



New Analytical Method for Analysis of 6PPD-Q

ALS are at the forefront of the analysis of emerging contaminants including capabilities to test for 6PPD-quinone (6PPD-Q) also called 2-amino-5-[(4-methylpentan-2-yl)amino]cyclohexa-2,5-diene-1,4-dione, or N-(1,3-Dimethylbutyl)-N'-phenyl-p phenylene-diamine-quinone. 6PPD-Q can leach from tyre-wear particles and has been found to be extremely toxic to species of fish. In urban stormwater runoff, 6PPD-Q can exceed acute toxicity thresholds for several salmonid species.

Transformation Byproduct from Tyre Anti-Oxidant

6PPD is a very reactive compound and is intended to preferentially react with ozone at the road surface to prevent tyre degradation, to extend tyre lifespan, and to improve tyre safety characteristics. When 6PPD reacts with ozone, it converts to 6PPD-Q.

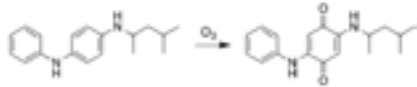


Figure 1 Ozonation Transformation of 6PPD to 6PPD-Q

Ozonation Transformation of 6PPD to 6PPD-Quinone

Due to its relatively high solubility in water, 6PPD-Q dissolves into runoff and finds its way into streams, and rivers during storms and high rainfall 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 persistence.

Fate and Transport Characteristics

Stormwater is the primary transport mechanism for 6PPD-q to surface water. Tyre wear products are generated as tyres 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. Stormwater is diverted to wastewater treatment works (WWTW) through combined sewer and stormwater systems. Studies investigating 6PPD-q removal in WWTW have had mixed results. Several studies showed a strong reduction or removal of 6PPD-q to non-detect levels Maurer et al, (2023), Seiwert et al, (2020) Zhang (2023), and another study showed an increase in mass in the effluent from



WWTW Johannessen (2022). More research is needed to follow up on this. The presence of 6PPD and 6PPD-q in biosolids from WWTW remains a data gap.

LC/MS/MS Analysis of 6PPD-Q

ALS laboratory in Canada now offers routine testing for 6PPD-Q in environmental waters, using an extensively validated in-house method. The test protocol uses Liquid Chromatography with Tandem Mass Spectrometry (LC-MS/MS), utilising Multiple Reaction Monitoring (MRM) of 3 independent mass transitions as shown in Figure 2. In combination with a selective Solid Phase Extraction and clean-up protocol, this robust analytical method offers definitive, confirmed identification and measurement of 6PPD-Q to ultra-trace levels of 0.001 µg/L (lower levels are possible). We ensure the highest possible accuracy and precision is achieved by using Isotope Dilution quantitation, where a deuterium-labelled 6PPD-Q analog

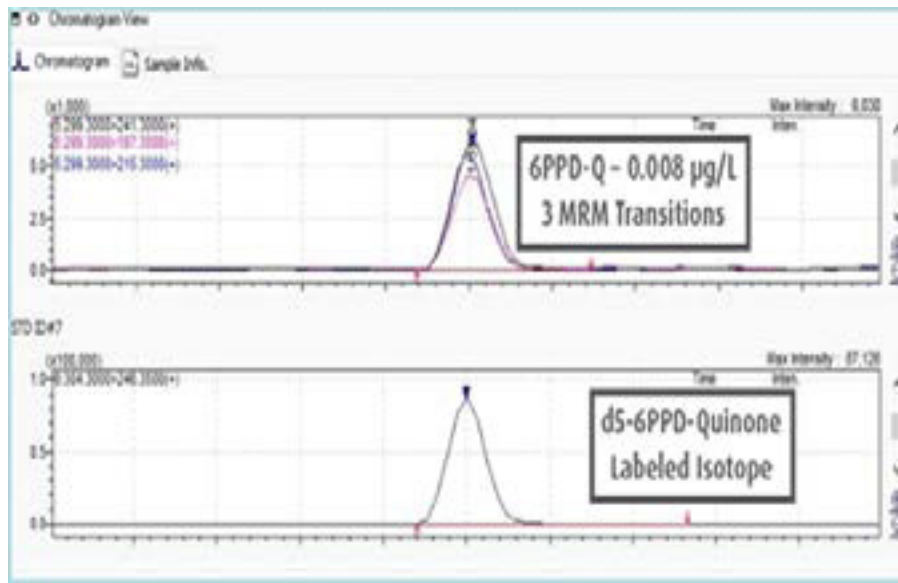


Figure 2 LC-MS/MS MRM Chromatogram

is added to all samples prior to concentration and analysis to correct for any sample matrix effects or sample processing losses.

The method may be used to characterise 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 surface waters, 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 100 mL amber glass bottles (provided by ALS) without preservation. Cool samples to $\leq 10^{\circ}\text{C}$ prior to shipment to the laboratory. ALS has adopted a holding time of 14 days (from sampling to extraction) based on draft United States Environmental Protection Agency (US EPA) Method 1634.

References

- Johannessen C, Metcalfe CD. The occurrence of tire wear compounds and their transformation products in municipal wastewater and drinking water treatment plants. *Environmental Monitoring and Assessment*. 2022;194(10):731. doi:10.1007/s10661-022-10450-9
- Maurer L, Carmona E, Machate O, Schulze T, Krauss M, Brack W. Contamination Pattern and Risk Assessment of Polar Compounds in Snow Melt: An Integrative Proxy of Road Runoffs. *Environmental Science & Technology*. 2023;57(10):4143–4152. doi:10.1021/acs.est.2c05784
- Seiwert B, Nihemaiti M, Troussier M, Weyrauch S, Reemtsma T. 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*. 2022;212:118122. doi:10.1016/j.watres.2022.118122
- Zhang H-Y, Huang Z, Liu Y-H, Hu L-X, He L-Y, Liu Y-S, Zhao J-L, Ying G-G. Occurrence and risks of 23 tire additives and their transformation products in an urban water system. *Environment International*. 2023;171:107715. doi:10.1016/j.envint.2022.107715
- United States Environmental Protection Agency (US EPA) Draft Method 1634 Determination of 6PPD-Quinone in Aqueous Matrices Using Liquid Chromatography with Tandem Mass Spectrometry LC-MS/MS). 2023
- CIWEM (2024) Highway Runoff and the Water Environment. Chartered Institution of Water and Environmental Management

For further information please contact:

Client Services Email: hawardencustomerservices@alsglobal.com