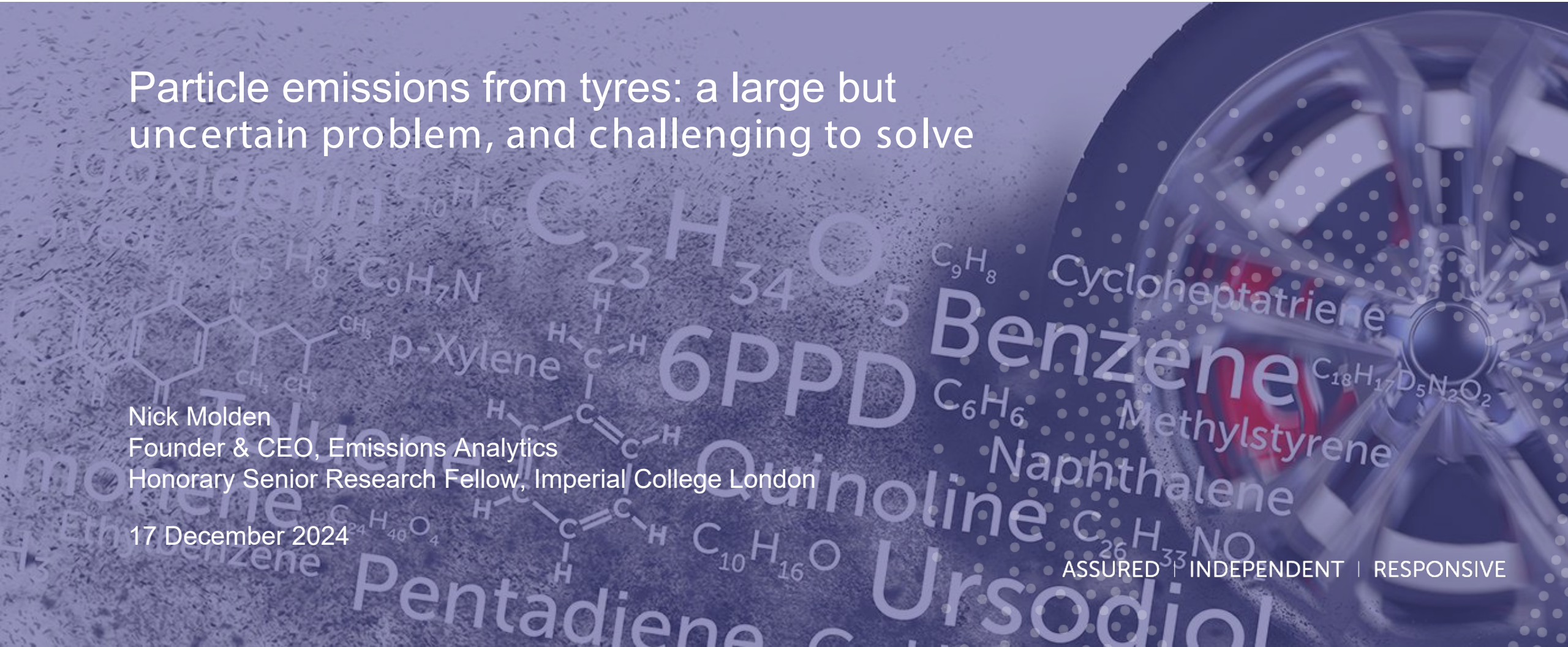
EMISSIONS ANALYTICS

Particle emissions from tyres: a large but uncertain problem, and challenging to solve



Nick Molden
Founder & CEO, Emissions Analytics
Honorary Senior Research Fellow, Imperial College London

17 December 2024

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Agenda

- Nature of tyre emissions
- Impacts on environment
- Emerging regulations in Europe and US
- Experimental approach
- Particle flows
- Chemical composition
- Further insights

The issue

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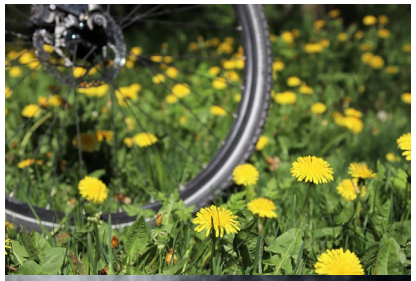
EQUA real-world test database

Setting the scene

- We study the holistic environmental impact of vehicles on the environment
- Working with industry and authorities
- To reconcile transportation with a sustainable environment

- The issue of tyre emissions is rising fast up the agenda
- We conduct a large volume of independent tests
- This presentation shares some of our findings so far
- We want to engage with as many of you as possible to find effective solutions

What are tyre emissions?



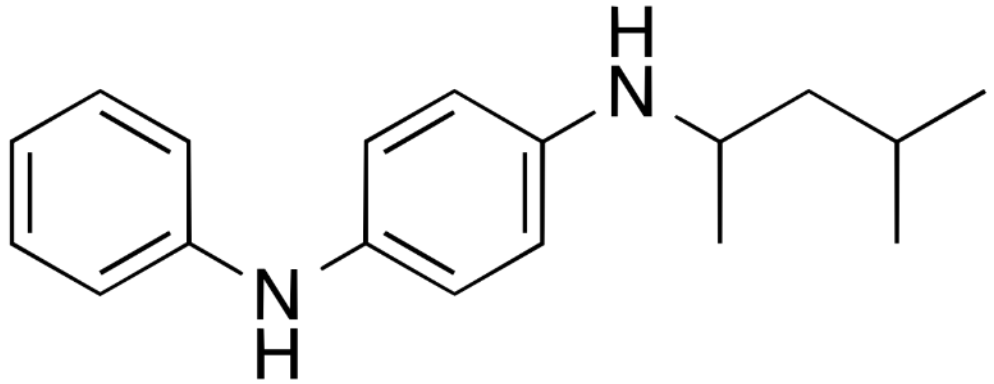
- “Sustainability”: reducing carbon emissions during production
- Alternative materials

- In-use pollution
- Larger and nano-particles
- Off-gassing volatile organics

- End-of-life tyres and recycling
- Rubber crumb
- Fuel source

Omnipresence of tyre wear emissions

- 6 million tonnes of tyre wear globally per year
- Or 1-4 kg per car per year
- Excluding 1-2 billion end-of-life tyres per year
- 7 thousand tonnes of 6PPD in the wear
- 135 ng of 6PPD and 6PPD-quinone in urine of average adult per day



What is 6PPD?

- N^1-(4-Methylpentan-2-yl)-N^4-phenylbenzene-1,4-diamine
- Preservative added during tyre making
- Anti-ozonant and anti-oxidant, to prevent cracking and degradation
- Reacts to create 6PPD-quinone
- Currently present in 100% of tyres sold in Europe and US
- Mass die-off of coho salmon linked to tyre wear in 2020 in Oregon

RESEARCH

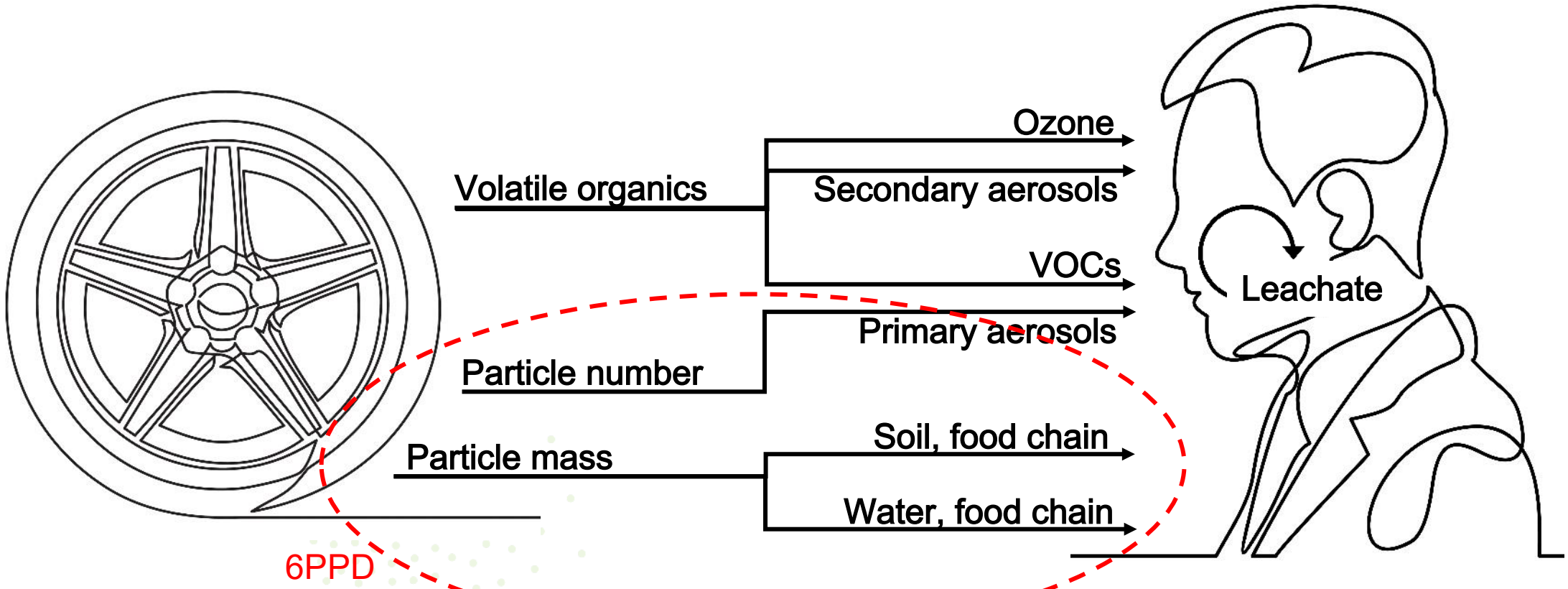
ECOTOXICOLOGY

A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon

Zhenyu Tian[1,2], Haoqi Zhao[3], Katherine T. Peter[1,2], Melissa Gonzalez[1,2], Jill Wetzel[4], Christopher Wu[1,2], Ximin Hu[3], Jasmine Prat[4], Emma Mudrock[4], Rachel Hettinger[1,2], Allan E. Cortina[1,2], Rajshree Ghosh Biswas[5], Flávio Vinicius Crizóstomo Kock[5], Ronald Soong[5], Amy Jenne[5], Bowen Du[6], Fan Hou[3], Huan He[3], Rachel Lundeen[1,2], Alicia Gilbreath[7], Rebecca Sutton[7], Nathaniel L. Scholz[8], Jay W. Davis[9], Michael C. Dodd[3], Andre Simpson[5], Jenifer K. McIntyre[4], Edward P. Kolodziej[1,2,3]*

In U.S. Pacific Northwest coho salmon (*Oncorhynchus kisutch*), stormwater exposure annually causes unexplained acute mortality when adult salmon migrate to urban creeks to reproduce. By investigating this phenomenon, we identified a highly toxic quinone transformation product of *N*-(1,3-dimethylbutyl)-*N*′-phenyl-p-phenylenediamine (6PPD), a globally ubiquitous tire rubber antioxidant. Retrospective 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 liter) at toxic concentrations (median lethal concentration of 0.8 ± 0.16 micrograms per liter). These results reveal unanticipated risks of 6PPD antioxidants to an aquatic species and imply toxicological relevance for dissipated tire rubber residues.

Multiple vectors



Electric vehicles making the problem worse

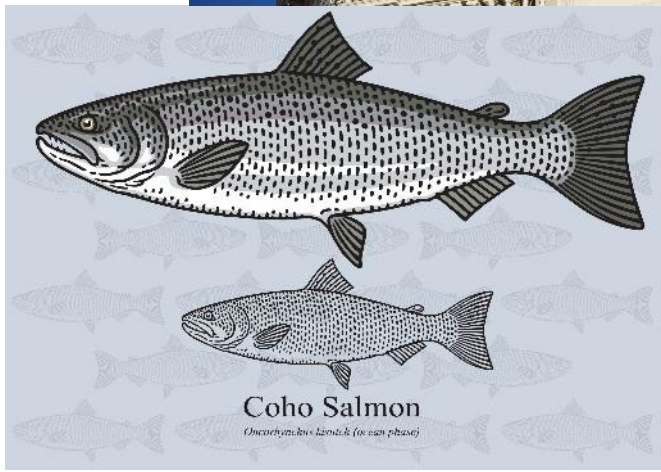
- 37 mg/km tyre wear is x8 maximum permissible tailpipe mass emissions
- 0.02 mg/km is actual, real -world tailpipe mass emissions from latest cars
- And cars are getting heavier
- +30% vehicle mass ⇒ +21% tyre wear
- As result, tyre emissions could be x1,850 higher
- https://www.emissionsanalytics.com/news/gaining-traction-losing-tread

Emerging regulation – EU

- “Euro 7” proposes to set limit values for distance -specific mass emissions
- More details required on how this would be enforced for replacement tyres
- Test method being developed by Task Force on Tyre Abrasion at UNECE
- Likely introduction in 2028/9
- Ignores chemical composition of tyres
- REACH already limits 8 polycyclic aromatic hydrocarbons

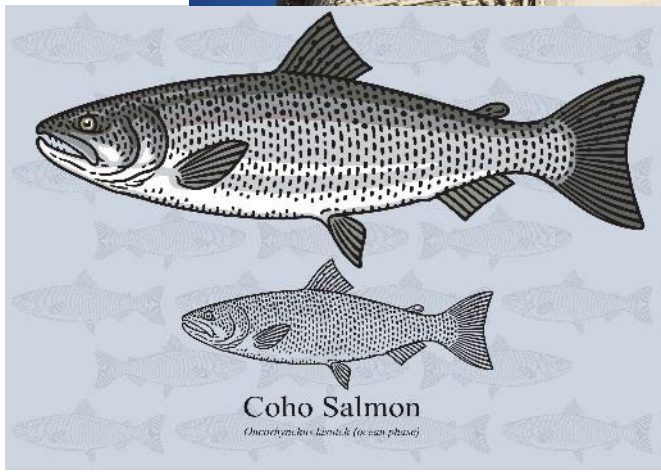
Emerging regulation – US (1)

- California 6PPD rule introduced in 2023
- To address mass die-off of coho salmon (https://www.emissionsanalytics.com/news/fishy)
- Forces tyre manufacturers to investigate alternatives to 6PPD
- Or remove from sale
- Accelerated timeline – November 2023
- Multi-stage, but one-off review only
- Other West Coast states to follow with variations on this approach



Emerging regulation – US (2)

- US Tire Manufacturers' Association has put together consortium of 32 companies
- 60 initial candidate compounds identified
- 7 potential substitutes selected for further analysis
- Notice of Compliance from the California Department of Toxic Substances Control (DTSC) for its revised Preliminary (Stage 1) Alternatives Analysis report in August 2024
- Consortium's Stage 2 report is due to DTSC on in August 2026, with an annual progress report due in August 2025
- Industry "optimistic" than they will find a way to "…replace or materially reduce 6PPD…"



Experimental approach

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On-vehicle sampling – principles

- Universal fitment across vehicles
- Fits to any and all wheels on a vehicle
- No vehicle modification required
- Articulates as the vehicle steers
- Safe and road-legal
- Can be coupled with any detector
- And collecting plates/receptacle
- Patent-pending

➢ Mass, number and physical collection

Reverse-engineering the tyre

- Two-dimensional gas chromatography with mass spectrometry
- INSIGHT flow modulator from SepSolve Analytical for separation
- BENCH-TOF time-of flight mass spectrometer
- Multi-stage pyrolysis method

BTAS brake and tyres analysis system

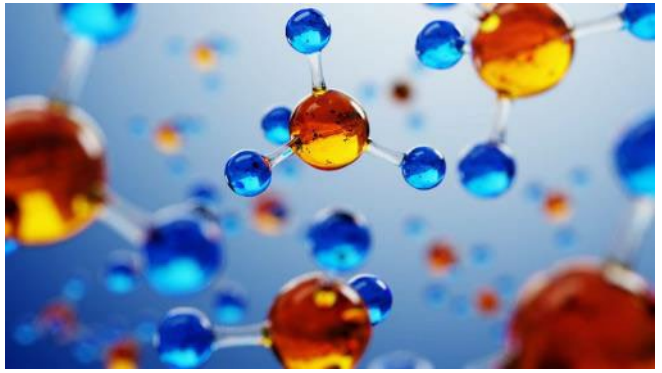
Test programme

- 501 new tyres tested
- Split between US and Europe
- Sourced from retail and wholesale
- Tread block samples taken
- Untargeted Pyrolysis-GCxGC-TOF-MS analysis undertaken
- Full organic compound identification and quantification

Complexities of tyre analysis

Pyr-GCxGC-TOF-MS

Breakdown products



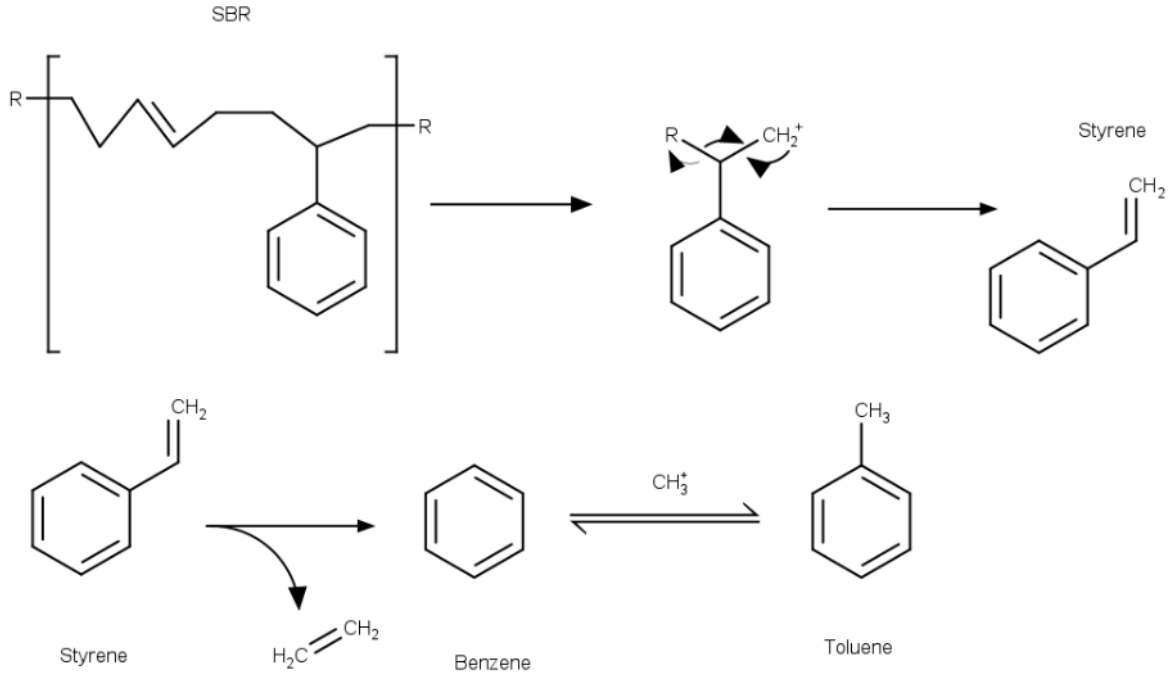
Potential toxicity

TD-GCxGC-TOF-MS

Reaction products

Understanding breakdown products – example

- Unlikely that benzene or toluene are being used in tyre formulation as they are highly regulated
- More likely, they are being formed during analysis from the styrene-butadiene rubber (SBR) pyrolytically cracking
- Styrene and a-methylstyrene are the main pyrolysis products of SBR but do not turn up frequently in the analysis
- Styrene is likely hydrogenated to give ethylbenzene, or decomposed to benzene, which in turn can be methylated to toluene



Particle flows

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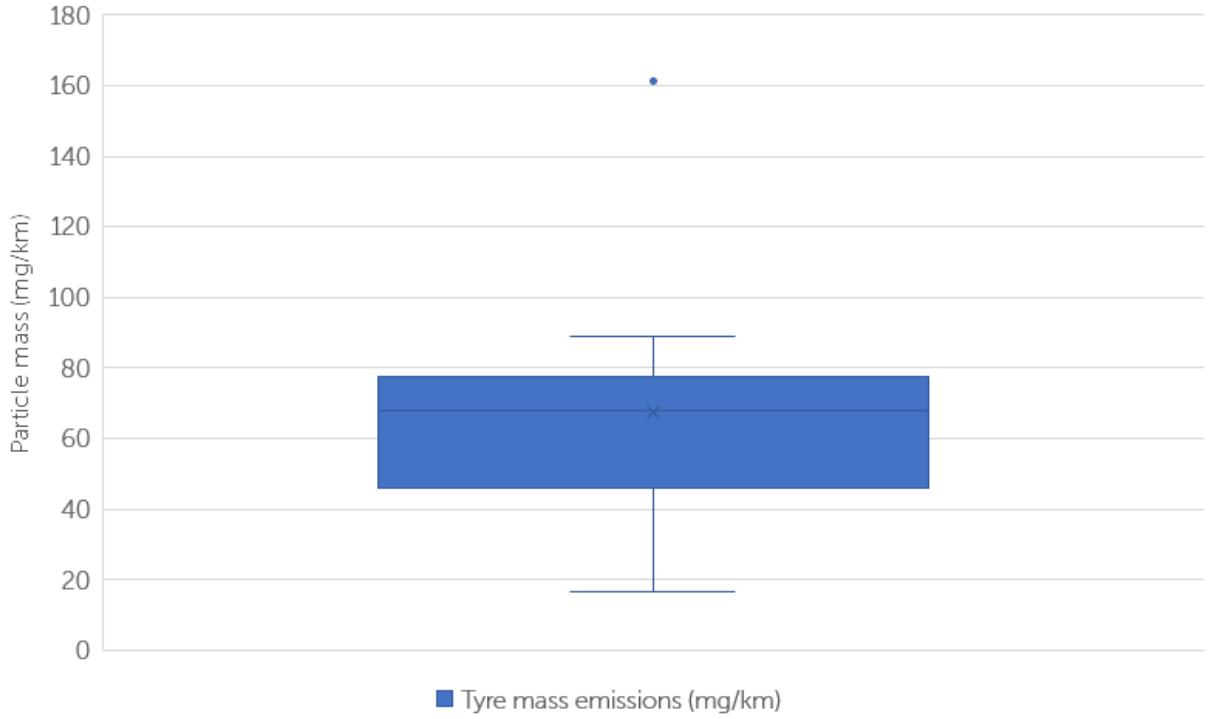
EQUA real-world test database

Tyre mass emissions

- 18 different models of tyre
- Tested from new
- Public highway
- Majority motorway by distance
- Average total distance ~5,000 km

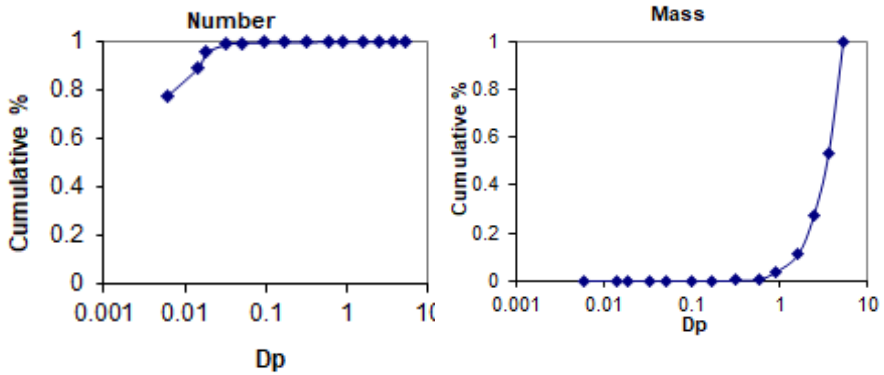
- 67 mg/km mean
- Inter-quartile range: 46-77 mg/km
- Outliers

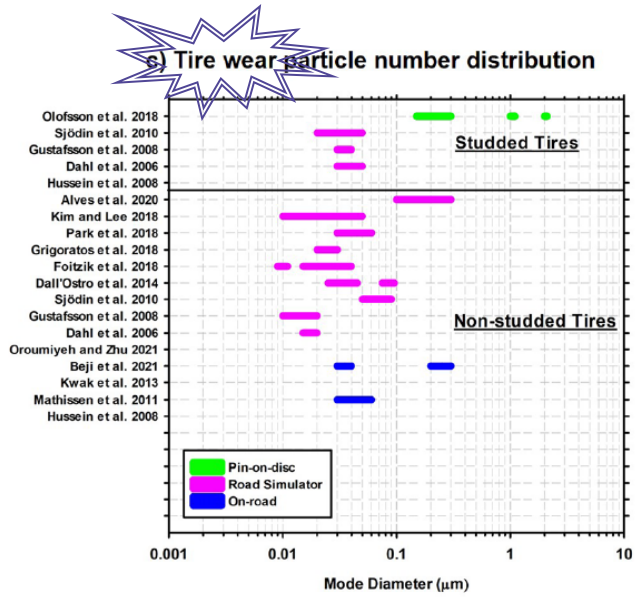


Ultrafine particles from tyres

- On-road test with ‘normal’ dynamics
- 11% of PM10 is below 2.5 µm diameter
- Ultrafines account for 92% by number
- But what interference from road wear, resuspended material and brake wear? Currently unknown in real -world testing
- Then add in secondary organic aerosols
- Absolute PM10 and PM2.5 emissions factors have high uncertainty, and growing evidence that these factors are relatively low

➢ Tyres are a problem for air, soil and water



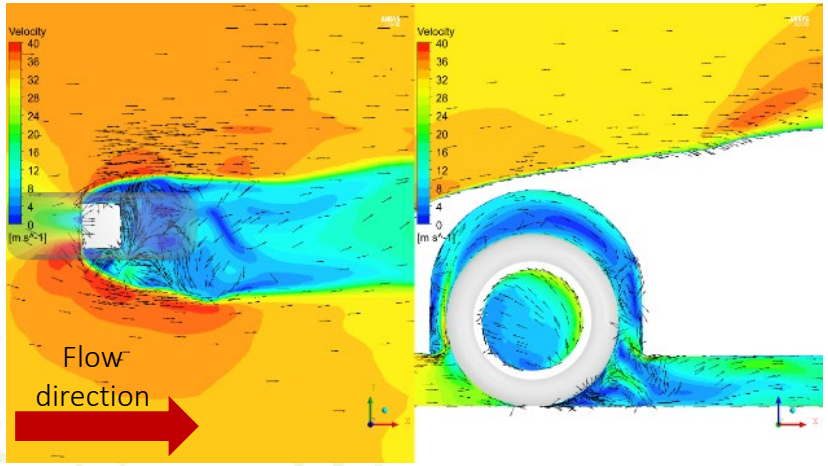


Particle trajectories

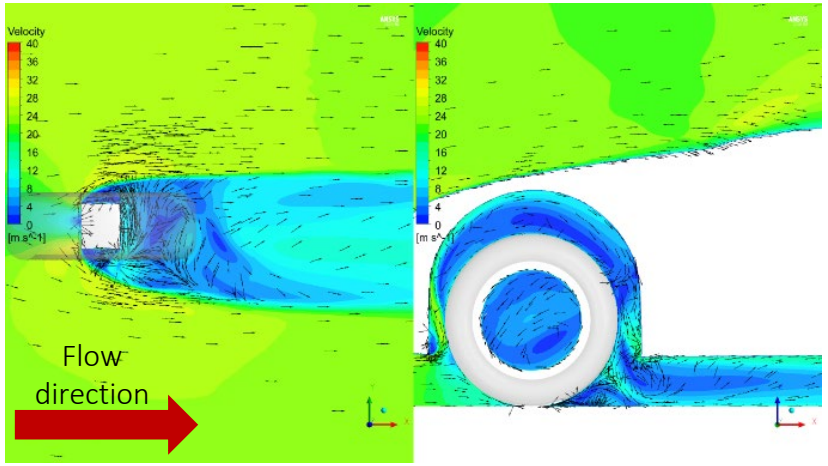
- Dynamic trajectory of particles instantaneously introduced at tyre/road contact patch
- Size range of particles from 10 nm to 100 microns

Speed dependency

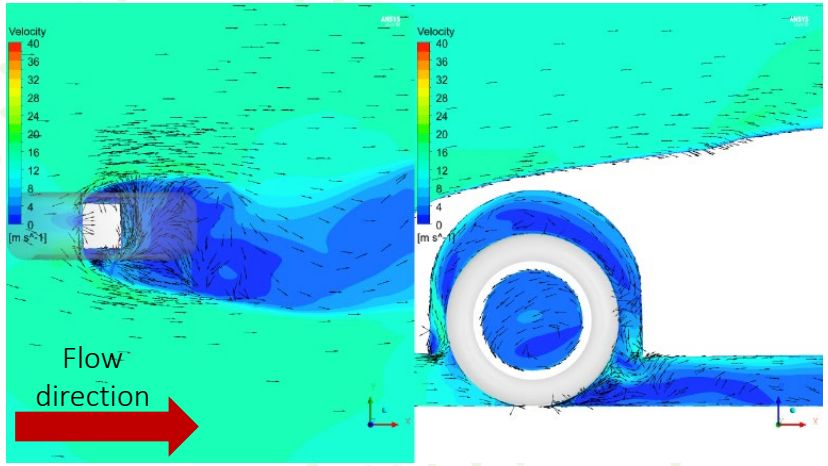
70 [mph]



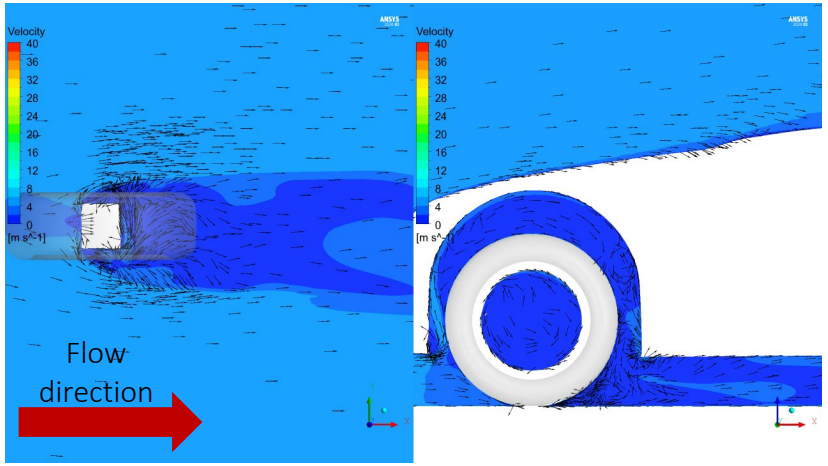
50 [mph]



30 [mph]

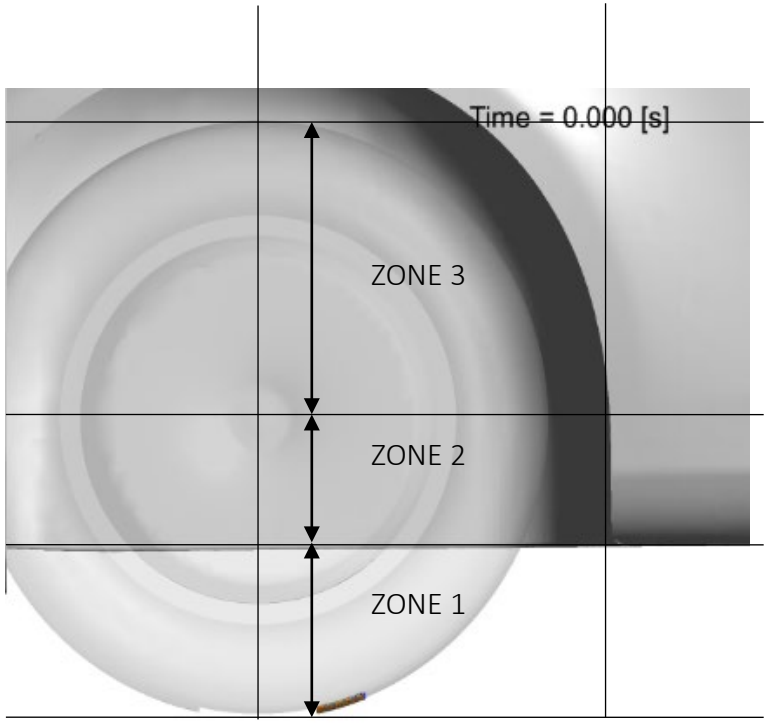


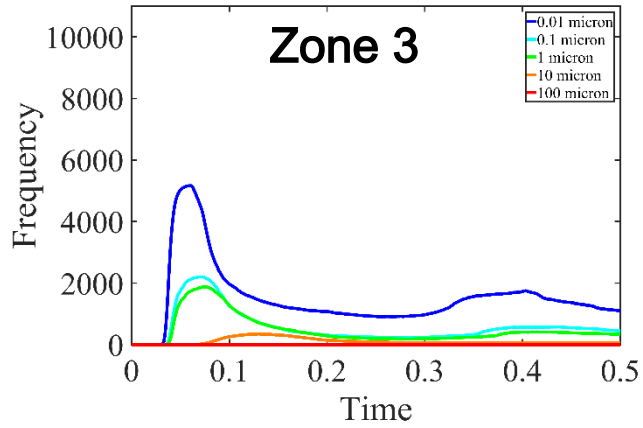
10 [mph]

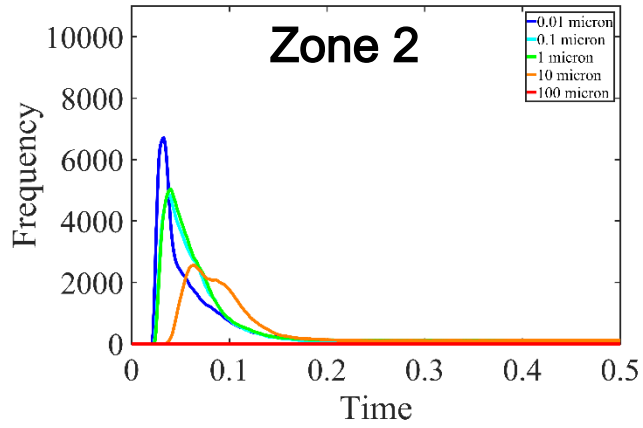


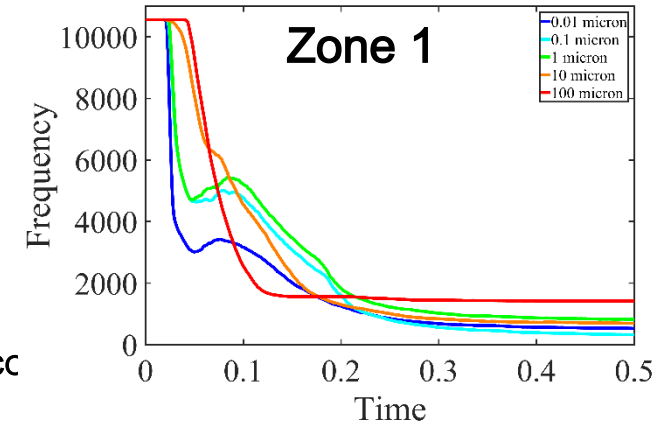
Location dependency

- Instantaneous particle concentration over time
- By size class
- By collection location









Chemical composition

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EQUA real-world test database

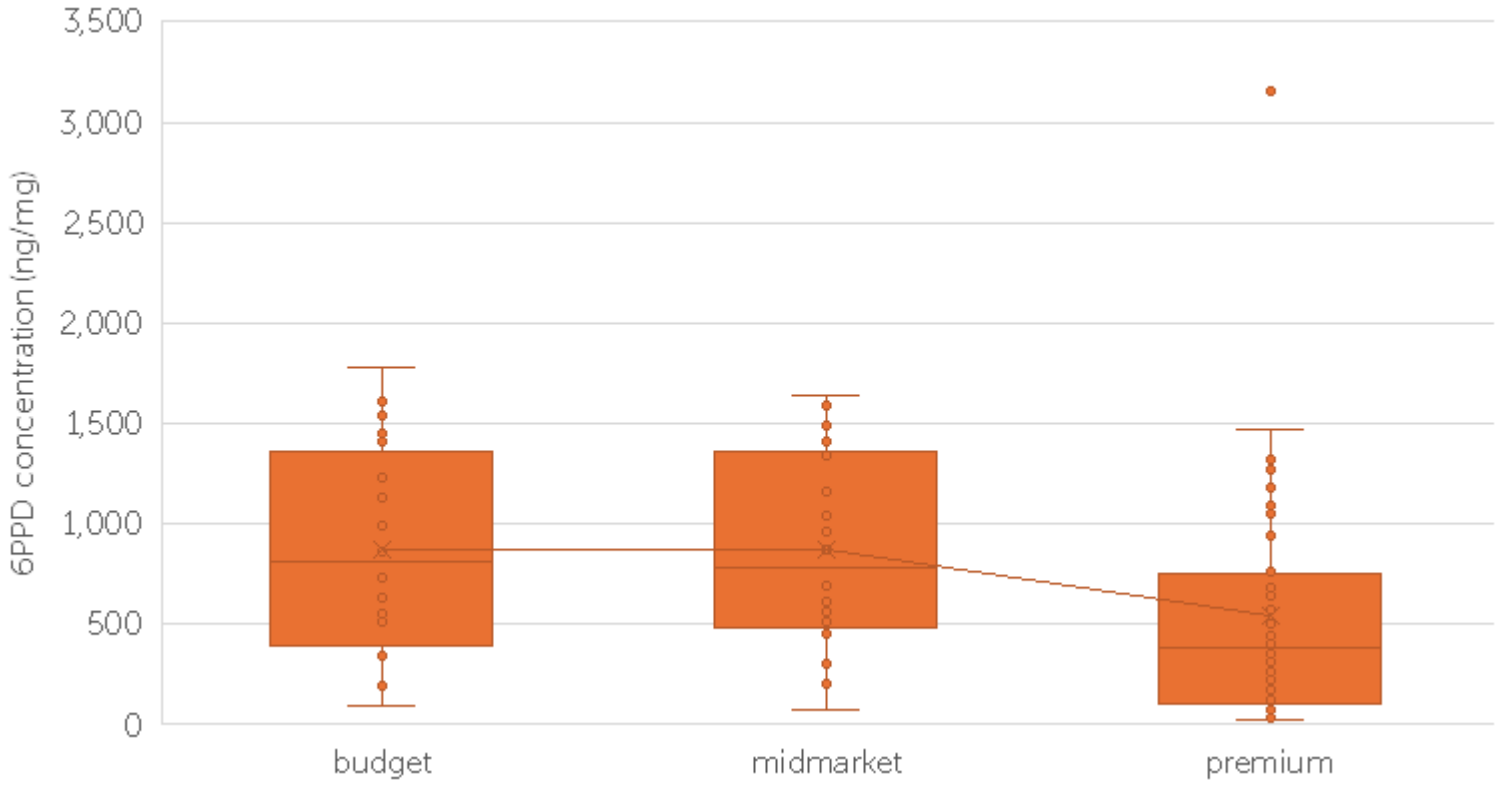
US car tyres contain less 6PPD than Europe

- Similarly lower 6PPD for pick-ups and vans
- But similar concentrations for heavy-duty vehicles
- 6PPD concentrations in the US are similar whatever the tyre application

ng/mg	Light	Medium	Heavy
USA	701	743	775
Europe	1,541	1,243	795
Difference: US vs Europe	(55%)	(40%)	(3%)

Premium tyres have less 6PPD in Europe…

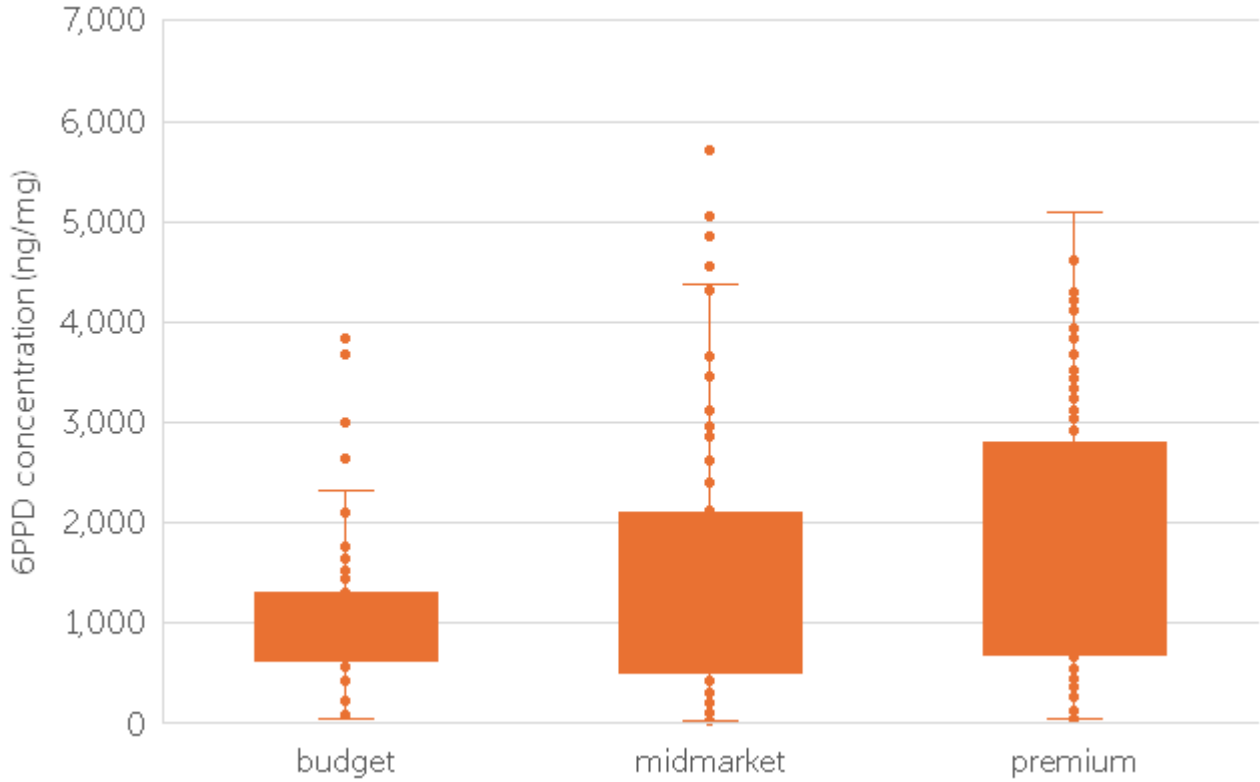
- Product segment determined by list price
- Premium tyres have 53% lower 6PPD concentrations than budget tyres
- Wide variability within each category
- Similar average concentrations between budget and midmarket tyres



BTAS brake and tyres analysis system

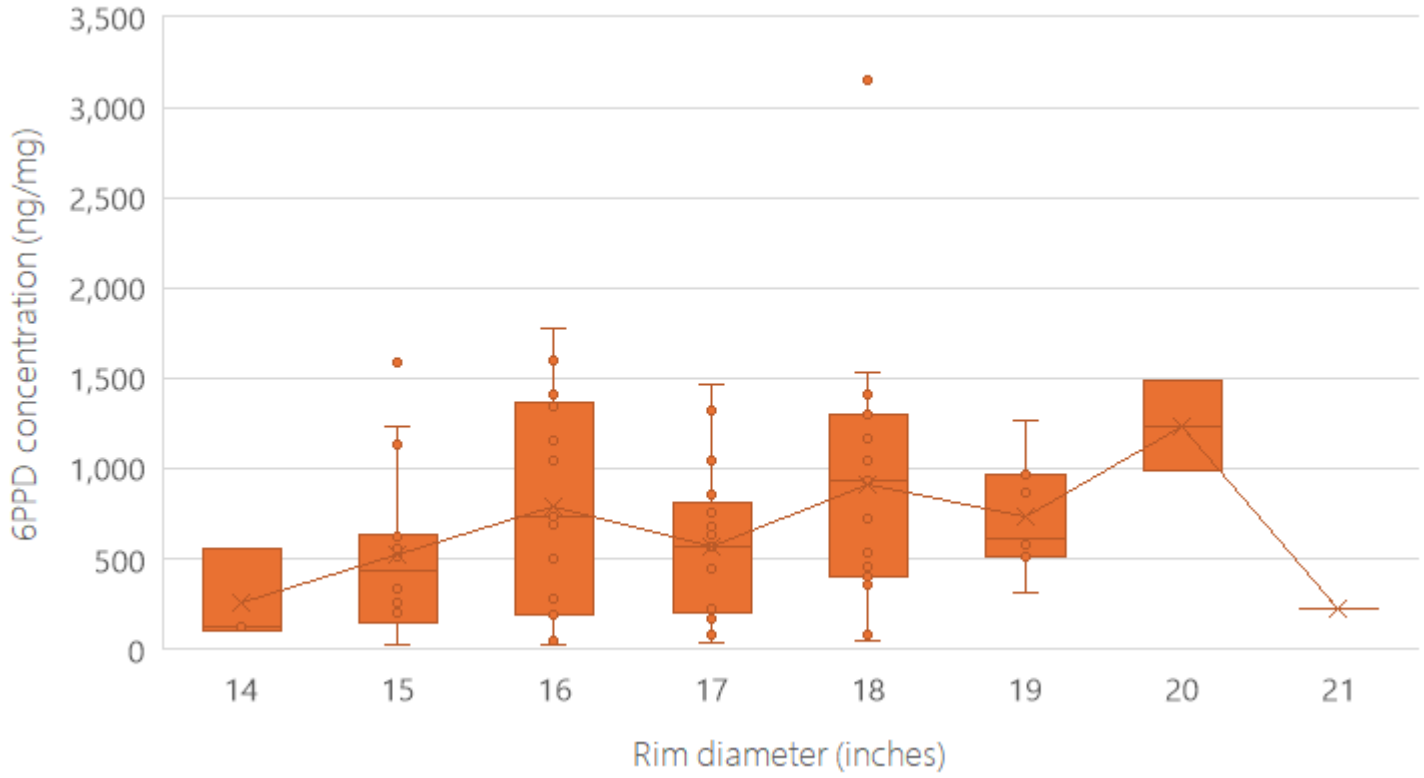
…but more 6PPD in the US

- Premium tyres have 67% higher 6PPD concentrations than budget tyres
- Different profiles of manufacturers, manufacture locations and usage cases



6PPD increases with tyre diameter in the US

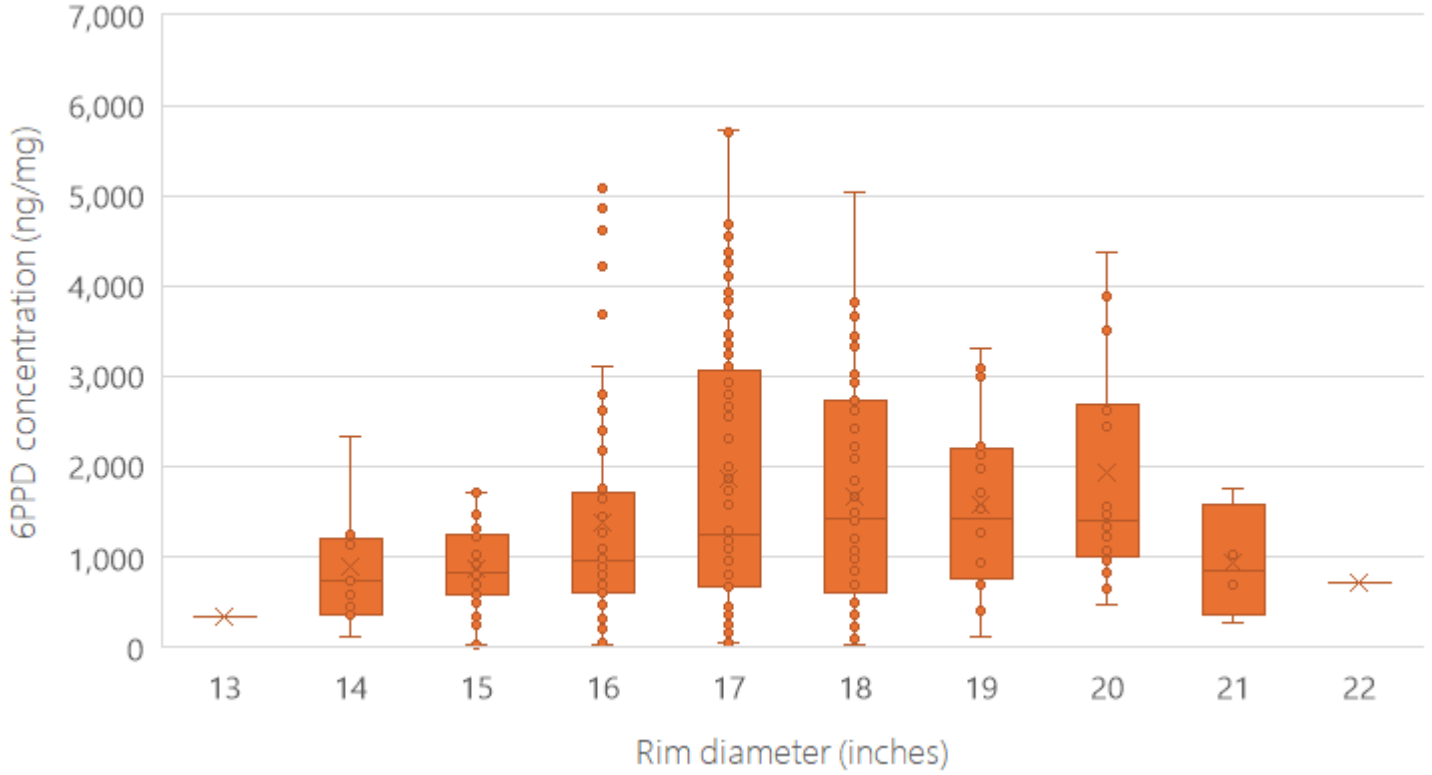
- Significant variability within rim categories, but clear positive correction
- 20” tyres on average have 6PPD concentrations x4.8 compared to 14” tyres
- Similar trends not seen with tyre width



BTAS brake and tyres analysis system

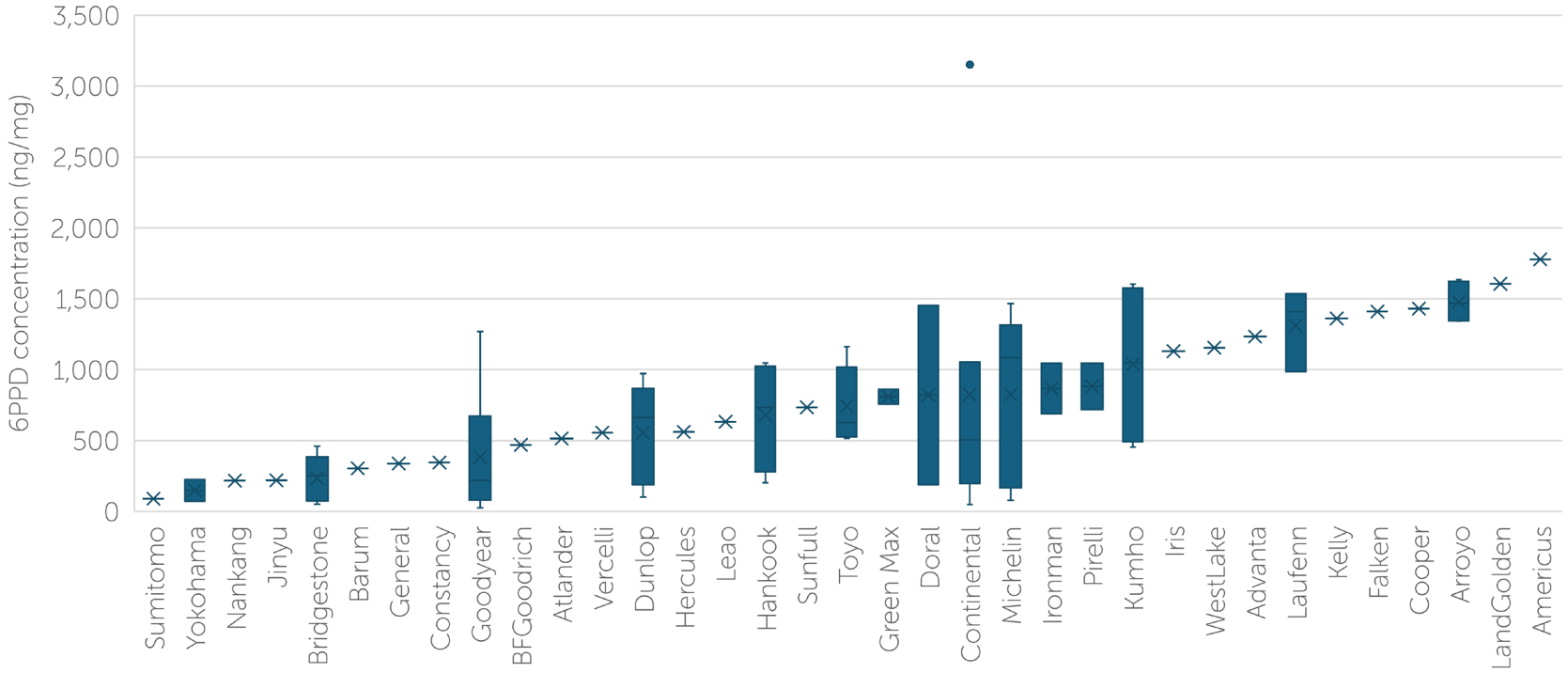
…true also in Europe, but less so

- Significant variability within rim categories, but clear positive correlation
- 20” tyres on average have 6PPD concentrations 88% higher than 14” tyres
- Similar trends not seen with tyre width



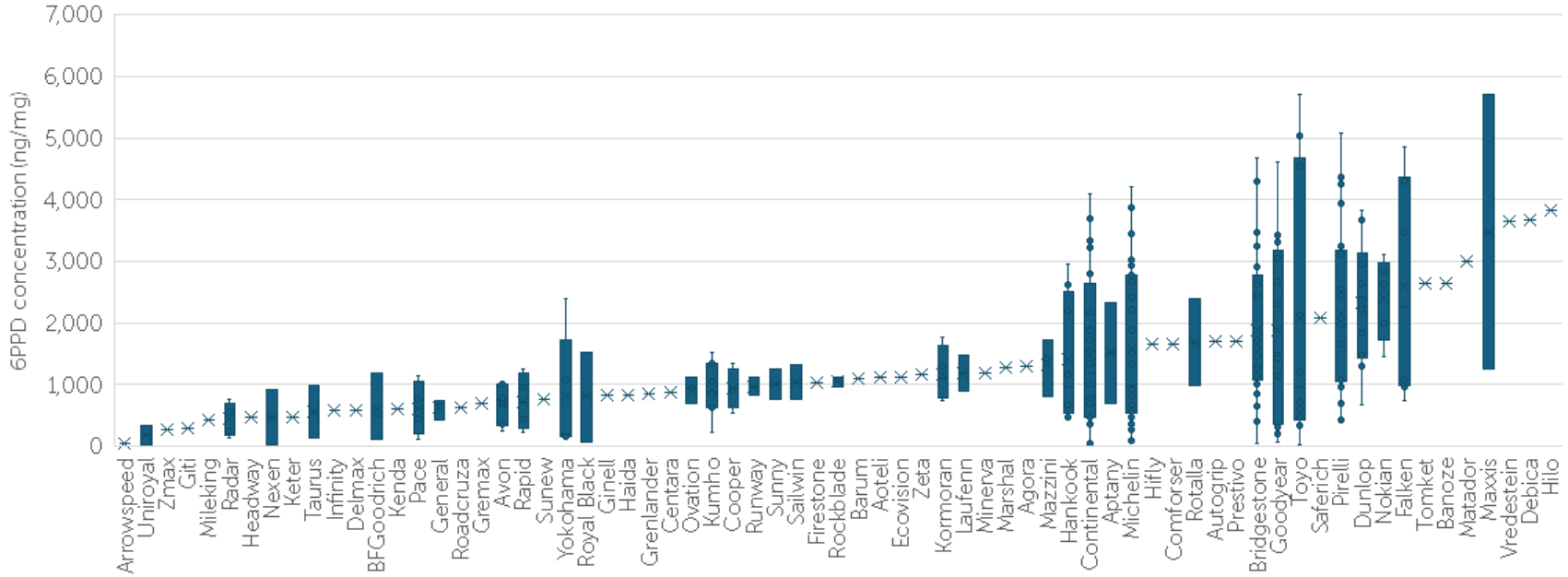
Manufacturer rankings – US car tyres

- Of manufacturers with multiple tyres tested…
- Yokohama has lowest 6PPD, 79% below average
- Arroyo has highest, x2.1 average
- Variability with each OE product range



Manufacturer rankings – EU car tyres

- Yokohama also at low end in Europe
- Established European and US manufacturers clustering in 1,500-2,500 ng/mg range
- Large variability points towards efficacy of limit value



Alternatives to 6PPD

- Highest concentrations of 6PPD and its alternatives tend to be found in winter tyres
- Tyre manufacturers experimenting with 6PPD substitution

Michelin Alpin 6 225/50 R17 98H

Details

Region	Europe	Fuel Efficiency Class	n/a
Tyre Type	Light	Wet Grip Class	n/a
Market Segment	Premium	Rolling Noise Class	n/a
Tyre Size	225/50 R17	Rolling Noise Level	n/a
Load Rating	98	Use in Severe Snow	n/a
Speed Rating	H	Use in Severe Ice	n/a
Country of Manufacture	Spain		
Year of Manufacture	2019		
Week of Manufacture	49		

Top 10 substances found from target list

CAS #	Substance	Concentration
		µg/mg
793-24-8	6PPD N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine	3.926
101-72-4	IPPD N-Isopropyl-N'-phenyl-pphenylenediamine	2.071
147-47-7	TMQ 1,2-Dihydro-2,2,4-trimethylquinoline	0.170
122-39-4	DPA diphenylamine	0.126
494-19-9	IDB iminodibenzyl	0.010
5650-10-2	IP-DPA isopropyl-diphenylamine	0.007
552-82-9	DPMA diphenylmethylamine	0.002
6267-02-3	DM-AD dimethyl-acridan	0.000

6PPD and Alternatives

For more information about this target list, visit .

Search:

Tyre	Total concentration	Substances found
	µg/mg	# (% of list)
Toyo Observe S944 225/50 R17 98V XL	6.668	9 (15.79%)
Michelin Alpin 6 225/50 R17 98H	6.312	8 (14.04%)
Maxxis Premitra Snow WPG 225/50 R17 98V	6.192	8 (14.04%)
Michelin Alpin 6 215/55 R17 98V XL	5.605	7 (12.28%)
Toyo Snowprox S954 235/40 R18 95V	5.542	8 (14.04%)

All winter tyres

Wider compounds of interest

- 15,916 unique compounds so far identified from tyres
- Six notable compounds of potential concern…

Compound	Formula	Uses	Chronic effects (non -cancer)	Cancer risk
Aniline	$C_6H_5NH_2$	Chemical intermediate; solvent	Cyanosis; irritant to eyes, skin, upper respiratory	EPA probably carcinogen
Diphenylamine	$C_{12}H_{11}N$	Antioxidant	Skin, eye irritant; kidney, bladder, liver damage	Not likely
Ethylbenzene	C_8H_{10}	Styrene intermediate; solvent	Acute respiratory; eye irritation; dizziness	n/a
Naphthalene	$C_{10}H_8$	Intermediate in plasticisers, resins	Cataracts and retinal damage; respiratory inflammation	EPA possible carcinogen
Phenol	C□H□O	Intermediate in phenolic resins	Weight loss; diarrhoea; stomach irritation; liver effects	n/a
Styrene	C_8H_8	Intermediate in plastics, resins	Effects on central nervous system	Possible link to leukaemia

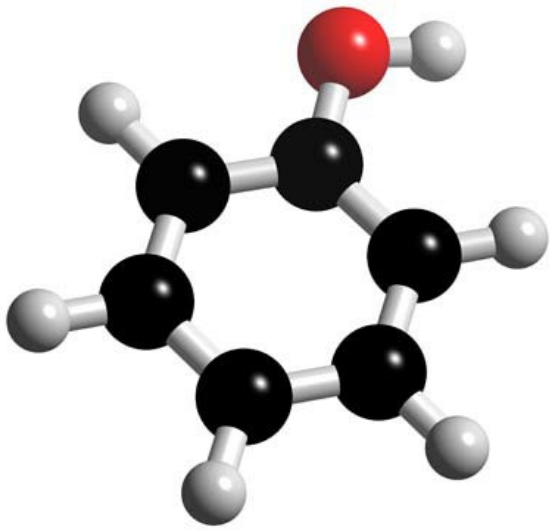
Hazards

Hazard code	Description
H300	Fatal if swallowed
H301	Toxic if swallowed
H302	Harmful if swallowed
H303	May be harmful if swallowed
H304	May be fatal if swallowed and enters airways
H305	May be harmful if swallowed and enters airways

- Globally Harmonized System of Classification and Labelling of Chemicals (GHS) – United Nations' standardised system
- Compounds identified CAS Registry Number, unique identifier assigned by US Chemical Abstracts Service
- European Chemicals Agency database of manufacturer disclosures
- 'Hazard codes' describe different effects, from irritants to carcinogens
- Each compound can have multiple hazard codes
- Which can be weighted together using a severity index

$$\text{Overall toxicity factor} = \sum_{i=1}^{n} \text{Number of hazard codes}_i \times \text{Compound concentration in sample } (\mu g/mg)_i$$

Potential toxicity



ng/mg	Toxicity factor	Relative to 6PPD
6PPD	22	1.0
IPPD	13	0.6
Aniline	52	2.4
Diphenylamine	33	1.5
Ethylbenzene	43	2.0
Naphthalene	37	1.7
Phenol	64	2.9
Styrene	37	1.7

Further insights

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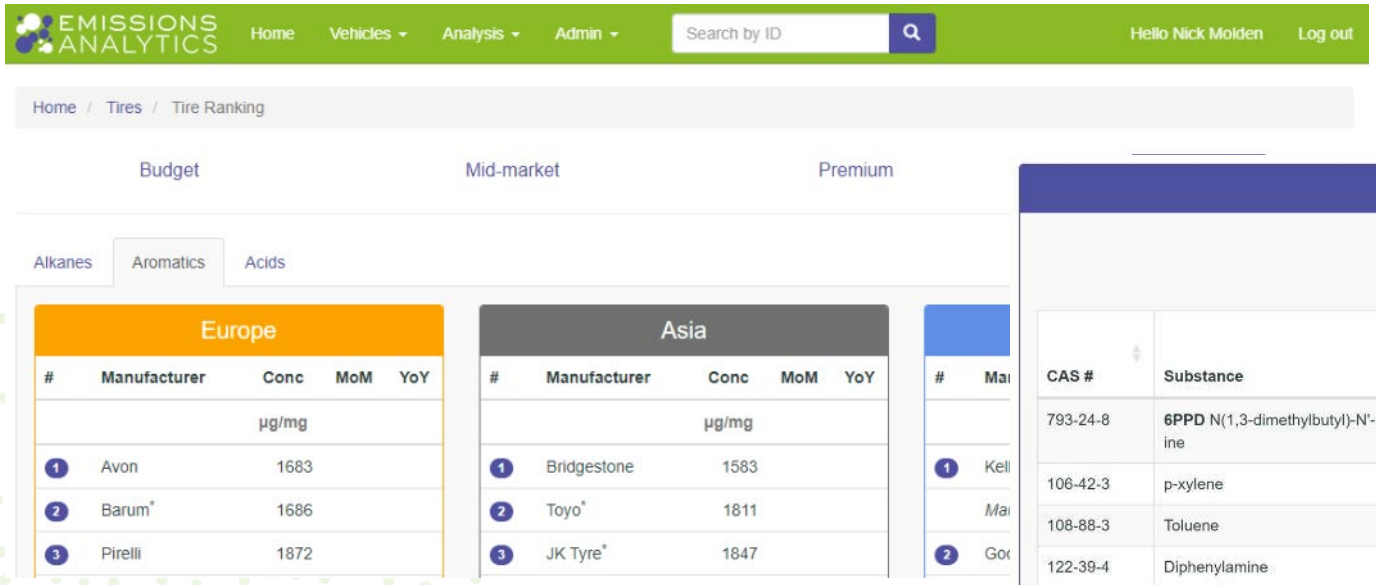
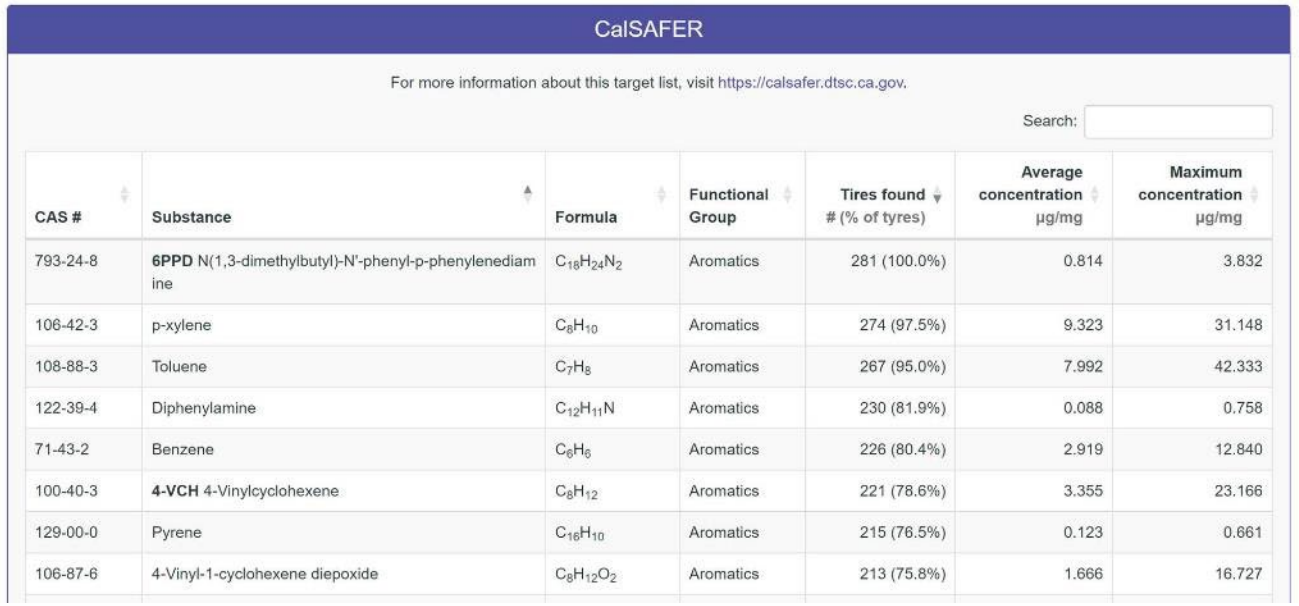
Tyre Emissions Research Consortium

https://www.linkedin.com/company/tyre -emissions-research-consortium

Tyre chemical fingerprint database





CalSAFER

For more information about this target list, visit https://calsafer.dtsc.ca.gov.

Search:

CAS #	Substance	Formula	Functional Group	Tires found # (% of tyres)	Average concentration µg/mg	Maximum concentration µg/mg
793-24-8	**6PPD** N(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine	$C_{18}H_{24}N_2$	Aromatics	281 (100.0%)	0.814	3.832
106-42-3	p-xylene	C_8H_{10}	Aromatics	274 (97.5%)	9.323	31.148
108-88-3	Toluene	C_7H_8	Aromatics	267 (95.0%)	7.992	42.333
122-39-4	Diphenylamine	$C_{12}H_{11}N$	Aromatics	230 (81.9%)	0.088	0.758
71-43-2	Benzene	C_6H_6	Aromatics	226 (80.4%)	2.919	12.840
100-40-3	**4-VCH** 4-Vinylcyclohexene	C_8H_{12}	Aromatics	221 (78.6%)	3.355	23.166
129-00-0	Pyrene	$C_{16}H_{10}$	Aromatics	215 (76.5%)	0.123	0.661
106-87-6	4-Vinyl-1-cyclohexene diepoxide	$C_8H_{12}O_2$	Aromatics	213 (75.8%)	1.666	16.727

- Substances of concern tracking
- For benchmarking, research and development

Tyre Insights subscription report

- First issue out now
- Four issues per year, delivered electronically

Human health effects

Tyre Wear Particles (TWPs) are respirable and will deposit in the lower airway, possibly exacerbating lung cancer and COPD risk.

TWPs tend to induce a negative cellular response, with inflammation increasing with dosage.

More research is required to distinguish the health impacts of TWPs from other Non-Exhaust Emissions.

The health effects of a particle are highly dependent on its physicochemical characteristics[1] and in this domain, Tyre Wear Particles (TWPs) are no different. It is well known that exposure to PM2.5, the size fraction of PM defined as respirable, can reach the lower airway. PM2.5 exacerbates asthma and chronic obstructive pulmonary disease (COPD), as well as causing death through lung cancer and other cardiovascular diseases[2]. These problems are exacerbated by the presence of Ultrafine particles (UFPs) where dp <100 nm a major component of TWPs are particularly worrisome as they reach and deposit efficiently in the alveolar region and cross cellular membranes[3].

There are few epidemiological studies, which are the golden standard of toxicological research on the health effects of TWPs, our literature search for these studies led to few results and it is worth noting that these studies can't differentiate effectively between all types of Non-Exhaust Emissions (NEEs) and most

References

1. Baensch-Baltruschat, B., Kocher, B., Stock, F. & Reifferscheid, G. *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 vol. 733 137823 (2020).

BTAS brake and tyres analysis system

Conferences

11-12 February, Prague

30 April-1 May,
California

Thank you.

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