EMISSIONS ANALYTICS

# Tire wear, chemical composition and toxicity

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# 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.

# Introduction

- Founded in 2011, headquartered in the UK
- Operations in UK, Germany, USA and South Korea
- Independent testing house specialising in real-world emissions testing
- Over 2,500 vehicles/machines tested across passenger, commercial and off-road
- >100 tires tests, >100 vehicle interior tests
- Largest commercially available database of real-world emissions data
- Work with regulators, OEMs, Tier 1/2 suppliers, fuel and chemical companies, fleets
- Chair of EU CEN Workshops 90 and 103
- Honorary Research Fellow, Imperial College London

# Agenda

1. Tire wear problem
2. Determining chemical composition
3. Measuring wear rates
4. Emissions toxicity
5. Environmental effects
6. Wider context



 

# The problem

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# The tire emissions problem

- Over 300,000 tonnes of tire 'rubber' are released in US/Europe annually
- Emissions rates are increasing while tailpipe emissions are falling
- Tires have complex, opaque chemistry
- Environmental propagation and health effects are poorly understood
- No real-world standard test method exists

➢ Independent insight and clarity urgently needed

# Vehicle emissions sources and trends

| Emissions source | Trend |
|---|---|
| | |
| Tailpipe | Extremely low on new cars; removing older, dirty cars is priority |
| Brakes | Significant, but declining as regenerative braking becomes the norm |
| Road wear | Low but growing, due to increasing vehicle weight, and toxic |
| Resuspension | Significant, but often less toxic |
| Tires | Significant, growing and toxic |

# Determinants of tire emissions

| Lever | Sensitivity | Execution |
|---|---|---|
| | | |
| Reduce speed | Limited effect on per-mile emissions | Easy |
| Change tire model | High, but needs new information | Easy |
| Drive and corner more smoothly | Effective in principle; compliance hard | Moderate |
| Reduce vehicle weight | High, but offset by regenerative braking | Moderate |
| Improve road surface | Eliminating potholes to reduce damage | Difficult |
| Avoid problematic weather conditions | Unpredictable | Difficult |

# Concept

*Chemical speciation*

x

*Tire wear rate*

x

*Compound toxicity*

=

*Environmental impact*

# Chemical analysis

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# Measurements – volatile organic compounds

- Two-dimensional gas chromatography with mass spectrometry from
- INSIGHT flow modulator from SepSolve Analytical for separation
- BENCH-TOF time-of flight mass spectrometer
- OPTIC-4 sample introduction

National Physical Laboratory

# Method development

- Objective to perform 'accelerated leaching'
- Quantify organic chemicals released over time
- Allow fair comparison between different tires
- Perform high volume of tests

➢ Quantification of measurement uncertainty – National Physical Laboratory, UK
➢ Initial results peer reviewed by domain experts
➢ Submission to EU consultation on tire wear published

# Uncertainty budget

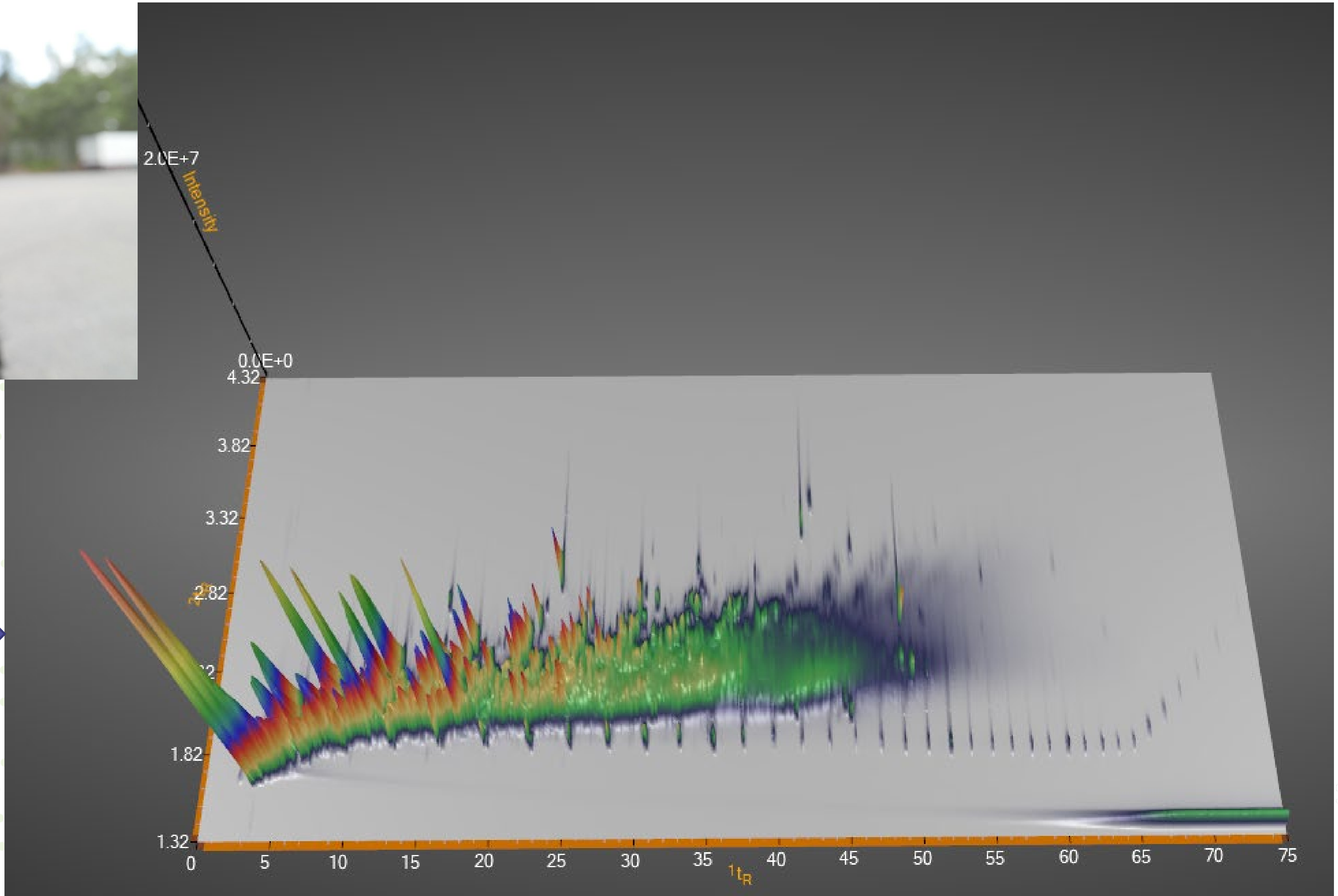
National Physical Laboratory

| Quantity | Relative uncertainty |
|---|---:|
| | |
| Mass of tire analysed | 0.7% |
| Peak area of sample – ion current | 3.5% |
| Compound extraction efficiency | 3.0% |
| Matrix match bias | 2.0% |
| Peak area of standard – ion current | 2.6% |
| Concentration of compound in stock solution | 1.5% |
| Volume of calibration compound on TD tube | 5.0% |
| Drift of instrument calibration | 44% |
| **Uncertainty total (k=1, 68%)** | 23% |
| **Uncertainty total (k=2, 95%)** | 47% |

- On parts-per-billion concentrati ons

Already significantly reduced

# Two-dimensional pyrolysis chromatogram



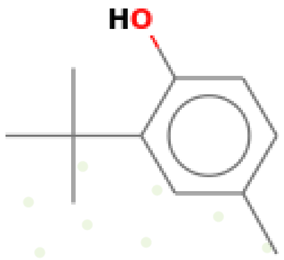
# Common, prevalent compounds in tires

| Compound; peak area % | Androstan-17-one, 3-ethyl-3-hydroxy-, (5α)- | Limonene | β-Guaiene | Longifolene | Ursodeoxycholic acid | Cyclohexane, 1,2,4-triethenyl- | Desogestrel | 2-[4-methyl-6-(2,6,6-trimethylcyclohex-1-enyl)hexa-1,3,5-trienyl]cyclohex-1-en-1-carboxaldehyde | Doconexent |
|---|---|---|---|---|---|---|---|---|---|
| | $C_{21}H_{34}O_2$ | $C_{10}H_{16}$ | $C_{15}H_{24}$ | $C_{15}H_{24}$ | $C_{24}H_{40}O_4$ | $C_{12}H_{18}$ | $C_{22}H_{30}O$ | $C_{23}H_{32}O$ | $C_{22}H_{32}O_2$ |
| Tyre 1 | 16.8 | 3.8 | 5.8 | 2.7 | 5.4 | 3.1 | 1.4 | 1.9 | 3.0 |
| Tyre 2 | 17.2 | 5.2 | 4.9 | 2.4 | 5.3 | 2.6 | 0.5 | 2.8 | 4.1 |
| Tyre 3 | 8.0 | 5.6 | 5.4 | 4.0 | 10.5 | 2.0 | 1.1 | 3.0 | 2.4 |
| Tyre 4 | 7.7 | 4.9 | 4.3 | 4.4 | 6.7 | 1.4 | | 2.3 | 0.6 |
| Tyre 5 | 6.3 | 2.7 | 3.9 | 1.6 | | 3.3 | 3.4 | | |
| Tyre 6 | 10.1 | 3.9 | 4.3 | 6.2 | 0.6 | 1.8 | 2.5 | 1.5 | |
| Tyre 7 | 10.9 | 4.9 | 5.2 | 5.6 | | 2.7 | 3.7 | 1.5 | |
| Tyre 8 | 10.9 | 4.3 | 4.7 | 5.1 | 2.8 | 2.4 | 2.4 | 1.8 | |
| Tyre 9 | 7.9 | 3.8 | 4.9 | 6.3 | 0.7 | 1.6 | 2.5 | 1.4 | |
| Tyre 10 | | 6.3 | | | | 4.3 | | | 4.1 |
| **Total** | 95.7 | 45.4 | 43.3 | 38.3 | 32.0 | 25.1 | 17.6 | 16.1 | 14.3 |
| **Description** | Unknown | terpenic pine herbal peppery | sweet woody dry guaiacwood spicy powdery | sweet woody rose medical fir needle; irritant to skin and eyes | Drug to dissolve cholesterol; irritant to skin and eyes | Eye, skin, respiratory irritant | Hormone | Unknown | Fatty acid |

- Fragrances – citrus, sweet, woody, spicy
- Irritants – eyes, skin
- High-order carbon compounds
- 2 unknowns

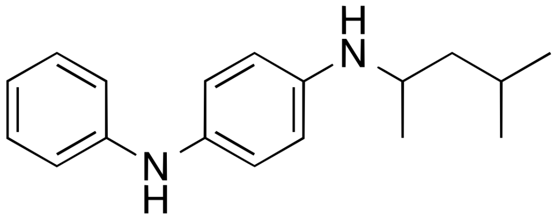
➢ Tire 10 has very different composition

# Notable compounds




Prevalent in Tire 8

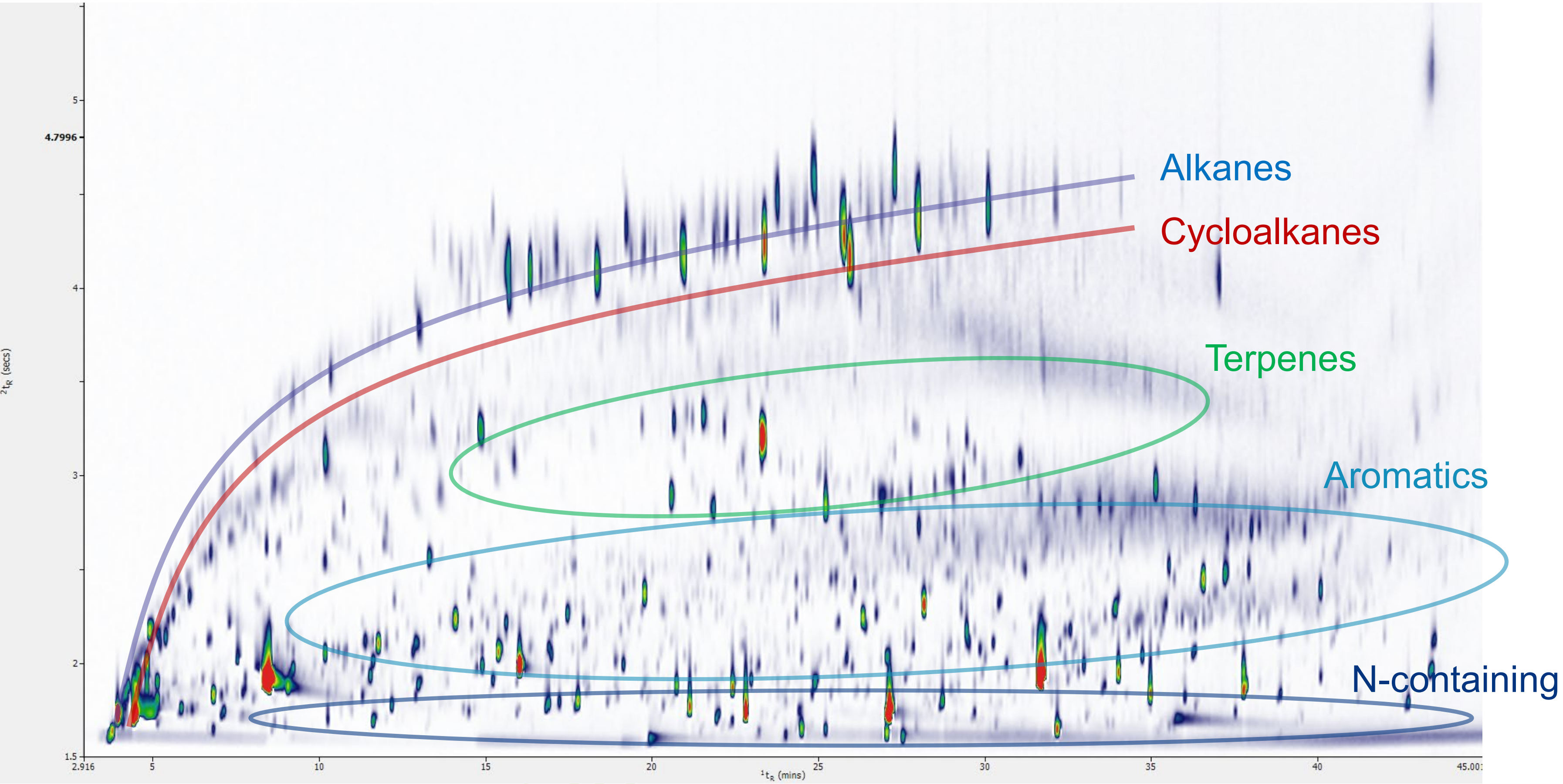
- phenol, 2-(1,1dimethylethyl)-4-methyl-
- Respiratory irritant, leathery smell




Prevalent in Tire 4, absent from Tire 5

- N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, aka 6PPD
- Preservative, reacts with ozone in the air
- 6PPD-quinone killed coho salmon in California

# Functional group classification




- Wide-ranging analytes identified

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

# Concentration by functional group

- Some compounds are deliberate additions, whereas others come in component mixtures such as carbon black
- Alkanes, etc are often irritants, but toxic in high concentration
- Aromatics, etc are more often carcinogenic and toxic at lower concentrations
- Significant variation in composition between brands and tires
- Ten tires shown, at high and low end of range of aromatics/PAHs – from 25% to 80%

| Concentration in sample (µg/mg) | Group 1<br>Acids, Amine and Alcohols | Group 2<br>Alkanes, Alkenes, Alkynes, Cyclo, Aldehydes and Ketones | Group 3<br>Aromatics and PAH |
|---|---|---|---|
| | | | |
| UKT137 | 1.1 | 58.3 | 49.5 |
| UKT026 | 1.9 | 85.3 | 51.2 |
| UKT160 | 2.9 | 69.0 | 52.5 |
| UKT152 | 2.5 | 66.6 | 52.6 |
| UKT210 | 0.9 | 49.5 | 53.4 |
| UKT138 | 5.1 | 63.8 | 194.4 |
| UKT141 | 2.4 | 73.9 | 201.7 |
| UKT171 | 1.4 | 48.1 | 206.7 |
| UKT147 | 1.7 | 72.6 | 287.3 |
| UKT243 | 12.8 | 265.4 | 451.5 |
| | | | |
| Average | 4.1 | 115.1 | 112.3 |
| Minimum | 0.6 | 32.8 | 49.5 |
| Median | 2.8 | 101.0 | 101.2 |
| Maximum | 21.2 | 265.4 | 451.5 |

# Wear rates

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# Total wear rates

- 14 different brands/models tested from new
- Mass loss over 1,000+ miles
- Whole vehicle mass loss (four wheels)
- Same vehicle, route, driver

- Total loss 73 mg/km
- Rate declines logarithmically as tire ages
- Lifetime mass loss estimated at 37 mg/km

| Tyre make | Total vehicle mass loss (mg/km) |
|---|---|
| | |
| Brand 1 | 161 |
| Brand 2 | 89 |
| Brand 3 | 81 |
| Brand 4 | 76 |
| Brand 5 | 75 |
| Brand 6 | 75 |
| Brand 7 | 73 |
| Brand 8 | 70 |
| Brand 9 | 66 |
| Brand 10 | 61 |
| Brand 11 | 61 |
| Brand 12 | 51 |
| Brand 13 | 45 |
| Brand 14 | 38 |
| | |
| Average | 73 |

# Speciated wear rates

- Match brand wear rate from new to compound speciation for particular tire
- Yields distance-specific emissions for each individual compound
- Can be expressed in functional groups
- Aromatics/PAHs wear at average 8.1 mg/km
- But with drill-down to individual compounds

| Mass emissions (mg/km) | Group 1<br>Acids, Amine and Alcohols | Group 2<br>Alkanes, Alkenes, Alkynes, Cyclo, Aldehyde and Ketone | Group 3<br>Aromatics and PAH |
|---|---|---|---|
| | | | |
| UKT137 | 0.081 | 4.249 | 3.606 |
| UKT026 | 0.139 | 6.222 | 3.735 |
| UKT160 | 0.211 | 5.031 | 3.826 |
| UKT152 | 0.181 | 4.860 | 3.834 |
| UKT210 | 0.067 | 3.606 | 3.895 |
| UKT138 | 0.370 | 4.654 | 14.175 |
| UKT141 | 0.174 | 5.392 | 14.709 |
| UKT171 | 0.102 | 3.504 | 15.073 |
| UKT147 | 0.124 | 5.292 | 20.951 |
| UKT243 | 0.937 | 19.353 | 32.924 |
| | | | |
| Average | 0.293 | 8.256 | 8.146 |
| Minimum | 0.045 | 2.392 | 3.606 |
| Median | 0.204 | 7.365 | 7.378 |
| Maximum | 1.548 | 19.353 | 32.924 |

# Toxicity analysis

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| 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 |

# Toxicity evaluation

- 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' described different effects, from irritants to carcinogens
- Each compound can have multiple hazard codes
- Different manufacturers can make different disclosures

➢ Method developed to synthesise into overall toxicity rating for a tire

# Toxicity evaluation

- Of 100 tires tested, on average…

- 410 organic compounds separated
- 78 organic compounds identified using NIST library
- 46 hazard codes cited

- Most and least toxic five tires shown
- Weighted toxicity factor, with mean indexed to 100
- Most toxic x6.7 least toxic

| Tire # | Weighted toxicity factor |
|---|---|
| | |
| | |
| UKT210 | 43 |
| UKT035 | 44 |
| UKT214 | 45 |
| UKT138 | 49 |
| UKT012 | 49 |
| UKT089 | 164 |
| UKT057 | 167 |
| UKT076 | 170 |
| UKT115 | 173 |
| UKT243 | 289 |
| | |
| Average | 100 |
| Minimum | 43 |
| Median | 97 |
| Maximum | 289 |

# Environmental effects

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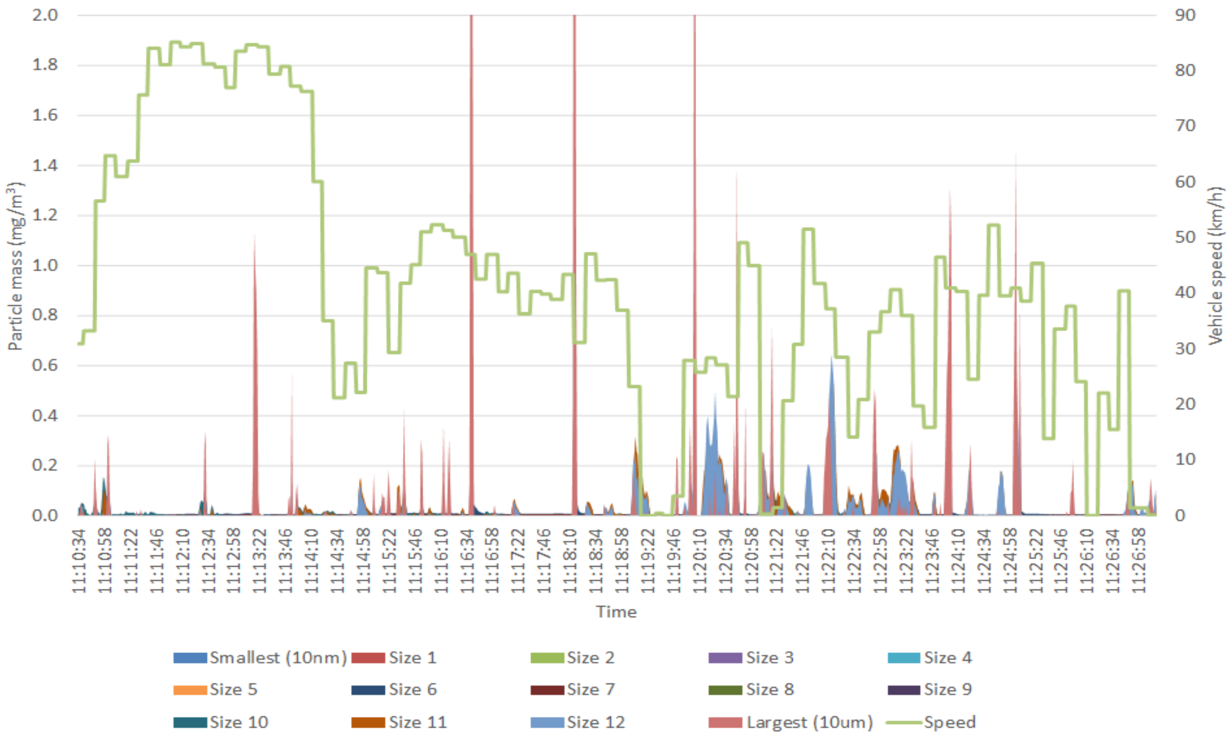
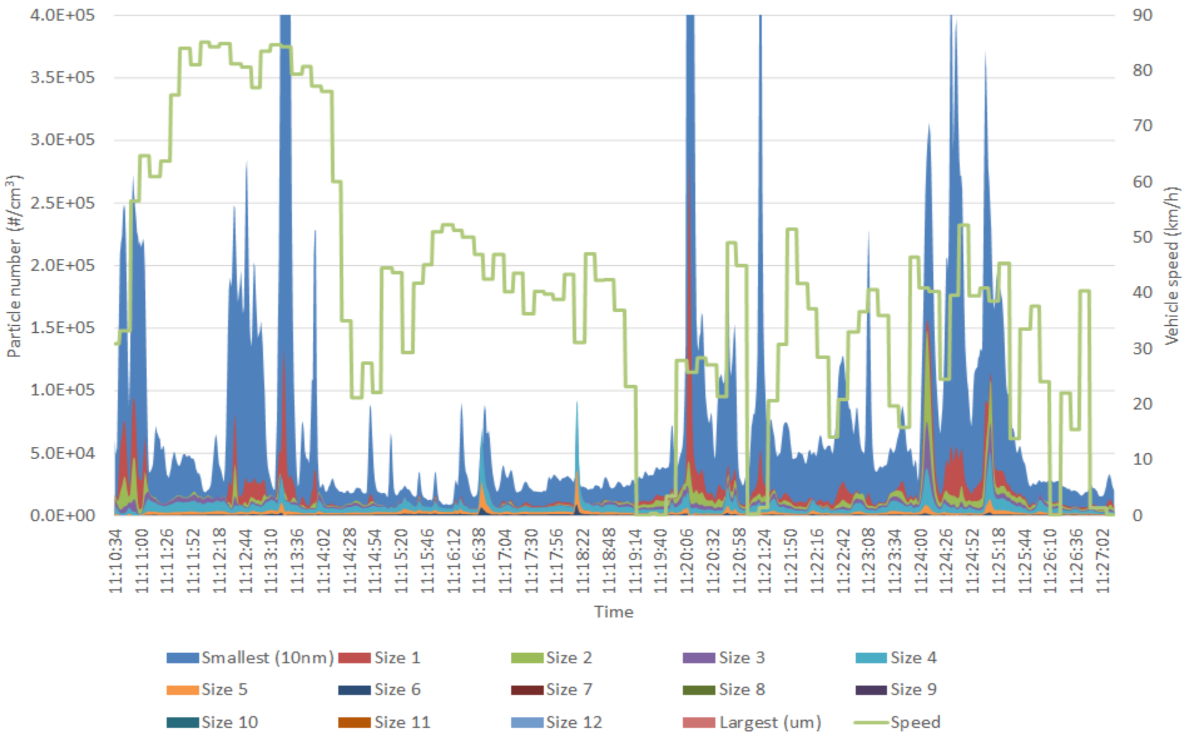
# Particle size distribution




TEMS tyre emissions measurement system

# Environmental propagation

- On-road test with 'normal' dynamics
- 11% of fine particle mass is below 2.5 µm diameter
- This material is likely to hang in the air for a period
- The rest is likely to go to soil and water
- But this mass accounts for almost 100% of particle number
- And ultrafines account for 92%
- Affect of desorped VOCs on air quality unknown

➢ Tires 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% |

# Wider context

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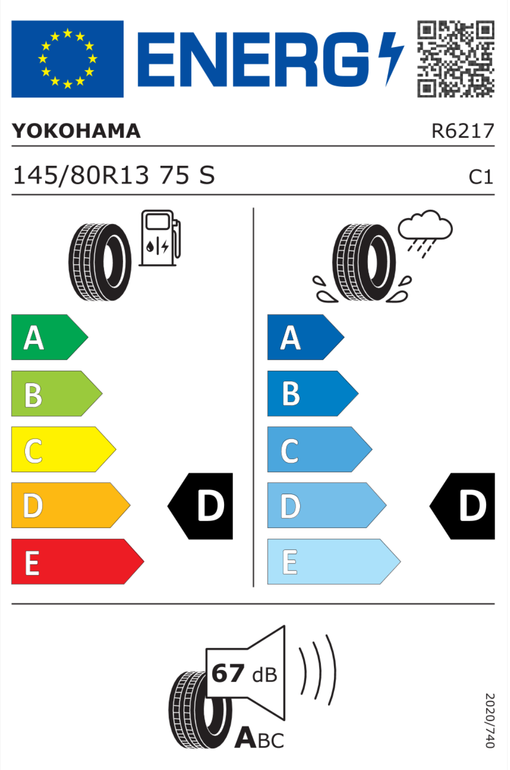
# Tire performance

- Official tire 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 tires without compromising performance




# Context of tailpipe emissions

- 37 mg/km tire wear is x8 maximum permissible tailpipe mass emissions
- 0.02 mg/km is actual, real-world tailpipe mass emissions from latest cars
- Tires are x1,850 times more polluting on this measure

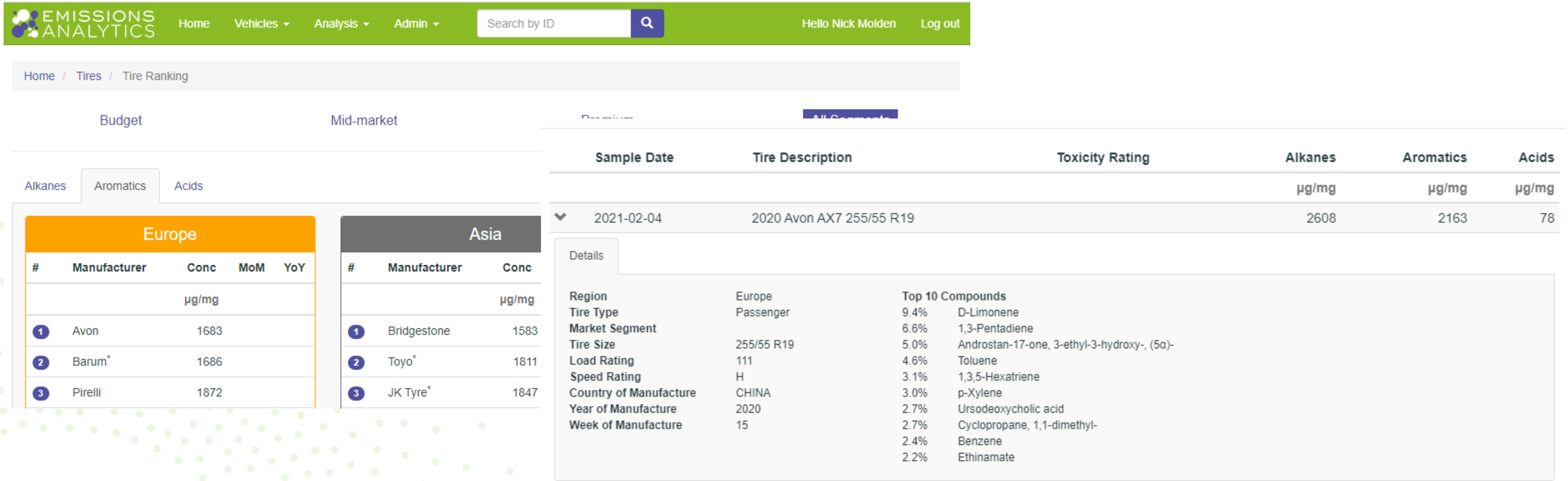
- 14.5 x $10^{11}$ #/km is x2.4 maximum permissible tailpipe number emissions
- 0.9 x $10^{11}$ #/km is actual gasoline PN, and 0.1 x $10^{11}$ #/km is actual diesel
- Tires are x29 times more polluting on this measures, averaged across fuel types

- Tire mass emissions increase by 21% for 500 kg extra mass, all else equal
- This increase is x389 the average tailpipe mass emission

# Summary

- Tire wear emissions are a material and growing concern
- For air, soil and water – and, indirectly, the human food chain
- Wear can be measured in real-world conditions
- Two-dimensional gas chromatography offers possibility of full chemical profiling
- Toxicity can be estimated from that
- Composition can be correlated to performance

# Subscription database




- Fingerprinting database to be launched in May 2022
- For benchmarking, research and development

# Thank you.

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