NTAA Primer 6PPD/6PPDQ

Purpose of this primer?

The NTAA Executive Committee (EC) requested a review of the information available for 6PPD and 6PPD-Quinone (6PPDQ) to better understand the concerns about this pollutant. This primer aims to consolidate current knowledge on the pollutant 6PPD/6PPDQ, providing the EC and the NTAA with an informed overview. Included in the following intro is an explanation of 6PPD/6PPDQ.

What is 6PPD? [1]

6PPD is an anti-degradation additive in rubber tires and other rubber products designed to prevent rubber tires from cracking, and to help prevent blowouts to preserve longevity of tires. 6PPD works to protect the rubber by aggressively scavenging ozone before the ozone can react with and degrade the rubber.

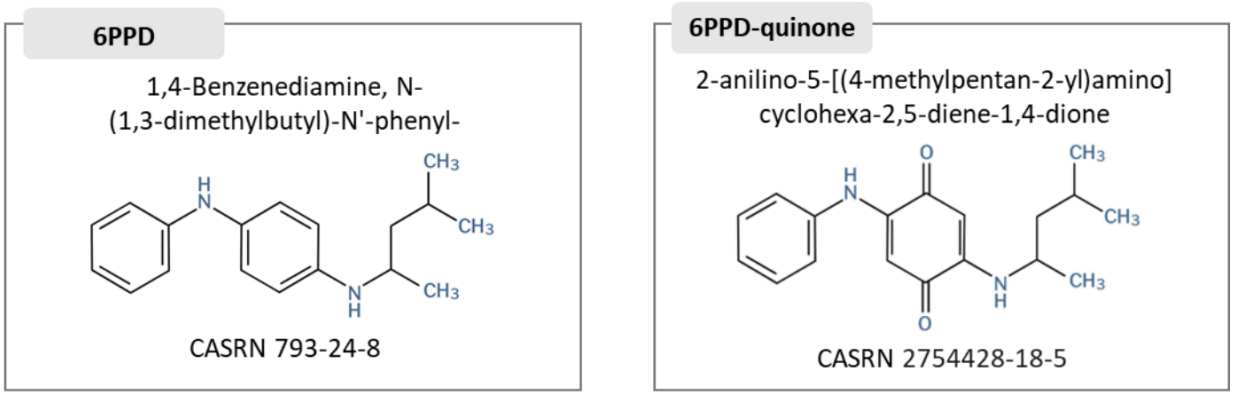

Figure 1. Chemical structures for 6PPD and 6PPD-quinone.

[1] https://6ppd.itrcweb.org/wp-content/uploads/2023/09/6PPD-Focus-Sheet-Web-Layout-9.pdf

What is 6PPDQ?

6PPD is produced through the combination of methyl isobutyl ketone, which has six carbon atoms, (hence the '6' in the name) with phenyl phenylenediam (PPD).[2] 6PPDQ is the byproduct of the reaction between the 6PPD and ozone, which creates 6PPD-quinone. The chemical is released when the tire wears or crumbles and deposits "Tire Wear Particles" (TWPs) on the roadway. The particles are "kicked" into the air which are then deposited along roadways and waterways. 6PPDQ is one of the most potent acute aquatic toxicants when compared to chemicals according to the Clean Water Act Aquatic Life Ambient Water Quality Criteria. 6PPD-quinone is highly toxic to some salmon (coho), trout (rainbow and book trout), and other aquatic species.

How does 6PPDQ move into the environment?

During rain events TWPs are washed into waterways, either directly from roadways or through drainage structures. Unfortunately, these drainage structures are only designed to reduce flooding, not contamination. Thus, drainage systems often flush pollutants and waste from streets directly into streams and rivers where fish are exposed to and die at relatively low concentrations of 6PPDQ. There is still a lot that is unknown about air transport and other aspects of how this pollutant interacts with the environment. For instance, it is unclear how far TWPs travel through the atmosphere before being deposited, whether 6PPDQ can bioaccumulate, and the extent to which it impacts terrestrial species. However, recent studies have found 6PPDQ in stormwater and surface waters on many continents as well as in airborne particulates, sediment, soil, rubber products, and human urine.

Furthermore, TWPs are not the only source of 6PPDQ. Other rubber products and applications in which tires are recycled or reused, such as shredded tires for landscaping, rubber reinforced roadways, and man-made reefs in oceans, can be sources of 6PPDQ.

How does 6PPDQ impact aquatic species?

The levels of 6PPDQ are highest during or following rain or snowmelt runoff[3] and have been measured in U.S. surface waters at concentrations above the LC_{50} (the concentration of a chemical in the water that is lethal to have of a test population) values (see Table 1)[4] for coho, brook trout, and potentially rainbow trout. The levels of 6PPDQ in the water column can remain elevated for days; the duration depends on how often and how much it rains, the site, and the characteristics of the receiving water. The extent and impacts of the

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[2] CompTox Chemicals Dashboard v2.5.0

[3] Johannessen C, Helm P, Lashuk B, Yargeau V, Metcalfe CD. The tire wear compounds 6PPD-quinone and 1,3-diphenylguanidine in an urban watershed. Archives of Environmental Contamination and Toxicology. 2021 Aug 4 [accessed 2021 Aug 5]. https://doi.org/10.1007/s00244-021-00878-4. doi:10.1007/s00244-021-00878-4

[4] https://6ppd.itrcweb.org/wp-content/uploads/2023/09/6PPD-Focus-Sheet-Web-Layout-9.pdf

chemical in estuaries and saltwater is still unknown. 6PPDQ is expected to sorb to sediment or particles[5] and has been measured in sediment in China.

Acute symptoms in fish mimic respiratory distress and include gasping at the water's surface, fin splaying, and loss of equilibrium.[6] Studies show acute symptoms can occur within 90 minutes of exposure above the LC50.[7] Studies are still needed to determine how 6PPDQ 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.[8] Other studies indicate the energy production at the cellular level may be disrupted.[9]

6PPDQ causes sublethal toxicity in other wild fish populations. Sublethal effects could impact growth and reproduction and make fish susceptible to other stressors, such as pathogens, higher temperatures, or other poor water quality parameters. Additional studies are needed to determine the concentrations of 6PPDQ that could result in adverse effects to salmonids, particularly to those populations that are protected under the Endangered Species Act (ESA). There is current litigation where environmental groups sued tire companies for violations of the ESA based on the use of PPDQ, resulting in a "taking" of endangered species. A "taking" under the ESA means any act that could significantly harm or disturb an endangered species or habitat, even if unintentional. In July 2024, the court denied a motion by the tire industry, to stay the case until EPA completes ongoing rulemaking efforts under TSCA. [10]

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[5] DTSC. Product-Chemical Profile for Motor Vehicle Tires Containing 6PPD - Department of Toxic Substances Control (DTSC).2022. https://dtsc.ca.gov/wp-content/uploads/sites/31/2022/05/6PPD-in-Tires-Priority-Product-Profile_FINAL-VERSION_accessible.pdf

[6] Scholz NL, Myers MS, McCarthy SG, Labenia JS, McIntyre JK, Ylitalo GM, Rhodes LD, Laetz CA, Stehr CM, French BL, et al. Recurrent die-offs of adult coho salmon returning to spawn in Puget Sound lowland urban streams. PLOS ONE.2011;6(12):e28013. doi:10.1371/journal.pone.0028013

[7] Tian Z, Zhao H, Peter KT, Gonzalez M, Wetzel J, Wu C, Hu X, Prat J, Mudrock E, Hettinger R, et al. A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon. Science. 2021;371(6525):185–189. doi:10.1126/science.abd6951

[8] Scholz NL, Myers MS, McCarthy SG, Labenia JS, McIntyre JK, Ylitalo GM, Rhodes LD, Laetz CA, Stehr CM, French BL, et al.
Recurrent die-offs of adult coho salmon returning to spawn in Puget Sound lowland urban streams. PLOS ONE.
2011;6(12):e28013. doi:10.1371/journal.pone.0028013

[9] Mahoney H, da Silva Junior FC, Roberts C, Schultz M, Ji X, Alcaraz AJ, Montgomery D, Selinger S, Challis JK, Giesy JP, et al.
Exposure to the tire rubber-derived contaminant 6PPD-quinone causes mitochondrial dysfunction in vitro. Environmental Science
& Technology Letters. 2022 Aug 4:acs.estlett.2c00431. doi:10.1021/acs.estlett.2c00431

[10] 2024 WL 3381032 United States District Court, N.D. California.
INSTITUTE FOR FISHERIES RESOURCES, et al., Plaintiffs,v. CONTINENTAL TIRE THE AMERICAS, LLC, et al., Defendants. Case No. 3:23-cv-05748-JD
Signed July 10, 2024

There is currently little data available to describe the environmental fate and transport of 6PPDQ, but data from several monitoring studies suggest that it persists longer in the environment than 6PPD (Ref. 31). One study found that 6PPDQ had a half-life of 33 hours in dechlorinated tap water compared to 5 hours for 6PPD (Ref. 16). The longer persistence of 6PPDQ in water indicates more potential exposure time to induce toxic effects in aquatic life (Ref. 16). Another study found that leachate from TWPs remain toxic after exposure to extreme heat (80 °C) for 72 hours, suggesting that 6PPDQ is stable under extreme heat conditions (Ref. 32). It is also likely that the polar carbonyl groups (added oxygen atoms from oxidation) may make 6PPDQ quinone more mobile in the environment than 6PPD[11].

What are potential air concerns about 6PPDQ?

6PPDQ, has been measured in particulate matter, including in airborne particles less than 2.5 µm (PM2.5),[12] road dust, and household dust.[13] TWPs may be airborne initially and could be transported long distances. The chemical and physical properties of 6PPDQ in the atmosphere are currently unknown.

Are there human health impacts from 6PPDQ?

There are only a few studies of 6PPDQ impacts on human health. This is particularly true of understanding the risk from other transformation products of 6PPD.[14] Studies in China found 6PPDQ in human urine with the highest concentrations in women and pregnant women.[15] The exposure route is unclear but inhalation, particularly for people living near roadways, is one important potential route. Ingestion may also come from contact with particles either through deposition or contact with other rubber products. However, 6PPD is also commonly used in hand sanitizers and has been documented to cause dermatitis in sensitive individuals, so exposure can come from other sources of 6PPD as well.[16]

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[11] Federal Register / Vol. 89, No. 223 / Tuesday, November 19, 2024 / Proposed Rules

[12] Zhang Y, Xu C, Zhang W, Qi Z, Song Y, Zhu L, Dong C, Chen J, Cai Z. p-Phenylenediamine antioxidants in PM2.5: The underestimated urban air pollutants. Environmental Science & Technology. 2021 Sep :acs.est.1c04500.doi:10.1021/acs.est.1c04500

[13] Huang W, Shi Y, Huang J, Deng C, Tang S, Liu X, Chen D. Occurrence of substituted p-phenylenediamine antioxidants in dusts. Environmental Science & Technology Letters. 2021;8(5):381–385. doi:10.1021/acs.estlett.1c00148 Zhang Y-J, Xu T-T, Ye D-M, Lin Z-Z, Wang F, Guo Y. 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. 2022 Apr 25 [accessed 2022 May 2]. https://doi.org/10.1021/acs.estlett.2c00193. doi:10.1021/acs.estlett.2c00193

[14] Hu X, Zhao HN, Tian Z, Peter KT, Dodd MC, Kolodziej EP. Transformation product formation upon heterogeneous ozonation of the tire rubber antioxidant 6PPD (n-(1,3-dimethylbutyl)-n'-phenyl-p-phenylenediamine). Environmental Science & Technology Letters. 2022 Apr 12 [accessed 2022Apr12https://doi.org/10.1021/acs.estlett.2c00187. doi:10.1021/acs.estlett.2c00187

[15] Du B, Liang B, Li Y, Shen M, Liu L-Y, Zeng L. 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. 2022;9(12):1056–1062. doi:10.1021/acs.estlett.2c00821

[16] ToxServices, LLC. N-(1,3-Dimethylbutyl)-N'-Phenyl-P-Phenylenediamine (6PPD) (CAS# 793-24-8) GreenScreen® for Safer Chemicals (GreenScreen®) Assessment. 2021. https://www.ezview.wa.gov/Portals/_1962/Documents/6ppd/GreenScreenExecutiveSummaryFor6PPD.pdf

Most studies on the health impacts of 6PPDQ are mice studies. Mice exposed to 6PPDQ show increased fat concentration in the liver and anemia. These studies indicate the impacts can be reversible. However, more study is needed to understand the full impacts and whether it bioaccumulates.[17]

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.

How does 6PPDQ potentially impact Tribes?

The impacts of 6PPDQ are not yet fully understood. More study is needed regarding both acute and chronic impact on humans due to the exposure of the pollutant. Further, the impacts of other 6PPD transformation products need to be studied. However, environmental justice is a concern because low-income minority communities are more likely to be located near roadways that cause 6PPDQ exposure from TWP.[18] Other environmental justice considerations that need additional study include the long-term

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[17] Fang L, Fang C, Di S, Yu Y, Wang C, Wang X, Jin Y. Oral exposure to tire rubber-derived contaminant 6PPD and 6PPD-quinone induce hepatotoxicity in mice. Science of The Total Environment. 2023;869:161836. doi:10.1016/j.scitotenv.2023.161836

[18] Rowangould GM. A census of the US near-roadway population: Public health and environmental justice considerations. Transportation Research, Part D: Transport and Environment. 2013;2013(25):59–67. doi:10.1016/j.trd.2013.08.003

impacts of 6PPD on subsistence fishers, better understanding of the impact on drinking water, and other exposure routes like contact with rubber products.

6PPDQ impacts Tribal nations by causing harm to important cultural and subsistence resources such as salmon and trout species. The threat to fish resources from 6PPD is exacerbated by other environmental factors, including climate change, loss of habitat, and changes in water quality and quantity. These combined factors can significantly impact Tribes' treaty rights and cultural practices.

As a result of these concerns, three Tribes, the Yurok Tribe, the Port Gamble S'Klallam Tribe, and the Puyallup Tribe of Indians petitioned EPA under Section 21 of the Toxic Substances Control Act ("TSCA"), 15 U.S.C. § 2620, to establish regulations prohibiting the manufacturing, processing, use, and distribution of 6PPD for and in tires under EPA's TSCA Section 6(a) authority, 15 U.S.C. § 2605(a), with such regulation to take effect as soon as practicable, in order to eliminate the unreasonable risk 6PPD in tires presents to the environment.[19]

How is 6PPDQ being monitored?

Monitoring methods are being developed by both EPA and the State of Washington for all media. Washington State's focus has been on stormwater monitoring[20] while EPA is developing methods for other media. At this point there is no verified method for regulatory testing.[21]

How can 6PPDQ run off be addressed?

Studies are being conducted to find alternatives to 6PPDQ as an additive to tires but to date none have been found.[22, 23]

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[19] Earth Justice letter to Administrator Regan, August 1, 2023

[20] Washington State Department of Ecology. Standard Operating Procedure (SOP): Extraction and Analysis of 6PPD-Quinone (Mel730136, Version 1.2). 2023.

[21] Johannessen C, Saini A, Zhang X, Harner T. Air monitoring of tire-derived chemicals in global megacities using passive samplers. Environmental Pollution. 2022;314:120206. doi:10.1016/j.envpol.2022.120206

[22] Sustainable Chemistry Catalyst. Collaborative Innovation Forum: Functional Substitutes to 6PPD in Tires. Meeting Report. 2023.https://static1.squarespace.com/static/633b3dd6649ed62926ed7271/t/63ee6cd15eb30a0fd4f0630d/1676569810601/6PPD-in-Tires-Innovation-Forum-Meeting-Report.pdf

[23] Washington State Department of Ecology. Technical Memo: Assessment of Potential Hazards of 6PPD and Alternatives. 2021. https://www.ezview.wa.gov/Portals/_1962/Documents/6ppd/6PPD%20Alternatives%20Technical%20Memo.pdf

Mitigation efforts – Washington State evaluated stormwater best management practices (BMPs) treatment mechanisms and rated their expected 6PPD and 6PPDQ removal effectiveness.[24] Several source control, flow control, and runoff treatment stormwater control measures were found to be potentially effective solutions. This research demonstrated that using stormwater retention and diverting it through bioretention soil mix (stormwater compost and sand), was an effective design component of a bioretention system.
(Figure 4) prevents acute mortality in coho.[25] [26]

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.

Are there any regulatory efforts to address 6PPDQ?

On November 19, 2024, EPA proposed to grant a petition filed under the Toxic Substances Control Act (TSCA) by Earthjustice on behalf of the Yurok Tribe, the Port Gamble S'Klallam Tribe, and the Puyallup Tribe of Indians, EPA committed to solicit and collect information from the public on the potential risks associated with N-(1,3- Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) (CASRN 793–24–8, DTXSID 9025114) and its transformation product, 6PPD-quinone(CASRN 2754428–18–5, DTXSID 301034849). EPA is soliciting that

[24] Navickis-Brasch A, Maurer M, Hoffman-Ballard T, Bator S, Diamond J. Stormwater Treatment of Tire Contaminants BestManagement Practices Effectiveness. 2022. p. 72. https://fortress.wa.gov/ecy/ezshare/wq/Permits/Flare/2019SWMMWW/Content/Resources/DocsForDownload/2022_SWTreatmentOfTireContaminants-BMPEffectiveness.pdf

[25] Spromberg JA, Baldwin DH, Damm SE, McIntyre JK, Huff M, Sloan CA, Anulacion BF, Davis JW, Scholz NL. Coho salmon spawner mortality in western US urban watersheds: bioinfiltration prevents lethal storm water impacts. Journal of Applied Ecology. 2016;53(2):398–407. doi:https://doi.org/10.1111/1365-2664.12534

[26] McIntyre JK, Davis JW, Hinman C, Macneale KH, Anulacion BF, Scholz NL, Stark JD. Soil bioretention protects juvenile salmonand their prey from the toxic impacts of urban stormwater runoff. Chemosphere. 2015;132:213–219. doi:10.1016/j.chemosphere.2014.12.052

information, along with information about potential alternatives and regulatory options to help inform the Agency's consideration of potential future regulatory actions under TSCA.[27]

Summary

6PPD is a chemical added to tires to support tire safety and longevity by scavenging ozone. 6PPDQ is the reaction byproduct created when 6PPD is exposed to ozone. 6PPDQ is highly toxic to some important aquatic species. Tire wear particles and releases from recycled tire products containing 6PPDQ that discharge into streams and rivers through storm and snow melt events may result in concentrations of 6PPDQ sufficient to cause fish kill events or sublethal impacts to sensitive populations.

Research is underway to understand all routes of transport and exposure from 6PPDQ and its full impacts in the environment to both aquatic and terrestrial species. Human health studies are also underway. Work is likewise being done to develop regulatory monitoring practices and in November 2024, EPA published a notice of proposed rulemaking to gather information to help inform the EPA's consideration of potential future regulatory action on 6PPD and 6PPDQ under the Toxic Substances Control Act.[28]

Further, releases of 6PPDQ have significant potential environmental justice impacts since low income and minority communities are more likely to reside along highways and highly traveled roadways.

Tribal Treaty rights and cultural lifeways are impacted because many of the fish species that are sensitive to 6PPDQ are important species for indigenous communities.

Mitigation of water quality impacts through stormwater BMPs, particularly through routing soil bioretention structures, has been shown to be a potentially effective solution.

NTAA will continue to track the evolution of the state of the knowledge of 6PPD and 6PPDQ to help keep Tribes informed and determine if further action from NTAA is needed.

[27] Federal Register / Vol. 89, No. 223 / Tuesday, November 19, 2024 / Proposed Rules
[28] EPA, Regulatory Investigation under the Toxic Substances Control Act: N-(1,3-Dimethylbutyl)-N'-Phenyl-P-Phenylenediamine and Its Transformation Product 6PPD-Quinone, 89 Fed. Reg. 91299 (Nov. 19, 2024).