# 6PPD-Quinone – Mystery Salmon Killer Identified by UW Researchers

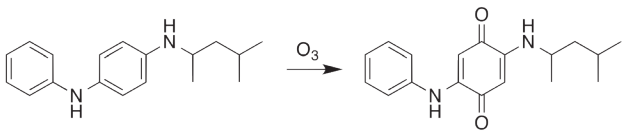
## Mystery Salmon Toxicant Identified – 6PPD-Q

"Urban Runoff Mortality Syndrome" (URMS) causes up to 90% of coho salmon to die before spawning in urban creeks impacted by stormwater runoff in the US Pacific Northwest, particularly in the Puget Sound region. For decades, scientists have been baffled by the cause of these high mortality rates, which occur after high rainfall events. In December 2020, a research group at the University of Washington reported some incredible scientific detective work that conclusively identified the mystery toxicant as 6PPD-Quinone (6PPD-Q).

6PPD-Q was shown to be acutely toxic to coho salmon at very low (sub-ppb) concentrations, but it is not yet known why other species of salmon, such as chum, seem to be far less sensitive to this chemical. The UW researchers identified 6PPD-Q in several streams in Washington and California, but fish-bearing streams around the world are likely to be impacted by this chemical, due to its ubiquitous nature and source.

## Transformation Byproduct from Tire Anti-Oxidant

The source of 6PPD-Quinone, the newly identified toxicant, was confirmed by the UW researchers to be a byproduct of 6PPD, a widely used anti-oxidant which is added to car and truck tires at relatively high levels of 0.4-2%. 6PPD is a very reactive compound, and is intended to preferentially react with ozone at the road surface to prevent tire degradation, to extend tire lifespan, and to improve tire safety characteristics. When 6PPD reacts with ozone, it converts to 6PPD-quinone.




*Ozonation Transformation of 6PPD to 6PPD-Quinone*

As tires wear, tread wear particles (TWPs – a category of microplastics) are deposited on and around road surfaces. Due to its relatively high solubility in water, 6PPD-Quinone dissolves into runoff and finds its way into creeks, streams, and rivers during storms and high rainfall events. Microplastics are already a major environmental concern for many reasons (refer to EnviroMail 28 for more information); acute salmon toxicity due to 6PPD-Quinone provides a clear link to ecological harm from microplastics.

The LC-50 for 6PPD-Quinone to coho salmon is very low at 0.8 µg/L. Concentrations lethal to coho salmon have frequently been exceeded in Washington State streams during high stormwater runoff events.

Environmental testing for the 6PPD source material is expected to be of much greater difficulty and lesser value in comparison to testing for 6PPD-Q. 6PPD has low water solubility, and is highly reactive by design; its aqueous half-life has been reported as being only a few hours under neutral pH conditions, even in sterile water. In comparison, 6PPD-Q has much higher toxicity, mobility, and stability characteristics.

## Long-Term Environmental Solutions

Given the ubiquitous global usage and distribution of 6PPD today, a long term solution to this problem likely requires the re-engineering of automobile tire formulations to use anti-degradants that do not generate toxic byproducts like 6PPD-quinone. Alternative short-term solutions in highly impacted fish-bearing streams could involve stormwater treatment or diversion, but these strategies would be cost-prohibitive on a large scale.

Much more research is needed to determine the toxicity impacts of 6PPD-Quinone to other salmon and aquatic species, to other ecological receptors, and even to humans.

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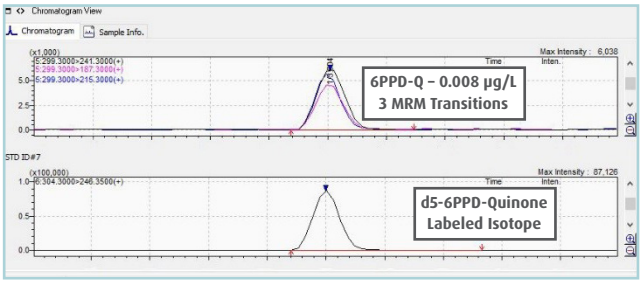
## LC/MS/MS Analysis of 6PPD-Quinone

ALS recognized the urgency of this issue when this story broke in December 2020, and immediately began work on the development of a robust and sensitive test method for 6PPD-Quinone. The ALS Waterloo laboratory now offers routine testing for 6PPD-Quinone in environmental waters, using an extensively validated in-house method. Our test protocol utilizes LC/MS/MS triple quadrupole technology, with Multiple Reaction Monitoring (MRM) of 3 independent mass transitions. In combination with a selective Solid Phase Extraction and cleanup protocol, this robust analytical method offers definitive, confirmed identification and measurement of 6PPD-Q to ultra-trace levels of 0.002 µg/L (lower levels are possible – please contact us if required). We ensure the highest possible accuracy and precision is achieved by using Isotope Dilution quantitation, where a deuterium-labelled 6PPD-Quinone analog is added to all samples prior to concentration and analysis to correct for any sample matrix effects or sample processing losses.




*LC/MS/MS MRM Chromatogram*

The ALS Canada method for 6PPD-Q may be used to characterize source inputs such as urban runoff or even landfill leachate, but also has more than enough sensitivity to support temporal monitoring of 6PPD-Q concentrations in creeks and streams, tracking concentrations before, during, and after rainfall events, with detection limits well below thresholds expected to cause acute toxicity to salmon.

## Sampling Requirements

Environmental water samples may be conveniently collected in 60 mL Polyethylene bottles (provided by ALS) without preservation. For testing of chlorinated waters, samples should be preserved with sodium thiosulfate (provided by request). Cool samples to ≤ 10°C prior to shipment to the laboratory. ALS has adopted a conservative hold time for this method of 7 days (from sampling to extraction). ALS Waterloo has submitted an application for ISO 17025 accreditation for this method to CALA, our accrediting body. Contact us or refer to ALS Waterloo's CALA scope of accreditation for updates on when formal accreditation has been granted.

Please contact your ALS Account Manager for further details about this important new test.

**References:**

Z. Tian et al., A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon, Science 10.1126/science.abd6951 (2020).