPD and 6PPD-q were detected in human urine in a Chinese study.[17] Pregnant women's urine had the highest levels of 6PPD and 6PPD-q out of all the demographic groups in the study.[17] One predicted route of exposure to these chemicals is inhalation of particulates, with the highest potential for exposure occurring near traffic (see Figure 2). Ingestion and incidental contact with rubber products or dust may be other sources of exposure to the chemicals.[42] 6PPD and 6PPD-q are present in tire crumb rubber, and these compounds have been identified in the bioaccessible fraction after extraction of crumb rubber with simulated gastrointestinal fluid, implying they may be absorbed after ingestion.[43] The risk of 6PPD and 6PPD-q to people who consume high levels of aquatic species has yet to be characterized. There are limited studies on the bioaccumulative properties of 6PPD and 6PPD-q. Fang and colleagues suggest that 6PPD and 6PPD-q may bioaccumulate in the livers of lab mice[40]; however, additional information regarding absorption, distribution, metabolism, and excretion by the exposed mice is needed to draw this conclusion. Contaminated sources for drinking water could potentially result in exposure depending on the source water and treatment method. Research is ongoing to address this question. Johannessen and colleagues reported negative findings in treated drinking water from two Canadian facilities.[44] No test results for U.S. drinking waters have been reported.

Environmental Justice and Tribal Government Considerations

The extent of 6PPD and 6PPD-q impacts on vulnerable populations and overburdened communities will be determined as knowledge advances. Communities near roadways are disproportionally comprised lower-income people and people of color, making the potential impacts of airborne 6PPD and 6PPD-q on these communities a notable environmental justice concern.[45,46] Environmental justice considerations include but are not limited to food safety of fish consumption, drinking and recreational water safety, use of recycled rubber products, traffic proximity and air particulate matter exposure, socioeconomic impacts to subsistence and commercial fishers, and cumulative impacts.

Salmonid mortality, which can be caused by 6PPD-q, other toxic chemicals, climate change, habitat loss, and additional factors,[18] disproportionately impacts tribal nations in North America by threatening tribal treaty rights, access to traditional foods, and the cultural and economic well-being of Indigenous peoples. Fishing rights for many tribal nations are guaranteed by treaties that have been signed, ratified, and reaffirmed by the U.S. government. Concerns for tribal nations around 6PPD-q include impaired salmon recovery and hatchery efforts, sublethal impacts to fishes, reduced ecosystem resilience, and cumulative impacts to fishes and peoples.

Fate and Transport

Stormwater is the primary transport mechanism for 6PPD-q to surface water. TWPs are generated as tires roll across the road, particularly during acceleration, braking, and turning. These particles, and the chemicals they contain, collect in road dust until stormwater transports them into the aquatic environment. In many cities in the United States, stormwater is diverted to wastewater treatment plants (WWTPs) through combined sewer and stormwater systems. Studies investigating 6PPD-q removal in WWTPs' have had mixed results. Several studies showed a strong reduction or removal of 6PPD-q to nondetect levels,[10,47,48] and another study showed an increase in mass in the effluent from the WWTP.[49] More research is needed to follow up on this. The presence of 6PPD and 6PPD-q in biosolids from WWTP remains a data gap.

The levels of 6PPD-q are highest during or following rain or snowmelt runoff[8,47] and have been measured in U.S. surface waters at concentrations above the LC_{50} values (see Table 1) for coho, brook trout, and potentially rainbow trout.[1,2] The levels of 6PPD-q in the water column can stay elevated for days[6,8]; the duration depends on the frequency of inputs, the site, and the characteristics of the receiving water. Fate and transport of the chemicals in estuaries and saltwater has not yet been characterized. 6PPD-q is expected to sorb to sediment or particles[18,50] and has been measured in sediment in China.[15] Additionally, TWPs may be airborne initially and could be transported long distances. The chemical and physical properties of 6PPD-q in the atmosphere are currently unknown. Notably, 6PPD-q has been measured in particulate matter, including in airborne particles less than 2.5 µm ($PM_{2.5}$),[14,51,52] road dust,[12,53] and household dust.[12] The highest detections and concentration ranges measured in various environmental media are provided in Table 2).Table 2Table 2. 6PPD-quinone concentrations measured in roadway runoff, surface water, sediment, and particulate matter-2.5.

Media	Concentration Range	Notes	References
Roadway runoff	ND – 2.43 µg/L	Highest detection was in China by Cao et al.	2,6,9,10,54
Surface water	ND – 2.8 µg/L*	Highest detection was in the Don River in Toronto, Canada, roughly 35× higher than median coho LC_{50}. Loading generally correlates with the amount of rainfall.	2,7,8,54–56
Sediment	ND – 18.2 ng/g	Highest in urban river sediment, present in deep sea sediment in China.	15
Particulate matter (up to $PM_{2.5}$)	0.1 – 7,250 pg/m^3	Highest detection alongside a road in Guangzhou, China.	14,51,52

*Median LC_{50} for coho (0.08 µg/L), brook trout (0.59 µg/L), and rainbow trout (1.0 µg/L) (see Table 1).

Notes: µg/L = microgram per liter, ng/g = nanogram per gram dry weight, ND = nondetect, pg/m^3 = picogram per cubic meter

Monitoring and Analytical Methods

Monitoring for 6PPD and 6PPD-q in air, soil, surfaces, and water is challenging because environmentally relevant concentrations may be low and presence may be intermittent. Sampling studies indicate that 6PPD-q is detected at higher concentrations during or following rain and snowmelt events that occur following an extended dry period.[8,56] The rate of transport of stormwater and exposure to aquatic life increase with percent impervious surface within a watershed.[8,56] Studies have shown that 6PPD-q can persist for days in urban areas during or following storm events.[8,57] Efforts are underway by the state of Washington to evaluate passive sampling technologies and effectiveness.

The U.S. Environmental Protection Agency is developing a 6PPD-q test method for surface water and stormwater that is projected to be available late in 2023. *Standard Operating Procedure (SOP): Extraction and Analysis of 6PPD-q* (Mel730136, Version 1.2)[58] contains procedures for the extraction and the qualitative and quantitative analysis of 6PPD-q by triple quadrupole mass spectrometry. The standard operating procedure recommends the sample collection, preservation, storage, and holding times. In addition, several commercial and research laboratories can test for 6PPD-q in water.

Other media. Standardized methods are currently in development for sediment and biological tissues. 6PPD-q has been measured in the air by academic researchers,[14,51,52] but there is not a verified method for regulatory testing.

Stormwater Best Management Practices

Stormwater research is focused on determining the effectiveness of existing and new BMPs at 6PPD-q removal, modifying stormwater systems to improve 6PPD-q removal, adding BMP retrofits to urban roadways that lack adequate space for green infrastructure, and refining green stormwater infrastructure to maximize 6PPD-q filtration.

Effective Stormwater Mitigation Technologies. A recent Washington State publication[59] evaluated stormwater BMP treatment mechanisms and rated their expected 6PPD and 6PPD-q removal effectiveness. Several source control, flow control, and runoff treatment stormwater control measures were found to be potentially effective solutions. Washington State is funding research to verify the efficacy of these BMPs and stormwater control measures.

Researchers have demonstrated that running stormwater through the bioretention soil mix (stormwater compost and sand) that is designed as a component of a bioretention system (Figure 3) prevents acute mortality in coho.[60,61] Research to optimize the depth and composition of the bioretention soil mix to maximize the effectiveness and longevity of the system is ongoing. Additionally, different media are being tested to reduce potential nutrient leaching from bioretention BMPs. Preliminary results of a study representing an accelerated timeline of 10 water years by passing water contaminated with 6PPD-q through a laboratory-managed bioretention soil mix shows prevention of coho mortality over the 18-month study period; the results of this study are being prepared by McIntyre and colleagues.

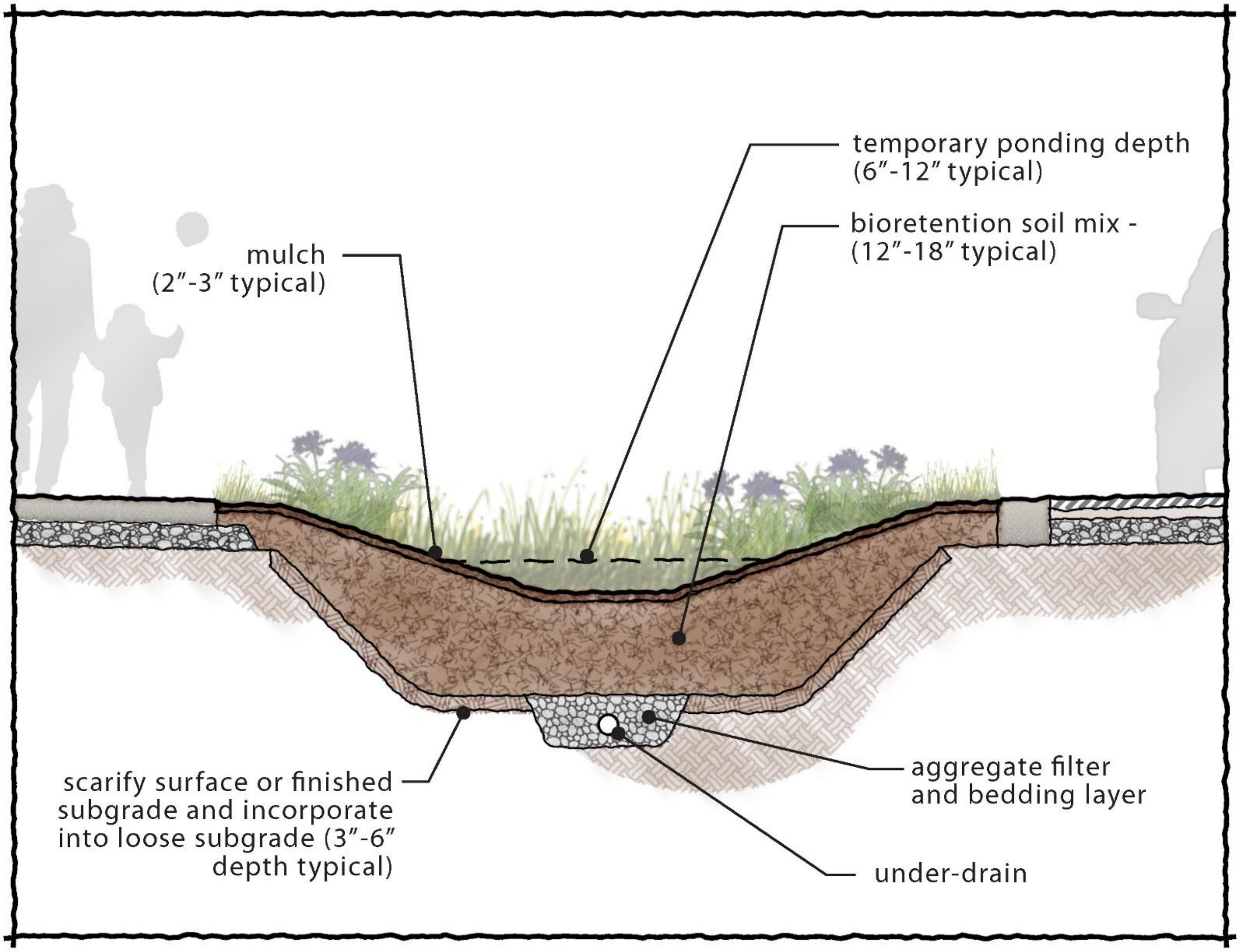


Figure 3. Typical bioretention system with design features. Current research is focused on optimizing the depth and composition of the bioretention soil mix. Courtesy of AHBL, Inc.

Researchers are also using compost-amended biofiltration swales comprising topsoil, compost, and vegetation (Figure 4) to determine the effectiveness of biofiltration systems alongside roadways; the results of this study are being prepared by Tian and colleagues. Preliminary results of the study show variability in compost-amended biofiltration swales performance across seasonal and storm specific parameters, with an efficiency of up to 80+% removal of 6PPD-q.

Identifying Vulnerable Aquatic Areas.
Washington State is developing strategies to focus sampling and stormwater mitigation efforts in locations where 6PPD-q is having a critical environmental impact. The development of these strategies is based on collaboration with tribal governments, community engagement, and available GIS mapping tools containing parameters that are assumed to influence concentrations of 6PPD-q in surface waters.

Figure 4. Example of a compost-amended biofiltration swale. Stormwater is filtered as it flows along the grass in the swale and infiltrates into the topsoil and compost. Photo: Washington State Department of Transportation.

Factors used to identify these areas include, but are not limited to, level of traffic, impervious surfaces, precipitation, media composition that stormwater travels through to get to receiving water, size of the receiving water, and the presence of sensitive species.

Other ongoing research includes the effectiveness of permeable pavement to capture tire particles, analysis of different compost medias and biochar to determine the effectiveness of organic matter in bioretention systems, and evaluation of existing street-sweeping technologies and practices (timing and frequency) on removal of 6PPD and 6PPD-q from roadways.

Alternatives to the Use of 6PPD in Tires

Identifying and deploying alternatives to 6PPD in tires can ultimately reduce or eliminate 6PPD-q in the environment. Currently, 6PPD is necessary for tire safety and to extend the life of tires by preventing cracking and degradation caused by ozone. Discussions with tire manufacturers have revealed that an anti-degradant is not currently available to replace 6PPD. Tires are complex products with tire safety as a principal design priority, and a fully functional anti-degradant is a necessity. Research is ongoing to identify safer alternative chemicals that provide the functionality of 6PPD in tires.[62] Due to the complexity of identifying, testing, and implementing a suitable alternative to 6PPD, the U.S. Tire Manufacturers Association cannot estimate the time frame for the replacement at this stage of the process. The states of California and Washington are pursuing policies to promote the advancement of alternatives to 6PPD in tires.

State Policies and Regulations

Washington State is developing a statewide action plan, funding research to fill in data gaps, assessing other potential tire anti-degradants, and developing specific data requirements and standards to assess the hazards of the alternatives. Technical Memo: Assessment of Potential Hazards of 6PPD and Alternatives[63] provides an overview of known toxicological hazards of chemicals that are or have been used as anti-degradants in tires. Washington State is currently developing hazard criteria to define “safer” when looking at alternatives to 6PPD. There is currently no estimated timeline for completion of the action plan or alternatives assessment. The Safer Products for Washington program, which aims to reduce toxic chemicals in consumer products, identified 6PPD as a priority chemical. Washington and California supported the Collaborative Innovation Forum: Functional substitutes to 6PPD in tires to develop a road map for identifying safer alternatives to 6PPD.[62]

California's Department of Toxic Substances Control will begin regulating 6PPD in motor vehicles through the Safer Consumer Products Program on October 1, 2023. These regulations require tire manufacturers to analyze the hazards and adverse environmental impacts of potential alternatives to 6PPD, as well as evaluate the benefits and tradeoffs of replacing 6PPD. This process leverages the technical expertise of the tire manufacturers and enables them to meet vehicle safety and consumer product safety requirements, while providing a rigorous, transparent, and scientific framework to evaluate and compare potential alternatives to 6PPD. The tire manufacturers' initial screening of potential alternatives is due on March 29, 2024.

6PPD is on Minnesota's Toxic Free Kids Act Chemicals of High Concern List,[64] and the state's legislature appropriated nearly half a million dollars for research on 6PPD-q and its effect on state fishes.[65] Maine also includes 6PPD on its Chemicals of Concern list.[66]

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This fact sheet incorporates data through July 2023.

The **Interstate Technology and Regulatory Council** (ITRC) is a state-led environmental coalition working to create innovative solutions and best management practices. ITRC produces documents and training that broaden and deepen technical knowledge and expedite quality regulatory decision-making while protecting human health and the environment. In January 2023, ITRC started the Tire Anti-degradants (6PPD) Team to provide guidance documents and tools on 6PPD and 6PPD-quinone for environmental officials.

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Glossary

Number

4-hydroxydiphenylamine (4-HDPA)
A transformation product of 6PPD. Visit USEPA's CompTox Dashboard for more information on this chemical.

6PPD-q
6PPD-quinone

A

Active sampling
The use of a pump to collect water or air for analysis.

Adduct
The chemical product resulting from a chemical or toxicant covalently bonding to a biological molecule, such as a protein or DNA. The adduct produced from this reaction can prevent a molecule from functioning properly.

Aliquots
A portion of a larger sample, often divided equally into smaller portions.

Anadromous
Descriptor for fish that hatch and spawn in fresh water but migrate to feed in marine ecosystems.

Antioxidant
A chemical that prevent or delay a material degradation from reaction with oxygen (oxidation).

Antiozonant
A chemical or material used to protect against degradation from ozone. For example, 6PPD is a chemical additive to tire rubber that functions as an antiozonant.

Apical outcome
An endpoint or effect that is observed in a whole organism. The exact definition of an apical outcome varies by source and discipline but generally includes endpoints or effects directly relating to survival, reproduction, development, growth, and behavior.

Asphalt rubber–asphaltic concrete friction courses (AR-ACFC)
Asphaltic concrete friction courses (ACFCs) are the final riding surface on highways, where superior skid resistance is needed. AR-ACFC is an asphalt-rubber version of ACFC, where crumb rubber is blended with the asphalt cement to form an asphalt-rubber binder.

Autosamplers
Pumping devices that are either programmed or remotely triggered to start sampling at timed or flow-controlled intervals.

B

Best management practices (BMPs)
Structural, vegetative, or managerial practices used to treat, prevent, or reduce water pollution.

Bioaccumulation
The accumulation of substances, such as pesticides, or other chemicals in an organism. Bioaccumulation occurs when an organism absorbs a toxic substance at a rate greater than the rate at which the substance is lost.

Bioavailability
The amount of a chemical that is taken up by an organism from the environment and available to cause a biological response.

Bioconcentration factor (BCF)
The accumulation of a water-borne chemical in an organism that is exposed to the water. BCF is calculated as the ratio of the chemical concentration in the organism to the chemical concentration in the surrounding aquatic environment.

Bioretention
The use of chemical, biological, and physical properties of plants, microbes, and soil to improve water quality by removing pollutants during stormwater detention.

Biosolids
Also known as sewage sludge, biosolids are a semi-solid material that remains following wastewater treatment. Biosolids are often applied to land as nutrient rich fertilizer, with or without chemical and physical treatment prior to land application.

Blood–brain barrier
The properties of blood vessels that tightly regulate the movement of molecules, ions, and cells between circulating blood and the central nervous system. Relative to the permeabilities of capillaries and veins in other parts of the body, the blood–brain barrier is uniquely selective.

C

Carcinogenicity
The ability to cause cancer.

Cleanup level
A parameter-specific concentration or other regulatory limit that is considered protective of human health and the environment.

Coarse particulate matter
Inhalable particles with diameters between 2.5 and 10 micrometers, also referred to as PM_{10}. Coarse particulate matter is typically a mixture of solid particles and liquid droplets found suspended in air.

Co-benefits
Multiple positive outcomes or synergies that arise as the result of an environmental action or policy. For example, reducing particulate emissions of TRWP improves air quality and reduces the source mass of 6PPD to soil and surface water.

Column tests
Laboratory studies that measure contaminant removal from water or air passing through a porous media. For stormwater treatment, the results of these tests can be used to quantify hydraulic parameters (such as hydraulic conductivity) and treatment effectiveness (such as contaminant removal rates and capacity) during the design or evaluation of full-scale systems.

Combined sewer systems
Hydraulic structures and pipe networks that collect and convey both sewage and stormwater to a wastewater treatment plant. Most combined sewer systems allow combined sewage overflow to discharge to a receiving water body with minimal or no treatment during large storm events to protect the treatment works.

Contaminant of emerging concern (CEC)
A substance or microorganism, including physical, chemical, biological, or radiological materials known or anticipated in the environment, that may pose newly identified risks to human health or the environment. For more information, visit the ITRC CEC Team website.

Critical habitat

As defined by the Endangered Species Act, critical habitats are areas that contain physical or biological features that are essential to the conservation of the species. These habitats may require special management considerations or protection.

Crumb rubber
Tire rubber that is ground to between particle sizes ranging between 1.5 and 6.5 mm, with the steel and fibers removed. One use of crumb rubber is as a cushioning infill on artificial turf playing fields (NYSDOH 2018).

Cryo-milled tire tread (CMTT)
Particles generated from cutting strips of tire tread into small pieces that are subsequently frozen, hammer-milled (to break the strips into small fragments), and sieved. The Tire Industry Project developed the protocol for consistent production.

D

D5-6PPD-q
Internal standard used in the laboratory for quantification of 6PPD-q concentrations.

Degradants
Chemicals formed during the chemical degradation process.

E

EC_{10}
A statistically derived concentration of a substance at which an effect is expected in 10% of test subjects following exposure.

EC_{50}
The median effect concentration, which is a statistically derived concentration of a substance that is expected to result in an effect in 50% of test organisms following exposure.

Ecosystem services
The direct and indirect benefits that ecosystems provide to humans.

Enantiomer
A chemical that has two configurations, denoted with the prefixes *R*– and *S*-, that are mirror images of one another. Enantiomers have the same chemical formula and sequence of bonded atoms but exist in left- and right-handed orientations that cannot be superimposed over one another.

Enantioselective
A phenomenon or effect that is different between the enantiomer of a given chemical. For example, *R*-6PPD-q and *S*-6PPD-q share similar physicochemical properties but differ in their toxicities (Di et al. 2022).

Endothelial permeability
The ability or extent that blood vessels leak blood contents into surrounding tissues. Endothelial permeability is an essential property that facilitates normal vascularization of organs and tissues, but alterations to this process may indicate or result in disease.

Essential Fish Habitat (EFH)
EFH is defined by the Magnuson-Stevens Fishery Conservation and Management Act (MSA) as habitat necessary for to fish spawn, breed, feed or grow to maturity. These areas are designated for all federally managed fishes, but are distinct from 'critical habitat', which is only for species protected by the Endangered Species Act.

Essential Fish Habitat (EFH) consultation
Collaborative effort between NOAA Fisheries and other federal agencies on best practices to minimize environmental damage to fish habitat during coastal development.

F

Fine particulate matter
Inhalable particles with a diameter of 2.5 micrometers or less, also referred to as $PM_{2.5}$.

Finished drinking water
Water that has been completely treated in a treatment plant and is ready for distribution to and use by consumers but has not entered the water distribution system.

G

Geographic information systems (GIS)
The people, hardware, software, and data necessary to display and manage information about places, analyze spatial relationships and model spatial processes. GIS integrates geospatial data with descriptive information to help users understand patterns, relationships, and geographic context.

Grab sample or grab sampling
Collection of a discrete sample over a short time interval from a single location.

H

Habitat Areas of Particular Concern
A subset of essential fish habitats that are high priority areas for conservation, management, and research.

Half-life
The amount of time for a substance's concentration to decrease by 50%.

Hematocrit
The volume percentage of red blood cells in blood. Hematocrit depends on the number and size of red blood cells.

High-performance bioretention soil mixes (HPBSM)
Engineered soil layer for bioretention BMP designs in Washington State that is designed to achieve specific runoff treatment performance goals.

Hydrologic unit
A hierarchical system to delineate watersheds in the United States based on surface hydrologic features.

K

Keystone species
An organism (plant, animal, bacteria, or fungi) that is critical to the survival or other functions of organisms in an ecosystem.

K-rail barriers
Solid structure adjacent to a roadway. K-rail barriers, also referred to as Jersey barriers, are typically made of precast concrete or molded plastic.

L

LC_{50}
Median lethal concentration, which is a statistically derived concentration of a substance (in air or water) that is expected to result in the death of 50% of test organisms following exposure.

LD_{50}
Median lethal dose, which is a statistically derived dose of a substance that is expected to result in the death of 50% of test organisms following administration of the substance.

Lignin
A plant-based polymer with potential for use as a replacement tire anti-degradant.

M

Media filter
A treatment process that uses one or more layers of sand, peat, shredded tires, foam, crushed glass, geo-textile fabric, anthracite, crushed granite, or other material to remove specific types and sizes of particles from influent water, resulting in effective and efficient contaminant removal.

Metabolites
Byproducts (either intermediates or end products) formed by biological processes.

Migration rate
The speed at which a chemical travels through a specific substance.

Mucociliary action
A bodily function that protects the lungs from harmful substances by capturing airborne particulate matter and microorganisms in mucus and other fluids prior to removal from airways.

Municipal separate stormwater system (MS4)
A conveyance or system of conveyances that is owned by a state, city, town, village, or other public entity and is designed or used to collect or convey stormwater for discharge to waters of the United States. The conveyances in an MS4 system typically include features such as storm drains, pipes, and ditches. MS4s do not include combined sewers, sewage treatment

plants, or publicly owned treatment works.

N

Nominal
The assumed amount or concentration of a substance that is expected to be in an exposure medium. It is often based on a calculated dilution of a stock solution.

Nonpneumatic tires
Tires that are manufactured with a flexible, spoke-like structure on the inside of a rubber tread to fulfill the role of pressurized air in conventional tires.

No-observed-effect concentration (NOEC)
The highest concentration at which no effect was observed in test subjects.

O

Octanol-water coefficient (K_{ow})
The unitless ratio of a chemical concentration in 1-octanol (C_O) and water (C_W) in an octanol-water system at chemical equilibrium. Mathematically, $K_{ow} = C_O/C_W$.

Overburdened communities
As defined by Washington State in Provisional Community Engagement Plan for HEAL Act Implementation (2023), overburdened communities are “a geographic area where vulnerable populations face combined, multiple environmental harms and health impacts”.

Oxidative stress
A process that damages critical molecules such as deoxyribonucleic acid (DNA), proteins, and lipids, with the potential for other adverse molecular effects.

P

Particulate matter (PM)
A mixture of solid particles and liquid droplets found in the air.

Passive sampler or passive sampling
A device or technique that uses a non-powered device or biological organism to allow measurement of chemical concentrations in environmental media. Passive sampling allows chemical molecules to freely flow over time from the sampled medium to a receiving phase until equilibrium is achieved. For more information, visit the ITRC Passive Sampling Team Website.

Permeable pavement
Hard surfacing that allows rain, snow melt, or surface runoff to pass through and infiltrate into the ground below. Some types of permeable pavement temporarily retain infiltrating water in a reservoir that slowly drains into underlying layers and soil. Permeable pavement is a type of green infrastructure that is an alternative to traditional (low permeability) concrete and asphalt.

Phylogenetic
Relating to the evolutionary development and diversification of a species or group of organisms, or a particular feature of a single organism.

Physicochemical characteristics
Physical and chemical properties of a substance, which include molecular properties (such as molecular weight, and chemical structure) and bulk properties (such as solubility, partitioning coefficients, and volatility).

$PM_{0.1}$
Inhalable particles with a diameter less than 0.1 micrometers, also referred to as ultrafine particulate matter.

PM_{10}
Inhalable particles with a diameter between 2.5 and 10 micrometers, also referred to as coarse particulate matter. PM_{10} is

typically a mixture of solid particles and liquid droplets found suspended in air.

$PM_{2.5}$
Inhalable particles with a diameter of 2.5 micrometers or less, also referred to as fine particulate matter.

Point of entry
Location where a water supply line enters a building or other extraction point on a consumer's property, but before water is conveyed within the consumer's water supply pipes, tanks, or on-site treatment/conditioning systems.

Point of use
Location of water consumption and use, such as a tap, spigot, or faucet.

Pollution prevention
Actions taken to stop a pollutant from entering the environment or from reaching sensitive receptors.

Q

Quinones
Organic compounds that contain two carbonyl groups either in ortho (adjacent) or para (opposite) positions on a six-membered unsaturated ring or, in some cases, on different rings.

R

Racemate
A chemical mixture containing equal amounts of two enantiomers.

Read-across
A technique that uses data from a similar substance to predict toxicity for chemical that is not well investigated or understood.

Receptors
A person, plant, animal, habitat, or ecosystem potentially impacted by exposure to a chemical or other contaminant.

Remediation
The act or process of abating, cleaning up, containing, or removing a substance (usually hazardous or infectious) from the environment.

Road component
The non-tire debris portion of TRWP, which can include asphalt or concrete particles, brake-wear particles, and other debris released from cars.

Rubber modified asphalt (RMA)
A mixture of ground rubber from scrap tires and asphalt.

S

Salmonids
A family of ray finned fish that includes salmon, trout, char, grayling, and freshwater whitefish (in North America) and taimen and lenoks (in Eurasia).

Sediment
A solid material that is moved and deposited in the bottom of a waterbody.

Sensitization
A chemical or agent that causes or elicits an allergic response in animals or humans. There are two types of sensitization: skin or respiratory. A skin sensitizer will elicit an allergic response following skin or dermal contact. A respiratory sensitizer will induce hypersensitivity of the airways following inhalation of the chemical or agent.

Source control
Reducing or removing the pollutant from its origin rather than treating or removing it after release.

Source water

One or more bodies of water (e.g., rivers, streams, lakes, reservoirs, springs, and ground water) that provide water for consumption or use.

Specific surface area
Total surface area per unit mass.

Stormwater
Water originating from rain or snow melt that is routed to surface water by storm sewers, combined sewers, channels, or other engineered structures.

Stormwater control measures (SCMs)
Structural devices or techniques that slow the flow of runoff and remove pollutants. Some entities refer to SCMs as BMPs.

Surface runoff
Unconfined water flowing over land.

Surface water
Any aboveground water body, such as streams, rivers, lakes, wetlands, reservoirs, creeks, estuaries, and oceans.

T

Tire- and road-wear particle (TRWP)
TRWP are heterogeneous particles generated at the interface of the tire and road surface during driving.

Tire particles
Within this document, tire particles is used as an all-encompassing, generic term for particles generated from vehicle tires on both roads and in laboratory settings. The terminology surrounding tire particles continues to evolve, which leads to inconsistency in published literature on this topic.

Tire rubber
The polymer matrix of rubber in a tire that contains both natural rubber and synthetic polymers (butadiene rubber and styrene butadiene rubber). Tire rubber may also contain halobutyl rubber to help keep tires inflated.

Tire wear particles (TWP)
Within this document, TWP refers to the tire component of the tire and road wear particles (TRWP). These are generated from friction between the tire and a road during driving, braking, and turning. TWP are very unlikely to be found in the environment without the road-component.

Toxicokinetic
The absorption, distribution, metabolism, and excretion (ADME) of toxic substances.

Transformation products
A chemical created from metabolic, chemical, or environmental processes acting on a different (parent) compound.

Treatment facility
A series of devices and structures that treat wastewater, industrial wastes, and sludge. Treatment means any process that alters water quality to make it appropriate for a specific end use.

Trophic levels
The position of a species (or in some cases, types of species with similar feeding habitats) within a food chain or food web.

U

Ultrafine particulate matter
Inhalable particles with a diameter less than 0.1 micrometers, also referred to $PM_{0.1}$.

Urban runoff
Water from rain, melting snow, or outdoor-water-use that drains from impervious surfaces (roads, parking lots, roofs, etc.) and does not soak into the ground. Urban runoff may flow directly into water bodies or can be captured by stormwater infrastructure that may or may not include treatment prior to discharge. Urban runoff contains mixture of chemicals and contaminants.

Urban runoff mortality syndrome (URMS)
A phenomenon observed in lowland streams in the Puget Sound region of the Pacific Northwest where adult coho salmon die after returning to freshwater streams and before spawning.

Urban stream syndrome
The degradation of water quality and associated aquatic ecosystems in streams that receive urban runoff.

V

Vehicle miles traveled
The total distance of travel for all vehicles over a given time period (typically one year) in a specific geographic area.

Vulcanization
A chemical process used to harden rubbers via polymer cross-linking. Most commonly, vulcanization refers to the process of heating natural rubber in the presence of sulfur or other agents, but this term can also include processes for hardening synthetic rubbers.

Vulnerable populations
Groups of people that are more likely to be at higher risk for poor health outcomes in response to environmental harms, which can include, but are not limited to, racial or ethnic minorities, low-income populations, populations disproportionately impacted by environmental harms, and populations of workers experiencing environmental harms. (Source: Provisional Community Engagement Plan for HEAL Act Implementation, 2023).

Acronyms

α-syn PFF	alpha-synuclein preformed fibrils
µg/g	micrograms per gram
µg/kg	micrograms per kilogram
µL	microliter
µg/L	micrograms per liter
µg/m^3	micrograms per cubic meter
µg/mL	micrograms per milliliter
µm	micrometer
µM	micromolar
4-ADPA	4-aminodiphenylamine; CAS: 101-54-2
4-HDPA	4-hydroxydiphenylamine; CAS: 122-37-2
6PPD	N-(1,3-dimethylbutyl)-N’-phenyl-p-phenylenediamine; CAS: 793-24-8
6PPD-q	6PPD-quinone; CAS: 2754428-18-5
AA	alternatives assessment
ACN	acetonitrile; CAS: 75-05-8
ADME	absorption, distribution, metabolism, and excretion
ALP	alkaline phosphatase
ATP	adenosine triphosphate
ALT	alanine aminotransferase
ARAR	applicable or relevant and appropriate requirements
ASE	accelerated solvent extractor
AST	aspartate aminotransferase
BAF	bioaccumulation factor
BCFs	bioconcentration factors
BEH	bridged ethyl-siloxane/silica hybrid
B-IBI	Benthic Index of Biotic Integrity
BMC	Brake Manufacturers Council
BMP	best management practice
cc	cubic centimeter
CEC	contaminants of emerging concern
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
cm	centimeter
CMTT	cryo-milled tire tread
CP-MIMS	condensed phase membrane introduction mass spectrometry
CSF	cerebral spinal fluid
CWA	Clean Water Act
DAPD	diaryl-p-phenylene diamine; CAS: 68953-84-4

DCM	dichloromethane; CAS: 75-09-2
dMRM	dynamic multiple reaction monitoring mode
DNA	deoxyribonucleic acid
DPPD	N,N’-diphenyl-1,4-phenylenediamine; CAS: 74-31-7
DQOs	data quality objectives
DTSC	(California) Department of Toxic Substances Control
DWTP	drinking water treatment plant
EC_{10}	10% effect concentration
EC_{50}	50% effect concentration
ECHA	European Chemicals Agency
EDTA	ethylenediaminetetraacetic acid; CAS: 60-00-4
EFH	essential fish habitat
EIS	extracted internal standard
Eco-SSLs	ecological soil screening levels
ESA	Endangered Species Act
ESI	electrospray ionization
FAF5	Freight Analysis Framework version 5
GAPS	Global Atmospheric Passive Sampling
GAPS-Megacities	Global Atmospheric Passive Sampling Network
GC	gas chromatography
GC/MS	gas chromatography / mass spectrometry
GC-QTOF-HRMS	gas chromatography–quadrupole time-of-flight–high-resolution mass spectrometry
GFF	glass fiber filter
GIS	geographic information system
g/L	grams per liter
HDPE	high-density polyethylene
Herrera	Herrera Environmental Consulting
HESI	heated electrospray ionization mode
HLB	hydrophilic-lipophilic-balanced
HPBSM	high-performance bioretention soil mixes
HPLC	high-performance liquid chromatography
HRGC/HRMS	high-resolution gas chromatography / high-resolution mass spectrometry
HRMS	high-resolution mass spectrometry
HSAID	hot-surface induced desolvation
HSS T3	high-strength silica, trifunctionally bonded
HUC	hydraulic unit code
ICP/MS	inductively coupled plasma / mass spectrometry
ID	inner diameter
IDL	instrument detection limit

ILC_{50}	internal median lethal concentration 50%
IPPD	phenyl-p-phenylenediamine; CAS: 101-72-4
IQL	instrument quantification limit
ISTD	internal standards
ITRC	Interstate Technology and Regulatory Council
KCEL	King County Environmental Laboratory
LC	liquid chromatography
LC_{10}	lethal concentration 10%
LC_{50}	lethal concentration 50%
LC-HRMS	liquid chromatography / high-resolution mass spectrometry
LC-MS	liquid chromatography / mass spectrometry
LC-MS/MS	liquid chromatography / tandem mass spectrometry
LC-QTOF-HRMS	liquid chromatography / quadrupole time-of-flight / high-resolution mass spectrometry
LD_{50}	median lethal dose
LOAEL	lowest observed adverse effect level
LOEC	lowest observed effect concentration
LOEL	lowest observed effect level
LOD	limit of detection
LOQ	limit of quantitation
LTCP	long-term control plan
LVSPE	large-volume solid-phase extraction
m	meters
m^3	cubic meter
MCLs	maximum contaminant levels
MDL	method detection limit
MEMA	Motor & Equipment Manufacturers Association
MeOH	methanol; CAS: 67-56-1
mg	milligram
mg/kg	milligrams per kilogram
mg/kg-bw	milligrams per kilogram of body weight
mg/L	milligrams per liter
mg/m^3	milligrams per cubic meter
mL	milliliter
ML	minimum level of quantification
mm	millimeter
mM	millimolar
mmol	millimol
mmol/L	millimole per liter
mol/L	mole per liter

MQL	method quantification limit
MRL	method reporting limit
MRM	multiple reaction monitoring mode
MS	mass spectrometry
MS2	tandem mass spectrometry
MS4	municipal separate storm sewer systems
MSA	Magnuson-Stevens Fishery Conservation and Management Act
MS/ddMS2	MS/ddMS2=mass spectrometry / data dependent tandem mass spectrometry
NAS	(USGS) Nonindigenous Aquatic Species
ND	nondetect
ng/g	nanograms per gram
ng/kg-bw/day	nanograms per kilogram of body weight per day
ng/L	nanograms per liter
ng/mg dw	nanogram per milligram dry weight
ng/mL	nanograms per milliliter
nM	nanometer
NOAA	National Oceanic and Atmospheric Administration
NOAEL	no observed adverse effect level
NOEC	no observed effect level concentration
NOEL	no observed effect level
NPDES	National Pollutant Discharge Elimination System
NREL	National Renewable Energy Laboratory
NWIFC	Northwest Indian Fisheries Commission
OECD	Organisation for Economic Co-Operation and Development
OW	(USEPA) Office of Water
PAH	polynuclear aromatic hydrocarbon
PAS	passive air sampler
PD	Parkinson’s disease
PDMS	polydimethylsiloxane
PE	polyethylene
PET	polyethylene terephthalate
PFF	preformed fibrils
PPD	para-phenylenediamine; CAS: 106-50-3
pg	picogram
pg/m^3	picograms per cubic meter
$PM_{0.1}$	ultrafine particulate matter, 0.1 micrometers or less in diameter
$PM_{2.5}$	fine particulate matter 2.5 micrometers or less in diameter
PM_{10}	coarse particulate matter, between 2.5 micrometers and 10 micrometers in diameter
POCIS	Polar Organic Chemical Integrative Sampler

POM	polyoxymethylene
PPDs	para-phenylenediamines, class of
PPD-q	para-phenylenediamines-quinone
PPE	personal protective equipment
ppm	parts per million
PRM	parallel reaction monitoring
PTFE	polytetrafluoroethylene
PUF	polyurethane foam
pyro-GC/MS	pyrolysis–gas chromatography / mass spectrometry
QTOF	quadrupole time-of-flight
QTOF/MS	quadrupole time-of-flight / mass spectrometry
QuEChERS	A solid-phase extraction method: Quick, Easy, Cheap, Effective, Rugged, and Safe
RAC	rubberized asphalt concrete
RARα	retinoic acid receptor α
RCRA	Resource Conservation and Recovery Act
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RI/FS	remedial investigation / feasibility study
RMA	rubber-modified asphalt
RNA	ribonucleic acid
RXRα	retinoid X receptor α
SCM	stormwater control measure
SD	standard deviation
SDWA	Safe Drinking Water Act
SIP	state implementation plan
SOP	standard operating procedure
SPE	solid-phase extraction
SRM	selected reaction monitoring
SSTD	surrogate standard
SWIFD	Statewide Integrated Fish Distribution
TAPE	Technology Assessment Protocol–Ecology
TCI	Tokyo Chemical Industry
TD	thermal desorption
TK	toxicokinetics
TMDL	Total Maximum Daily Load
TNC	The Nature Conservancy
TRC	Toronto Research Chemical
TRWP	tire- and road-wear particles
TSCA	Toxic Substances Control Act
TWA	time-weighted average
TWC	tire-wear contaminants

TWP	tire-wear particles
UHPLC	ultra-high–performance liquid chromatography
UPLC	ultra-performance liquid chromatography
UPLC-QTOF-MS/MS	ultra-performance liquid chromatography–quadrupole time-of-flight–tandem mass spectrometry
UPLC-TOF-MS	ultra-performance liquid chromatography–time-of-flight–mass spectrometry
URMS	urban runoff mortality syndrome
USDA	U.S. Department of Agriculture
USEPA	U.S. Environmental Protection Agency
USFWS	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
USTMA	U.S. Tire Manufacturers Association
VELMA	Visualizing Ecosystem Land Management Assessments
v/v	volume per volume
WA Ecology	Washington State Department of Ecology
WDFW	Washington (State) Department of Fish and Wildlife
WDOC	Washington State Department of Commerce
WET	whole effluent toxicity
WaTech Solutions	Washington (State) Technology Solutions
WQS	water quality standards
WSDOT	Washington State Department of Transportation
WSU	Washington State University
WWTP	wastewater treatment plants

Reference Text	Reference ID
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