AUTOMOTIVE TIRE TECHNOLOGY 2023

How to reduce emissions of micro particles from tyres to minimise health and environmental impact and avoid reputational damage

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EMISSIONS ANALYTICS

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Agenda

- How prevalent are tyre wear emissions?
- To what extent do they include micro plastics?
- What are their health and environmental effects?
- What are the options for reducing the impact?
- What reputation risks do tyre companies face?

The issue

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EQUA real-world test database

Omnipresence of tyre wear emissions

- 6 million tonnes of tyre wear globally per year
- Or 4 kg per car per year
- Excluding 1-2 billion end-of-life tyres per year
- Ultrafine particles (<100 nm) are airborne before eventually settling
- Fine particles settle on soil close to roadway
- Larger particles wash into the drainage system
- Multiple vectors for human inhalation or ingestion
- 135 ng of 6PPD and 6PPD-quinone in urine of average adult per day

Rapidly declining tailpipe emissions

- 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
- Tyres are x1,850 times more polluting on this measure

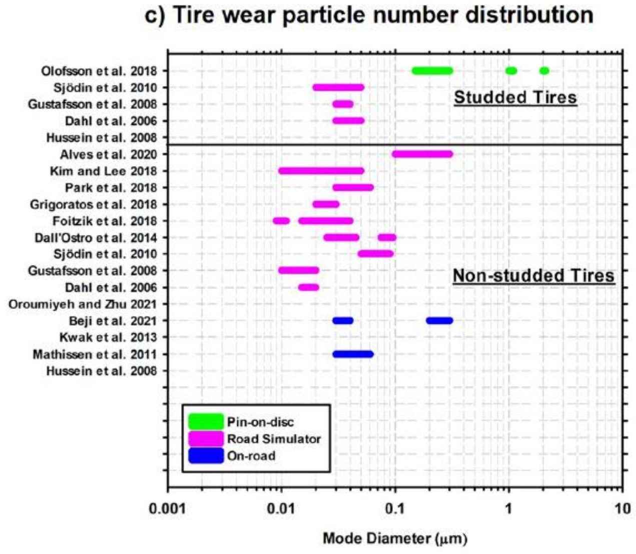
- 14.5×10^{11} #/km is x2.4 maximum permissible tailpipe number emissions
- 0.9×10^{11} #/km is actual gasoline PN, and 0.1×10^{11} #/km is actual diesel
- Tyres are x29 times more polluting on this measures, averaged across fuel types

Ultrafine particles from tyres

- On-road test with ‘normal’ dynamics
- 11% of fine particle mass is below 2.5 μm diameter
- This mass accounts for almost 100% of particle number
- And ultrafines account for 92% by number
- Other potential source of ultrafines is from combustion, but influence from other vehicles eliminated
- Results borne out in academic literature

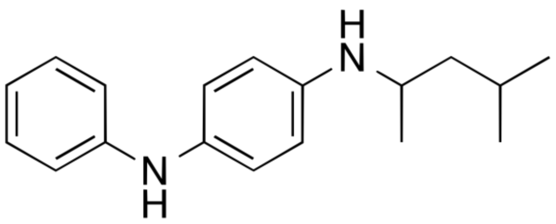
➢ Tyres are simultaneously a problem for air, soil and water

Particulate mass	mg/km
PM10	36.5
PM2.5	4.1
PM2.5 proportion of PM10	11%
Ultrafine proportion of PM10	0%
Particulate number	**#x10^11/km**
Down to 23 nm	1.1
Down to 6 nm	14.5
Fine as proportion of PM10	8%
Ultrafine as proportion of PM10	92%

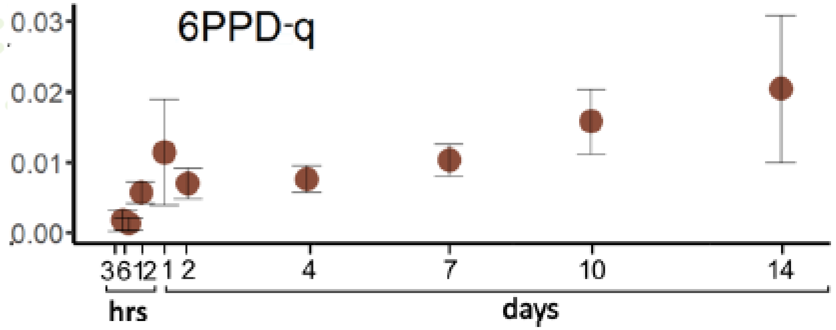


Derivative products

- Formation of 6PPD-quinone by oxidation of 6PPD preservative
- 6PPD-quinone killing coho salmon and trout in US
- Absorbed through roots of lettuce

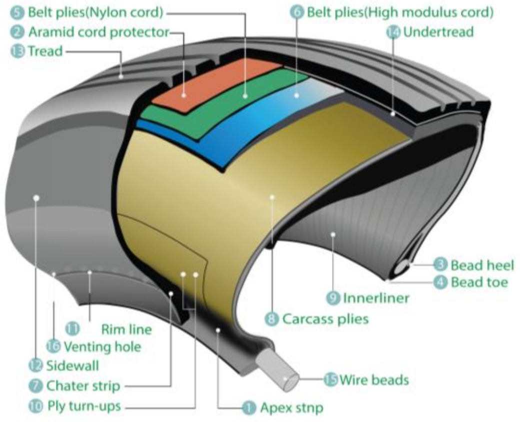


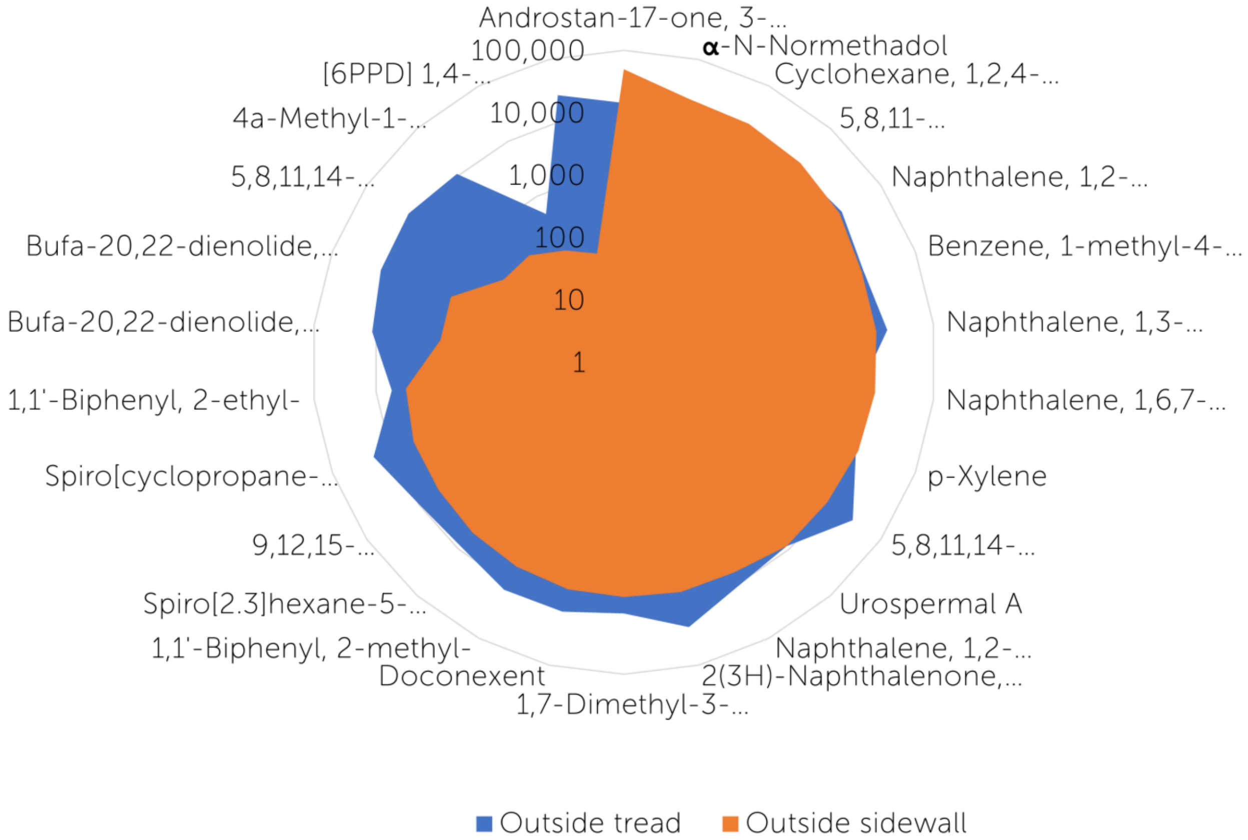
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, aka 6PPD



Secondary pollutants

- Secondary organic aerosol formation from off-gassed VOCs reacting in air
- Mainly from tyre sidewall, which can be different chemical composition from tread
- SOA Yield of 4.01 μg/m³ from toluene in recent research in Shanghai





TEMS tyre emissions measurement system

Experimental approach

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Concept

Tyre wear rate

x

Chemical speciation

x

Compound hazard

=

Potential environmental impact

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

Chemical fingerprinting

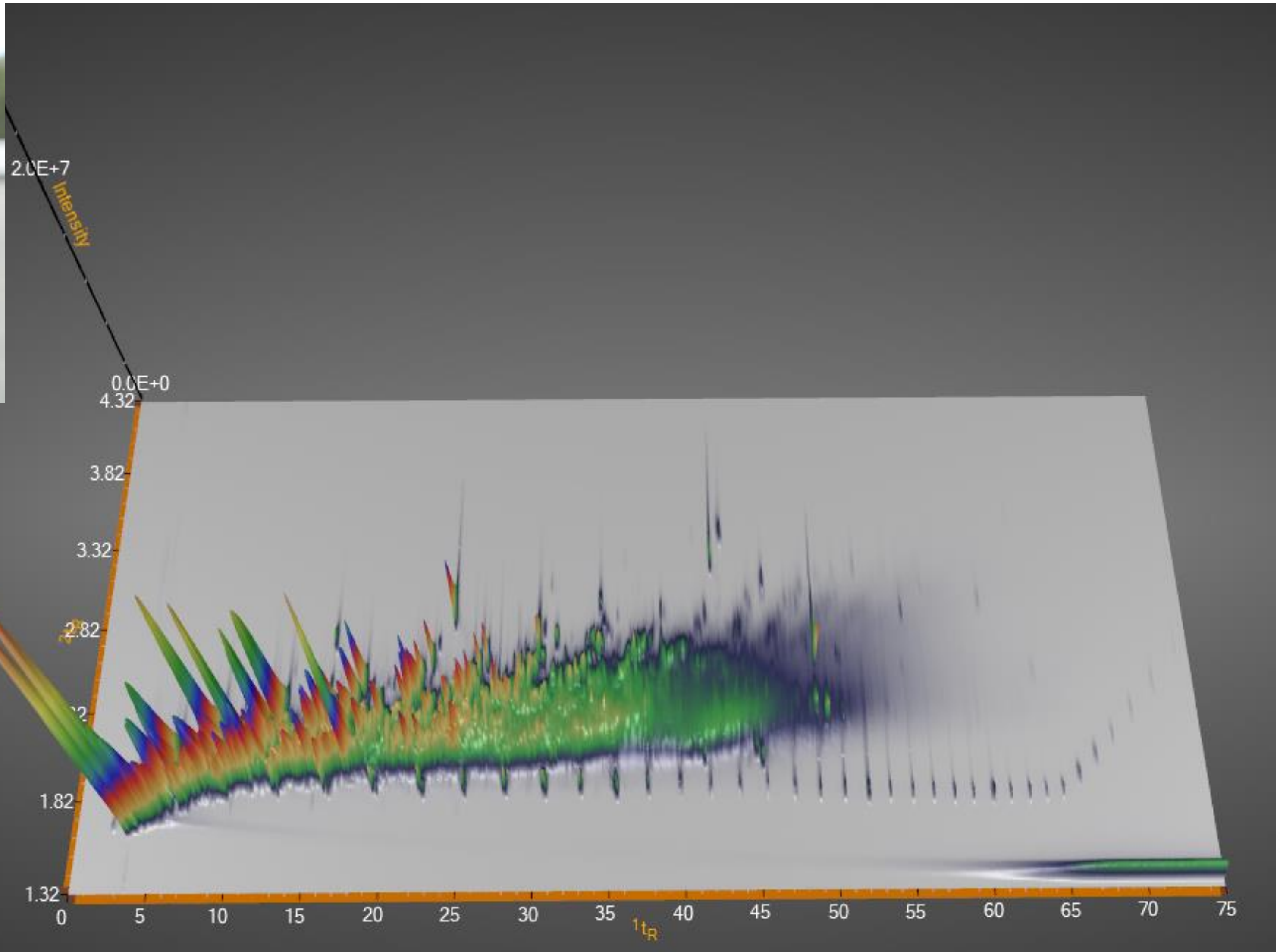
- Two-dimensional gas chromatography with mass spectrometry
- INSIGHT flow modulator from SepSolve Analytical for separation
- BENCH-TOF time-of flight mass spectrometer
- Multi-stage pyrolysis method

Analytical methodology

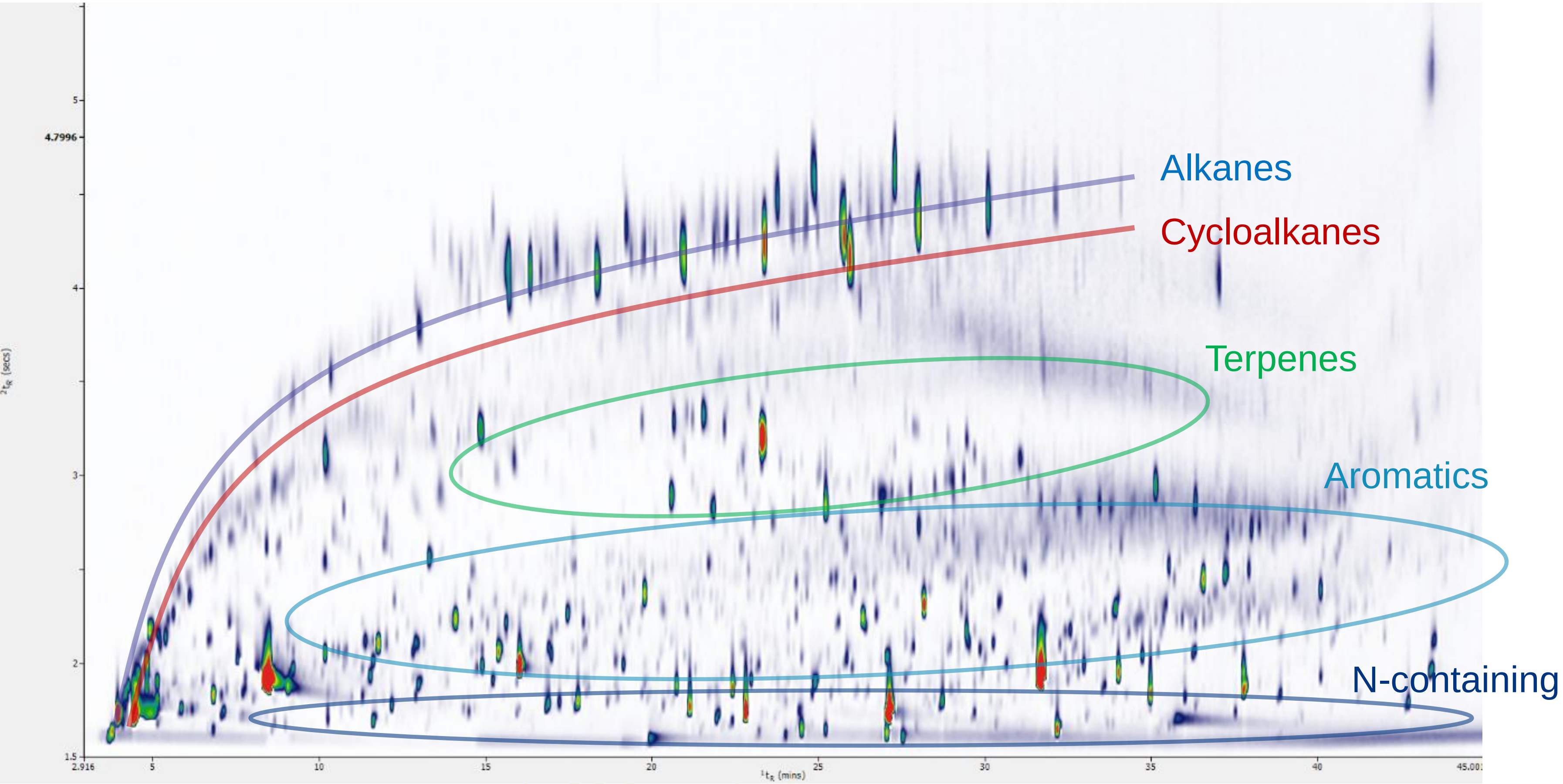
- *Are the compounds measured really in the originally tyre?*
- *Does the high temperature of the pyrolysis lead to compounds breaking down?*

- Due to the very rapid heating and then flushing out of the hot zone, the pyrolysates are likely to remain unchanged, with secondary reactions and pyrolysate aggregation occurring rarely (Shin Tsuge, 2012) (Xiao-Ming Ma, 2014).
- The degradation process is useful for understanding the structure of the polymer but also for determining what smaller molecules could possibly be formed and for example, leach into the environment (Ladak, 2021) (Greta Biale, 2021).

Two-dimensional pyrolysis chromatogram



Functional group classification



- Wide-ranging analytes identified

- Alkanes: lungs, liver, kidney, brain
- Cycloalkanes: headaches, dizziness
- Terpenes: aromas
- Aromatics: carcinogens
- N-containing: carcinogens

TEMS tyre emissions measurement system

Method development

- Objective to determine all compounds in tyre as sold to user
- Estimate potential to leach organic chemicals over time
- Quantification of measurement uncertainty – National Physical Laboratory, UK
- Required development of specialist spectral library
- Peer reviewed

➢ Allow fair comparison between different tyres

Tyre wear results

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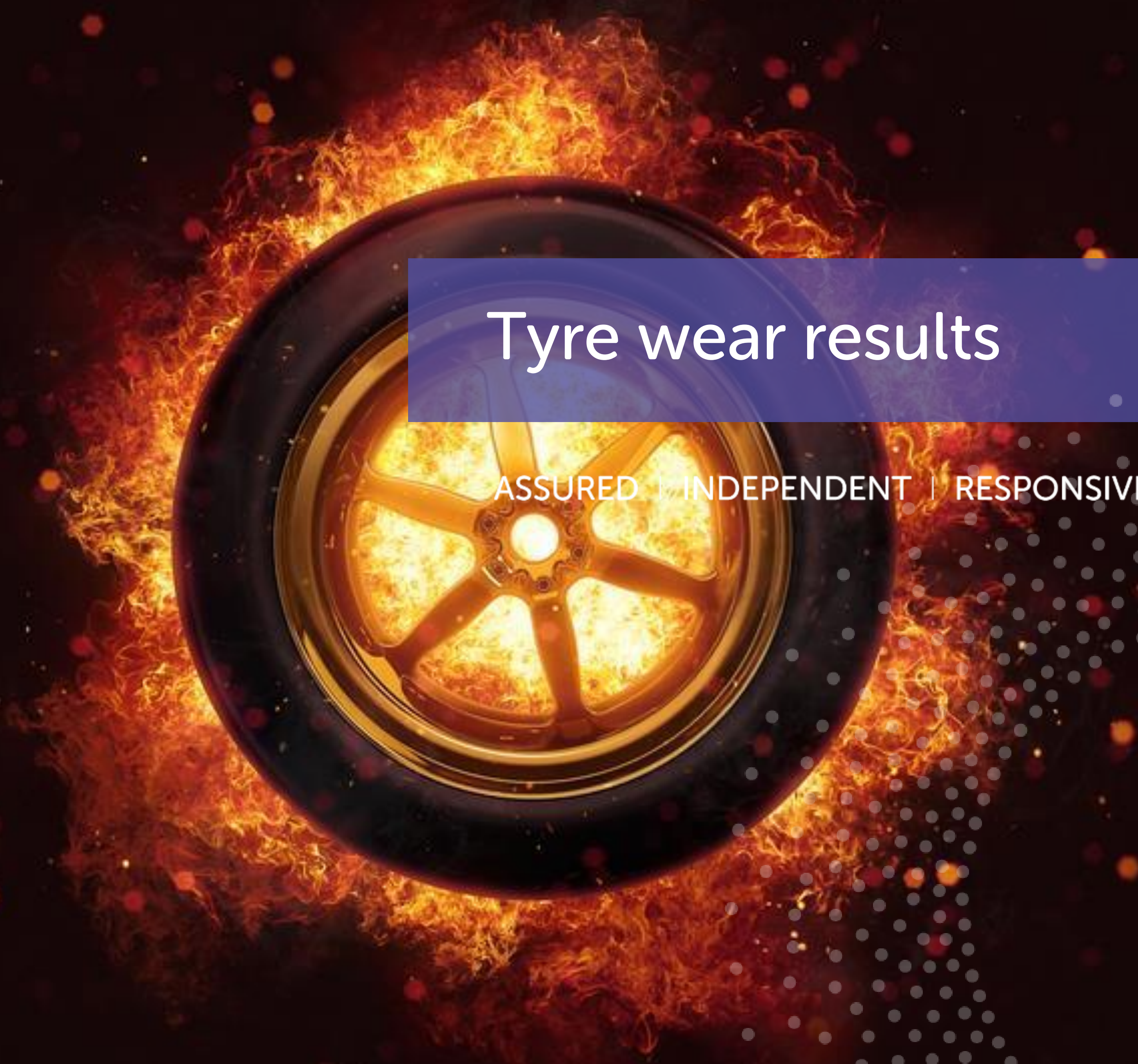


Comparative tyre wear results

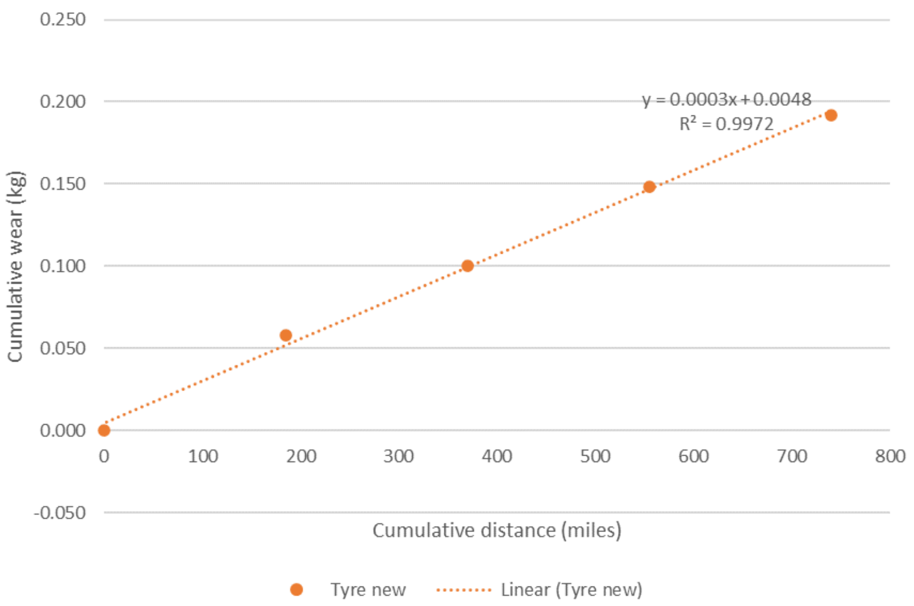
- 18 different models of tyre
- Tested from new
- 90% motorway driving by distance
- Public highway
- Average total distance 5,300 km

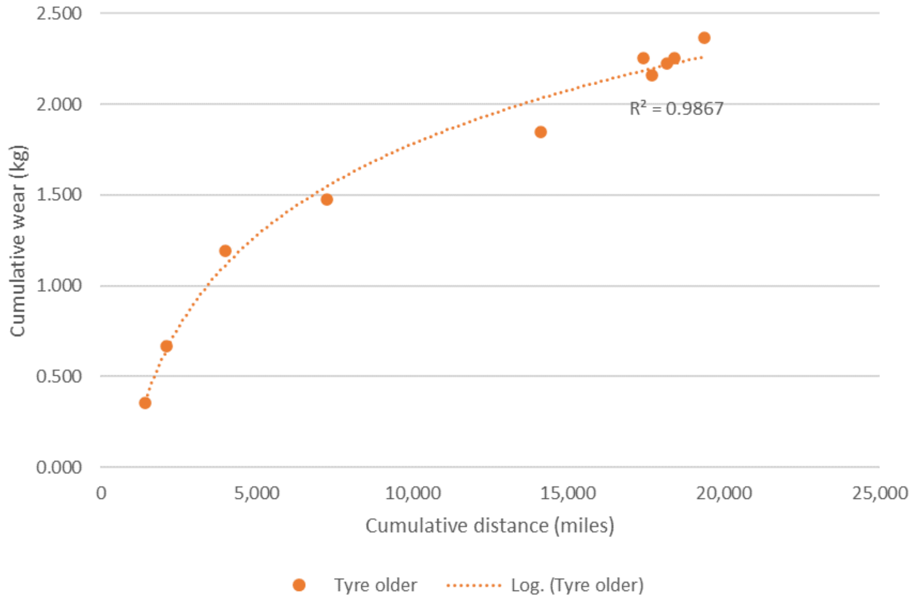
- 67 mg/km mean

Tire #	Manufacturer	Wear rate (mg/km)
1	Continental	161
2	Michelin	61
3	Sumitomo	38
4	Firestone	73
5	Avon	45
6	Kumho	75
7	Yokohama	89
8	Goodyear	75
9	Apollo	61
10	Kumho	51
11	Michelin	81
12	Hifly	76
13	Kumho	17
14	Rotola	66
15	Taurus	70
16	Bridgestone	46
17	Nankang	87
18	SnowRoad	44
	Average	67

Longitudinal results

- Continental Contisport 6 tyres on Mercedes C-Class/unladen
- Tyres tested from new
- Wear rate linear up to ~1,000 km
- Then approximately logarithmic trend up to ~30,000 km
- Shape of cumulative wear differs between models





TEMS tyre emissions measurement system

Chemical speciation

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Speciation

- Toluene equivalence used for quantification
- Proportion of the most toxic group – the aromatics and PAHs – varies between 25% and 80% across 100 tyres

Mass in sample (µg)	Group 1 Acids, Amine and Alcohols	Group 2 Alkanes, Alkenes, Alkynes, Cyclo, Aldehyde and Ketone	Group 3 Aromatics and PAH
UKT003	4.9	40.6	178.6
UKT009	2.2	66.1	65.0
UKT012	2.2	57.9	58.4
UKT013	2.4	119.2	98.4
UKT014	4.5	116.6	87.0
UKT016	4.9	132.8	73.3
UKT022	8.4	156.2	83.6
UKT023	2.6	95.6	69.8
UKT024	1.7	65.7	63.2
UKT025	8.9	194.9	69.9

Compound	Match Factor	Area %	Mass (ng)	Concentration (ng/mg)
1,3-Pentadiene	817	9.83	24,884	23,476
D-Limonene	789	6.58	16,660	15,717
Cyclohexene, 4-ethenyl-	667	4.95	12,526	11,817
Toluene	781	4.19	10,619	10,017
9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	729	3.05	7,727	7,290

Wear rates by brand

Compound release (μg/km) =
Tire wear rate (mg/km) x Compound concentration in sample (μg/mg)

- Distance-specific wear derived by brand and functional group
- Sevenfold difference in alkanes between highest and lowest
- Fourfold difference in aromatics across the range

Mass emissions (mg/km)	Group 1	Group 2	Group 3
Brand ID	Acids, Amine and Alcohols	Alkanes, Alkenes, Alkynes, Cyclo, Aldehyde and Ketone	Aromatics and PAH
1	0.339	2.823	12.407
2	0.162	5.780	5.262
3	0.328	8.507	6.346
4	0.332	8.968	4.947
5	0.370	9.391	5.057
...			
36	0.208	9.515	7.282
37	0.382	14.397	12.456
38	0.306	9.103	5.828
39	0.357	8.513	5.557
40	0.326	7.969	12.468
Average	0.286	8.050	9.088
Minimum	0.087	2.396	4.947
Median	0.247	7.739	8.037
Maximum	0.970	17.005	20.951

Compound hazard

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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

Toxicity potential factor

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

- Over 300 tyres now tested
- 410 organic compounds separated on average
- 46 hazard codes cited
- Challenge of compound identification
- 78 organic compounds identified using NIST library
- Bespoke spectral library resolves the remainder

Toxicity potential results

- Comparison across individual tyres in database
- Zero means absence of any substances of concern
- No tyre achieves this standard
- Factor of x6 from best to worst
- Worst is x3 the average

Tire #	Toxicity potential factor
UKT210	485
ULT035	493
UKT214	511
UKT138	550
UKT012	553
…	
UKT089	1,856
UKT057	1,893
UKT076	1,929
UKT115	1,961
UKT243	3,269
Average	1,132
Minimum	485
Median	1,093
Maximum	3,269

Potential solutions

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EQUA real-world test database

Reduce wear rates

- Almost a factor of x10 from the slowest to fastest wearing models
- 28% reduction would be achieved by eliminating fastest wearing half of the market
- Need to consider trade-offs with safety, noise and efficiency
- Proposed Euro 7 vehicle certification includes placeholder for tyre wear limits
- Preferred test method is on-road convoy
- Future introduction would put downward pressure on wear rates

Reduce potential toxicity

- Opportunity to remove the highest potential toxicity products
- Any scoring system would need to be validated against toxicological experiments
- Chemical disclosure could be extended, building on ECHA work
- Specific, high-toxicity chemicals could be banned
- Manufacturers could be forced to consider alternatives – as in California
- Limit values could be set on target chemicals – as REACH already does
- Consumer labelling to influence demand

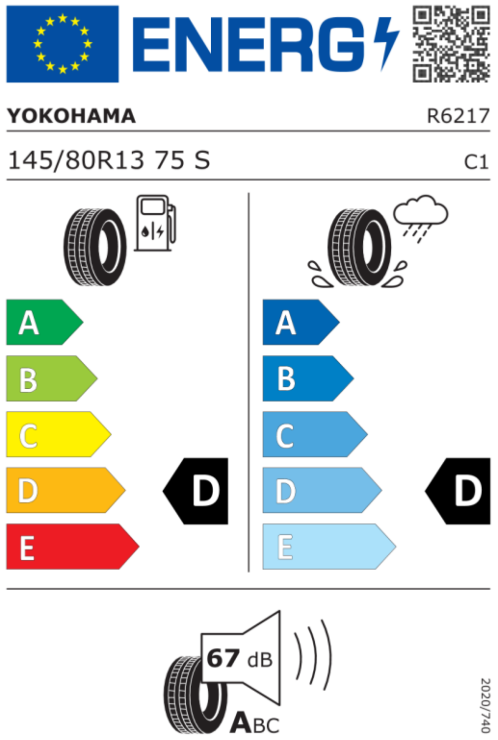
Targeted screening

- Compounds regulated under REACH, found in tyres
  - ($C_{18}H_{12}$) Chrysene
  - ($C_{18}H_{12}$) Benz[a]anthracene

- Other compounds of concern found
  - ($C_{18}H_{24}N_2$) [6PPD] 1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-
  - (C_7H_5NS) [BTZ] Benzothiazole
  - ($C_{15}H_{18}N_2$) [IPPD] 1,4-Benzenediamine, N-(1-methylethyl)-N'-phenyl-
  - ($C_7H_5NS_2$) [MBTZ] 2-Mercaptobenzothiazole
  - ($C_{18}H_{16}N_2$) [DPPD] 1,4-Benzenediamine, N,N'-diphenyl-

Consumer labelling

- Official tyre labels exist in multiple regions
- Current focus on rolling resistance, grip, weather and noise
- Pollutant emissions are currently excluded
- Closest proxy is 'tread wear rating' in US
- Price is important additional metric



- ➢ A standard method could allow toxicity rating to be added
- ➢ Immediately wear rates and composition can be correlated to performance, to aid development less toxic tyres without compromising performance

Innovative formulations

- Recapping tyres can significantly change toxicity of existing tyres
- Bio-based tyres can be lower toxicity potential and reduced aromatics, but not necessarily
- May increase aquatic toxicity while reducing human effects
- Tyres must be assessed individually

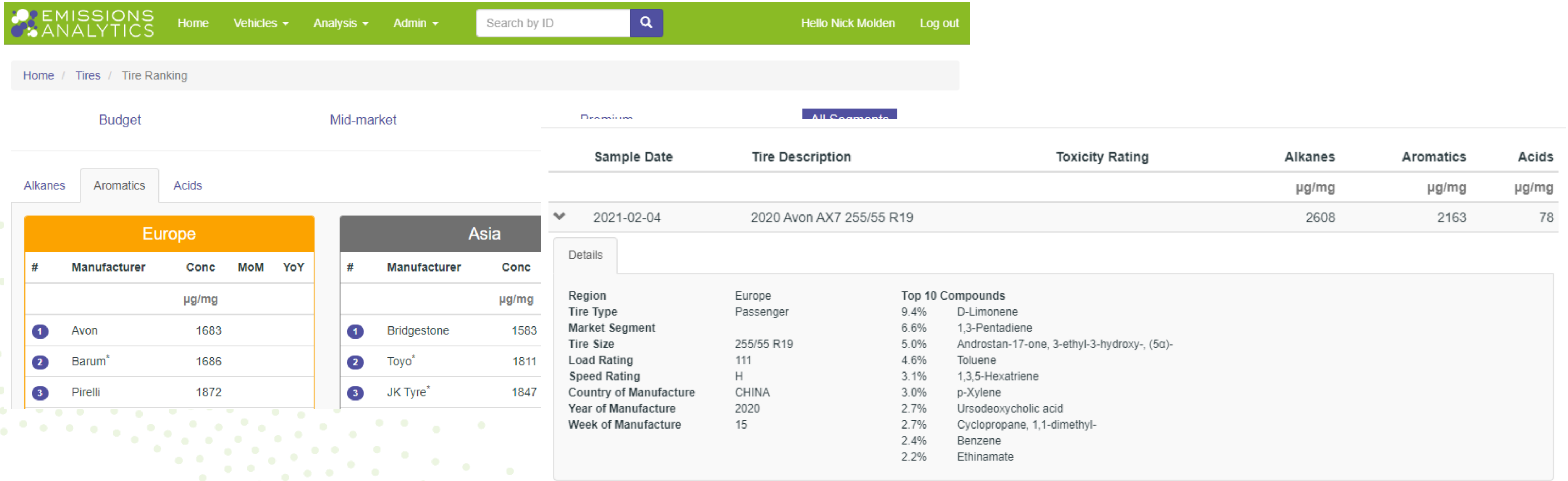
Tyre	Potential toxicity rating	Proportion of aromatics	
Goodyear	53	31%	As new
Goodyear	16	68%	Recapped
Goodyear	42	42%	Soy-based
Other bio-tyre	93	TBC	Non-automotive
Average	**53**	**48%**	

Summary

- Tyre wear emissions are all around and inside us
- Encompassing larger and smaller particles, but tyres also off-gas VOCs
- Real-world, real-time measurement is practical
- Chemical speciation and potential toxicity can be understood better
- A range of options for control or mitigation are now possible.

➢ Tyre wear emissions will rapidly become the dominant pollution from new vehicles

Subscription database



- Fingerprinting database now live
- For benchmarking, research and development

Thank you.

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Independent
Objectivity and candour are the driving forces in all our work, so you know the facts.

Responsive
We're fast on our feet so we can conduct emissions testing when and where we're needed.

EMISSIONS ANALYTICS

Our Belief

When it comes to the pursuit for improved air quality, we believe in the power of clarity, transparency and integrity. With real-world data we can meet emissions challenges – instilling trust and confidence in our industry partners and public.

It's with our commitment and independence we are able to make a significant contribution toward positive change and to achieve enduring results.