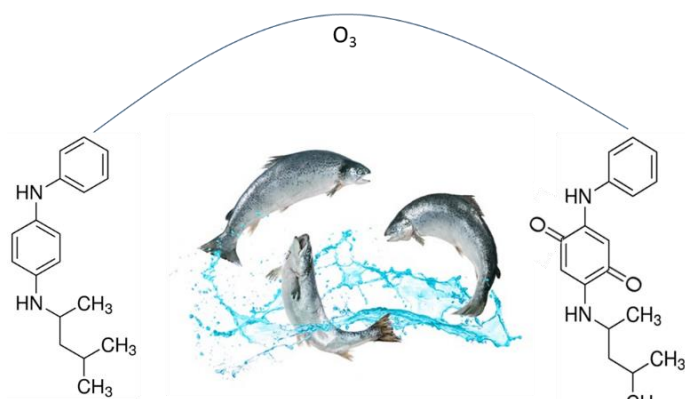


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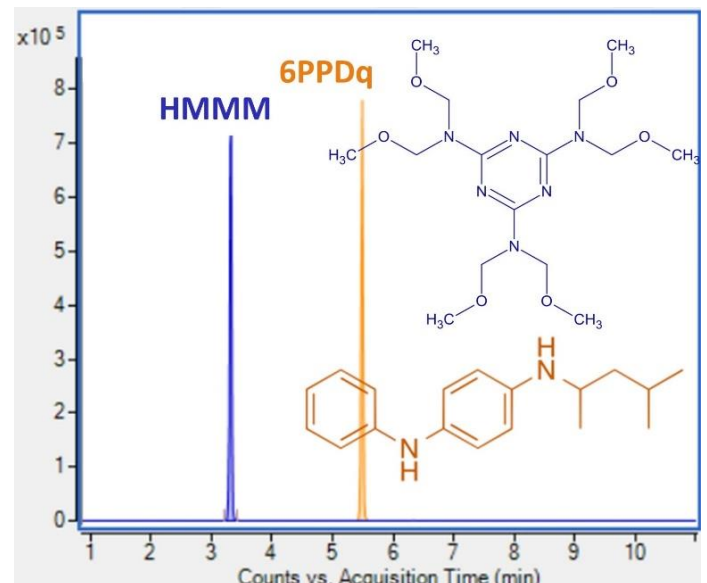
Urban Runoff Mortality Syndrome (URMS): 6-PPD quinone & HMMM

Eurofins Environment Testing Australia now offers the targeted analysis of 6-PPD quinone & HMMM by isotope dilution LC-MS/MS in wastewaters and stormwater run-off as well as playground rubber crumb samples. These emerging contaminants have been implicated in what is called Urban Runoff Mortality Syndrome (URMS) that gained notoriety in early 2021 when scientists from University of Washington using high-resolution accurate mass liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QToF-MS) documented tyre additives and their degradants viz 6-PPD and its ozonation product 6-PPD quinone that were responsible for the deaths of Coho salmon (*Oncorhynchus kisutch*) in Pacific Northwest America.



The parent compound, 6-PPD (N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine; CAS No. 793-24-8), is added to passenger and commercial vehicle tyre formulations as an antioxidant in concentrations up to 2% by weight. Following exposure to ozone, 6-PPD is rapidly transformed to the toxic 6-PPD-quinone.

Additionally, another common tyre additive, HMMM, (2-N,2-N,4-N,4-N,6-N,6-N-hexakis(methoxymethyl)-1,3,5-triazine-2,4,6-triamine; CAS No. 3089-11-0) has also been implicated as an aquatic toxicant and was detected in Australian surface waters by researchers from The University of Queensland in late 2020. Classed as emerging contaminants, our Team in Brisbane have developed a method to determine 6-PPD quinone and HMMM at parts per trillion (ppt) levels in surface water, sediments, and rubber crumb widely used in sports fields and playgrounds as well as some multipurpose outdoor activity areas.



There is a plethora of tyre additives in use, but there is little information on the composition of tyres imported into Australia, and this complex group of chemicals is largely under-studied. Under its REACH Regulationⁱ the European Chemicals Agency (ECHA) lists 6-PPD as a member of the PPD “family”, which further includes 7-PPD (N-(1,4-dimethylpentyl)-N'-phenyl benzene-1,4-diamine), 8-PPD (1,4-Benzenediamine, N-(1-methylheptyl)-N'-phenyl-), 7,7-PD (N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine), and 4,4-PD (N,N'-di-sec-butyl-p-phenylenediamine). As an example, 8-PPD is dissolved in wax and added primarily to the tyre sidewall at a rate of 30-100% by weight by some manufacturersⁱⁱ. LC-QTOF-MS is the ideal technical for this type of application because it is capable of non-targeted analysis that can characterise these unknown species.



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ECHA records that 6-PPDⁱⁱⁱ is not PBT (Persistent, Bioaccumulative and Toxic) or vPvB (very Persistent and very Bio-accumulative) (vPvB)^{iv} but does not list 6-PPD quinone specifically. Similarly, HMMM does not appear to be registered under REACH. However, during the preregistration process, HMMM was included on the so-called Annex III list of compounds with problematic properties, due to its suspected persistence and aquatic toxicity. Analysis of representative roadway runoff and stormwater-affected creeks of the U.S. West Coast indicated widespread occurrence of 6PPD-quinone (<0.3 to 19 micrograms per litre) at toxic concentrations (median lethal concentration of 0.8 ± 0.16 micrograms per litre). These results reveal unanticipated risks of 6-PPD antioxidants to an aquatic species and imply toxicological relevance for dissipated tire rubber residues.

Because of this research, the California Department of Toxic Substances Control (DTSC) identifies product-chemical combinations for consideration as Priority Products in accordance with the process identified in Article 3 of the Safer Consumer Products (SCP) regulations. DTSC has determined that motor vehicle tires containing N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) meet the key prioritisation criteria for listing a Priority Product:

- (1) There must be potential public and/or aquatic, avian, or terrestrial animal or plant organism exposure to the Candidate Chemical(s) in the product; and
- (2) There must be the potential for one or more exposures to contribute to or cause significant or widespread adverse impacts

ⁱ [Understanding REACH](#)

ⁱⁱ [Rubber composition](#) for a tyre sidewall

ⁱⁱⁱ [N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine](#)



Given the very recent discovery of 6-PPD-quinone, little is known about its effects on other aquatic organisms. However, it is potentially toxic to other economically important species that are closely related to Coho salmon such as species that inhabit our waterways viz rainbow trout (*Oncorhynchus mykiss*) and brown trout (*Salmo trutta*) that are a species of salmonid found widely in both Australia and New Zealand.

Water samples can be collected in specially cleaned bottles for the analysis of 6-PPD & 6-PPD quinone and HMMM with a targeted approach; adopting isotope dilution mass spectrometry and applying non-targeted analysis to determine compounds such as further degradation products can be identified using LC-QToF-MS. As the tyre-wear, components most likely fall into the microplastics category these can be identified using infra-red spectroscopic techniques by means of our specialised microplastics facility in our Melbourne laboratory.

Logistical Support

If you are interested in learning more or you have samples that you would like to have analysed then please contact your local Analytical Service Manager or one of our Business Development Team.

^{iv} [TC NES Subgroup](#) on identification of PBT and vPVP substances

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Contacts for further information

EnviroSales@eurofins.com +61 3 8564 5000

Technical Support

EnviroTechnical@eurofins.com

Melbourne Head Office

6 Monterey Road

Dandenong South, Vic. 3175

AUSTRALIA

ABN: 50 005 085 521

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