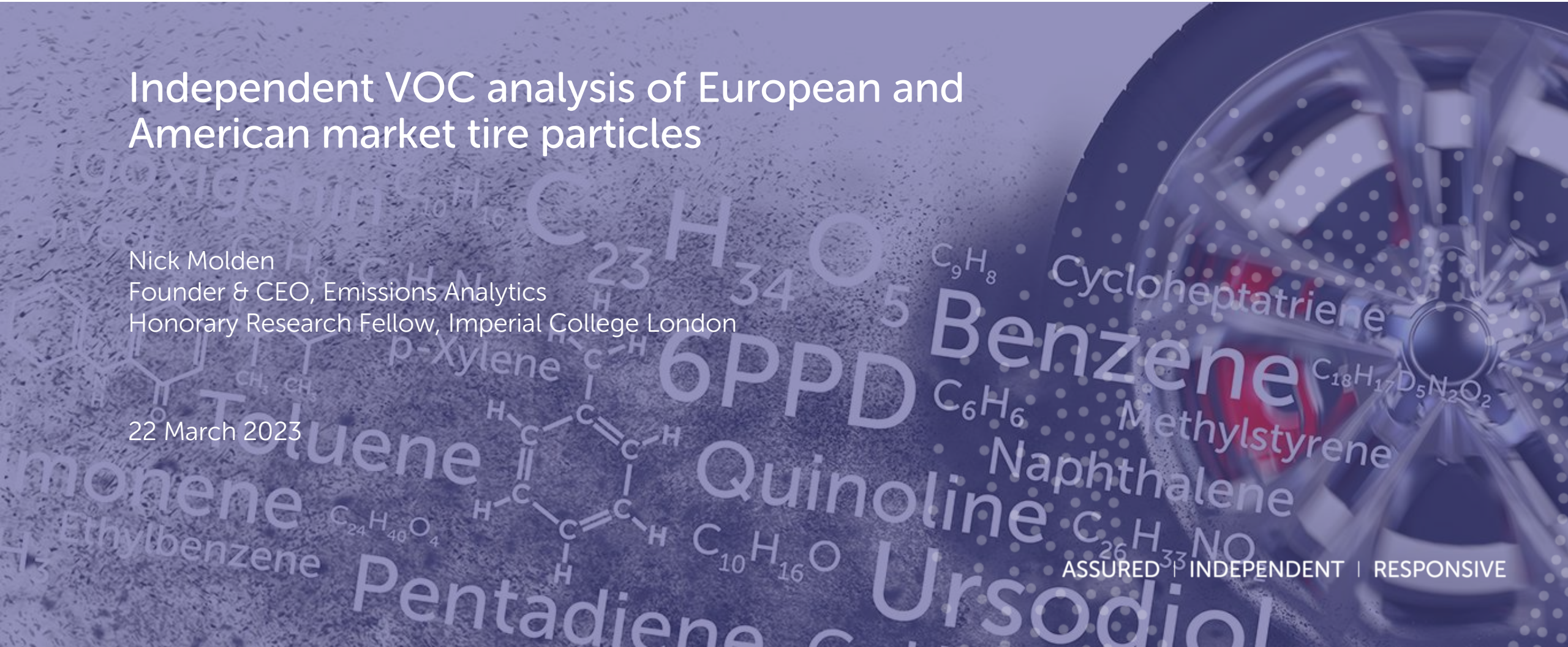
EMISSIONS ANALYTICS

Independent VOC analysis of European and American market tire particles

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

22 March 2023



Agenda

- How prevalent are tyre wear emissions?
- To what extent do they include micro plastics?
- What are their health and environmental effects?
- What is the chemical profile of tyres?
- How do European and US tyres compare?
- What are the options for reducing the impact?

The issue

ASSURED | INDEPENDENT | RESPONSIVE

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

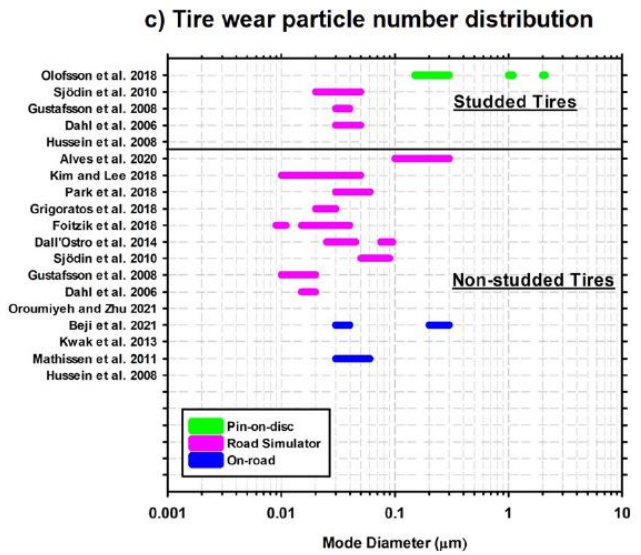
- 37 mg/km tyre wear is x8 maximum permissible tailpipe mass emissions
- 0.02 mg/km is actual, real-world tailpipe mass emissions from latest cars
- Tyres are x1,850 times more polluting on this measure

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

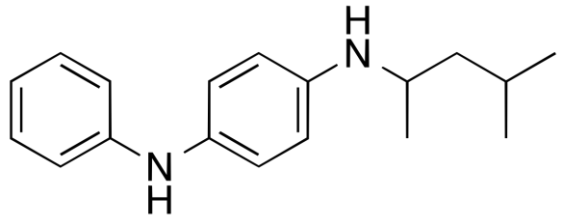
➢ Tyres are simultaneously a problem for air, soil and water

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%

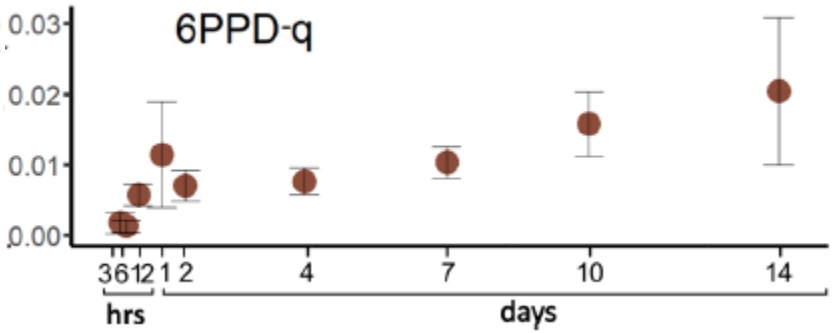


Derivative products

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

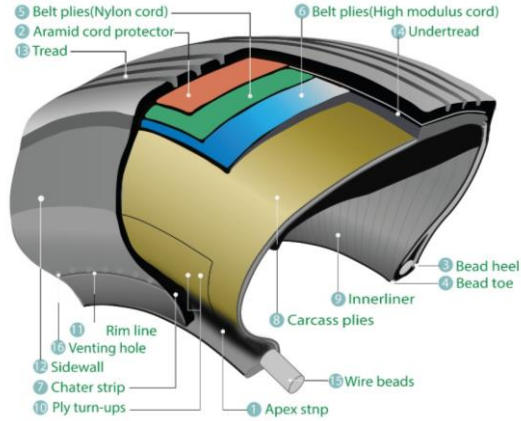


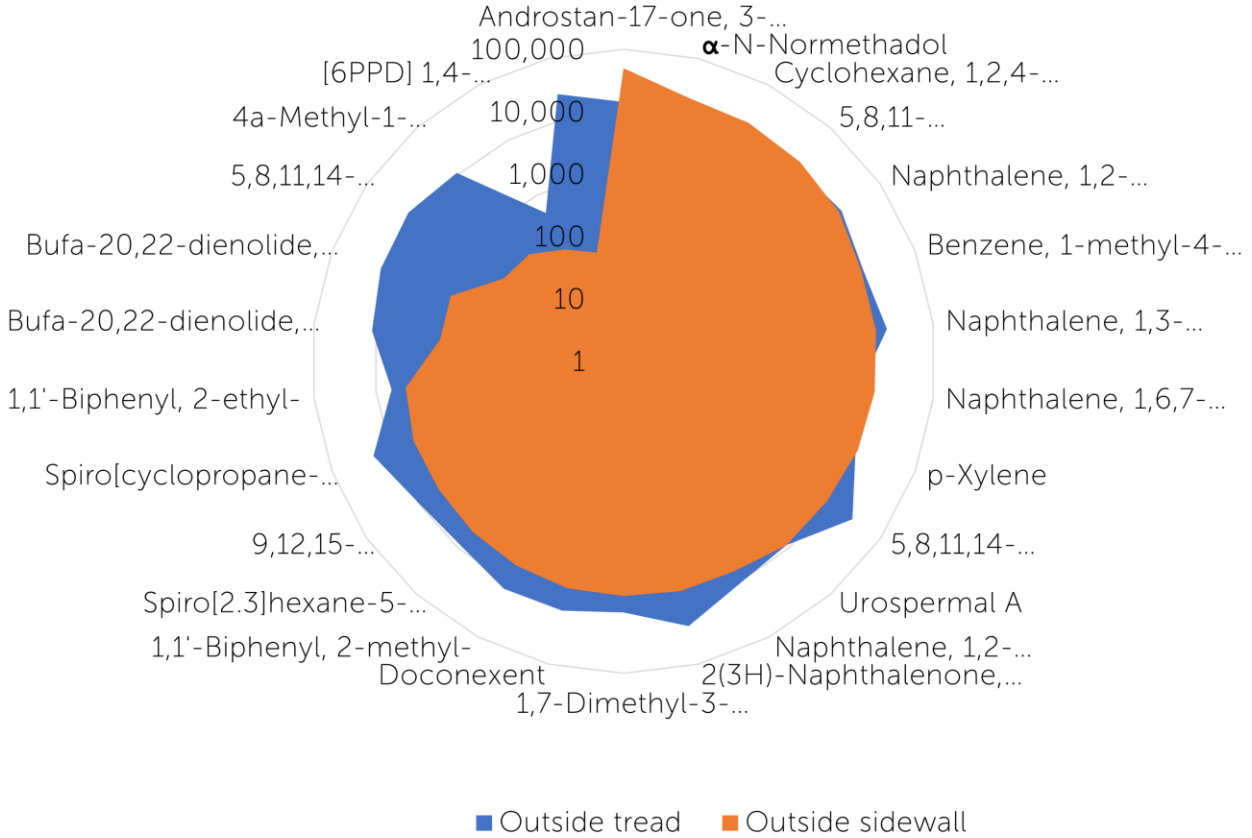
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, aka 6PPD



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/m^3 from toluene in recent research in Shanghai





BTAS brake and tyres analysis system

Experimental approach

ASSURED | INDEPENDENT | RESPONSIVE

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

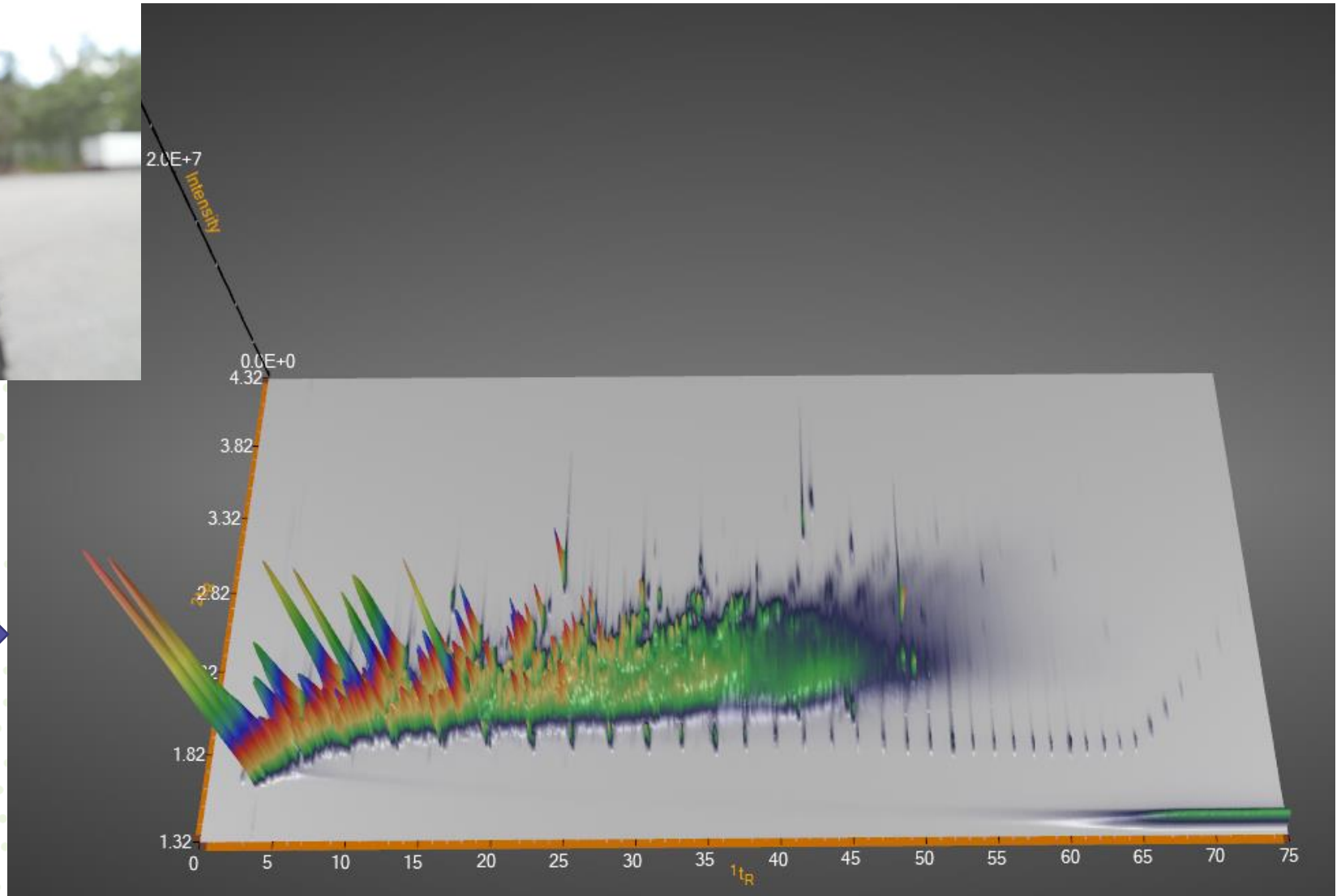
- Two-dimensional gas chromatography with mass spectrometry
- INSIGHT flow modulator from SepSolve Analytical for separation
- BENCH-TOF time-of flight mass spectrometer
- Multi-stage pyrolysis method

Analytical methodology

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

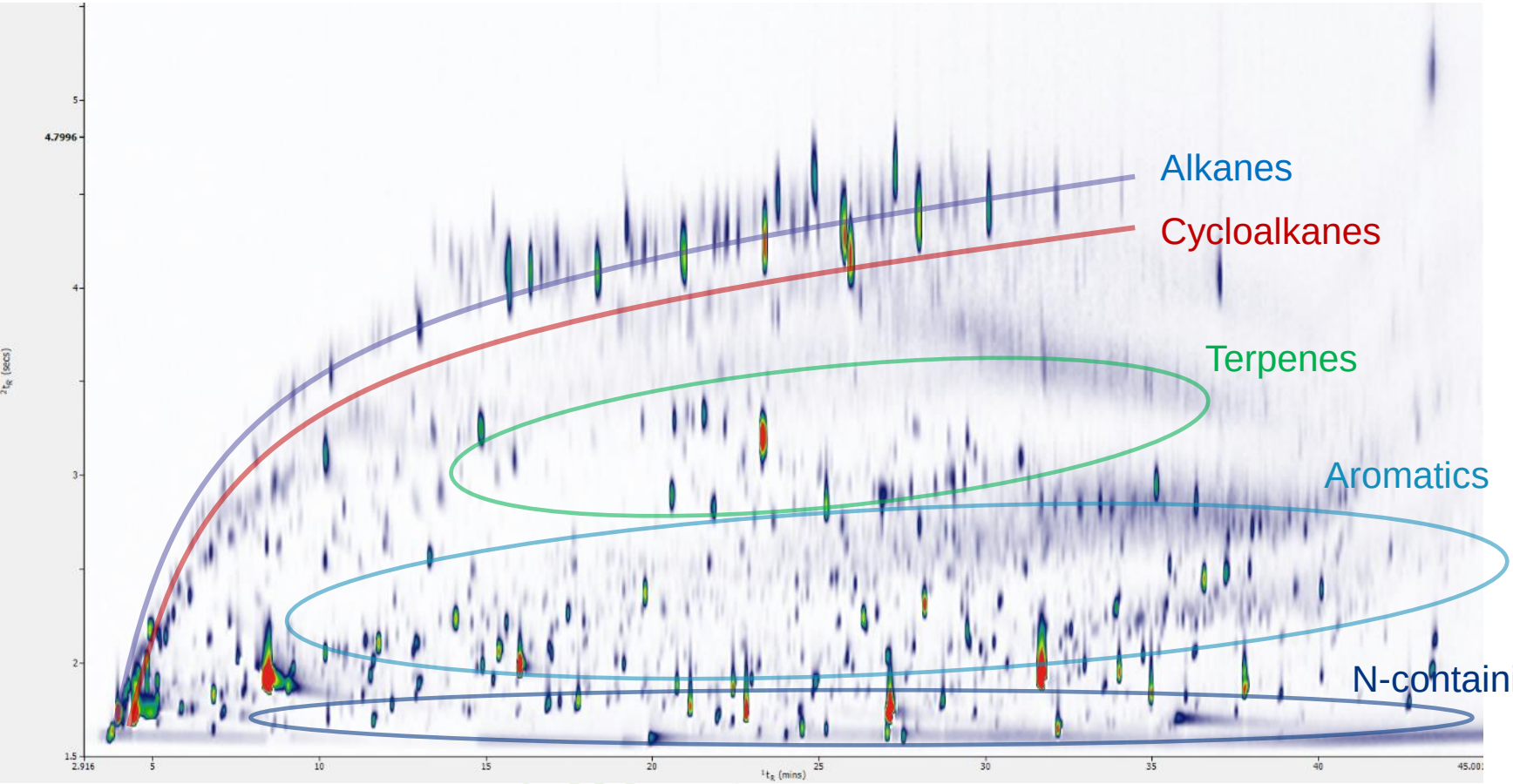
- Due to the very rapid heating and then flushing out of the hot zone, the pyrolysates are likely to remain unchanged, with secondary reactions and pyrolysate aggregation occurring rarely (Shin Tsuge, 2012) (Xiao-Ming Ma, 2014).
- The degradation process is useful for understanding the structure of the 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



BTAS brake and tyres analysis system

Functional group classification



- Wide-ranging analytes identified

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

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

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

Regional differences

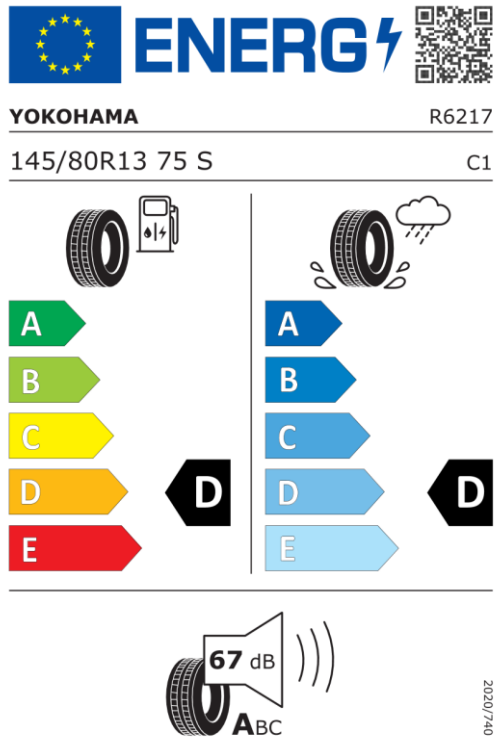
ASSURED | INDEPENDENT | RESPONSIVE

EQUA real-world test database

Regional labelling

- Official tyre labels exist in multiple regions
- Current focus on rolling resistance, grip, weather and noise in Europe
- Closest proxy is ‘tread wear rating’ in US
- Fuel economy is pre-eminent consideration in Europe
- Compared to durability in the US

➢ Differences likely to be seen in composition of tyres between regions



Comparison by target market – light duty

- 228 tyres analysed across Europe and North America
- Sourced from retail outlets
- Vent sprues from unused tyres
- Significantly lower aromatic content in US tyres, with lower toxicity potential
- Fewer alkanes in US tyres, but higher toxicity potential on average

	Europe	North America	Variance
Tyres analysed	185	43	
Average aromatics concentration (ng/mg)	226,021	94,181	-58%
Human toxicity potential	42	26	-38%
Marine toxicity potential	4	2	-37%
Average alkanes concentration (ng/mg)	123,907	70,354	-43%
Human toxicity potential	20	24	17%
Marine toxicity potential	3	3	-13%

Comparison by target market – heavy duty

- 55 tyres analysed
- Sourced from retail and New York City authorities
- Less aromatics and alkanes in US tyres
- High marine toxicity potential from US tyres, but mixed effects on human health

	Europe	North America	Variance
Tyres analysed	16	39	
Average aromatics concentration (ng/mg)	95,142	64,122	-33%
Human toxicity potential	26	21	-20%
Marine toxicity potential	2	2	14%
Average alkanes concentration (ng/mg)	133,963	100,328	-25%
Human toxicity potential	26	34	34%
Marine toxicity potential	4	4	13%

Aromatics by region of manufacture – light duty

ng/mg	Region of sale:		
	Europe	North America	Variance
Region of manufacture…			
Europe	206,703	118,039	-43%
North America	263,160	90,914	-65%
Asia	227,927	91,681	-60%
Other	279,381	94,050	-66%

- Tyres made for US market have lower aromatics from all sources
- Due to higher durability expectations?
- Tyres imported in Europe have highest aromatics
- May reflect more the OE and product mix than a like-for-like comparison

Aromatics by manufacturer– light duty

- Segmenting by manufacturer to achieve closer to like-for-like comparison
- Compound data available from both regions for 7 OEs
- One-third less aromatics in US tyres, but varies

ng/mg	Europe	North America	Variance
Bridgestone	111,252	99,670	-10%
Continental	183,670	111,757	-39%
Dunlop	98,757	95,704	-3%
Goodyear	217,062	92,521	-57%
Hankook	111,974	90,577	-19%
Kumho	182,072	90,015	-51%
Michelin	235,297	108,862	-54%
Average	162,869	98,444	-33%

Target compounds

ASSURED | INDEPENDENT | RESPONSIVE

EQUA real-world test database

Compounds of concern – marine

- Target compounds in tyres – sources including ChemSec SIN list, REACH, PEWS
- Average concentration of compound, where present in at least 10 European tyres
- Thousands of potential concerns can be seen at low concentrations
- 6PPD is not the only compound of concern for marine life

Compound name	Chemical formula	Europe average concentration (ng/mg)	American average concentration (ng/mg)	Potential effects - aquatic	Other potential effects - human
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine	$C_{18}H_{24}N_2$	531	513	Very toxic, long-lasting	Human fertility, skin irritation
Dimethyl selenide	C_2H_6Se	305		Very toxic, long-lasting	Toxic if inhaled, swallowed; organ damage
Naphthalene	$C_{10}H_8$	229	117	Very toxic, long-lasting	Harmful if swallowed; suspected carcinogen
Fluorene	$C_{13}H_{10}$	152	140	Very toxic, long-lasting	
1,2-dihydro-2,2,4-trimethylquinoline	$C_{12}H_{15}N$	148	53	Toxic, long-lasting	Harmful if swallowed
N-isopropyl-n'-phenyl-p-phenylenediamine [IPPD]	$C_{15}H_{18}N_2$	101		Very toxic, long-lasting	Harmful if swallowed; skin irritation
Chrysene [CHR]	$C_{18}H_{12}$	100		Very toxic, long-lasting	Potential carcinogen; suspected genetic effects
Retene [RET]	$C_{18}H_{18}$	29	1,083	Very toxic, long-lasting	

Compounds of concern – human

- Pattern of compounds of concern very different between Europe and America

Compound name	Chemical formula	Europe average concentration (ng/mg)	American average concentration (ng/mg)	Potential effects - human	Other potential effects - aquatic
Benzene, 1,3-dimethyl-	C_8H_{10}	2,352		May be fatal if swallowed or inhaled; serious eye, respiratory irritation	Harmful, long-lasting
p-Xylene	C_8H_{10}	2,142	210	May be fatal if swallowed or inhaled; serious eye, respiratory irritation	Harmful, long-lasting
Benzene	C_6H_6	1,077	171	May be fatal if swallowed or inhaled; organ damage; potential carcinogen; genetic effects; serious eye irritation	
Indene	C_9H_8	850	166	May be fatal if swallowed or inhaled; serious eye, skin irritation; suspected carcinogen	Toxic, long-lasting
Styrene	C_8H_8	681	30	May be fatal if swallowed or inhaled; eye, skin irritation; potential carcinogen	Harmful, long-lasting
Ethylbenzene	C_8H_{10}	269	520	Potential carcinogen; genetic effects; harmful if swallowed	Harmful, long-lasting
Acetonitrile cyanomethane	C_2H_3N	248	14	Toxic if swallowed, inhaled or skin contact; skin and eye damage; potential carcinogen	Toxic, long-lasting
Benzothiazole [BTZ]	C_7H_5NS	222	130	Toxic If swallowed, inhaled or skin contact; eye damage; organic damage	
Benzothiazole, 2-phenyl-	$C_{13}H_9NS$	77	197	Serious eye irritation	
2-(methylthio)benzothiazole [2-MTBT]	$C_8H_7NS_2$	33	97	Serious eye, skin and respiratory irritation	

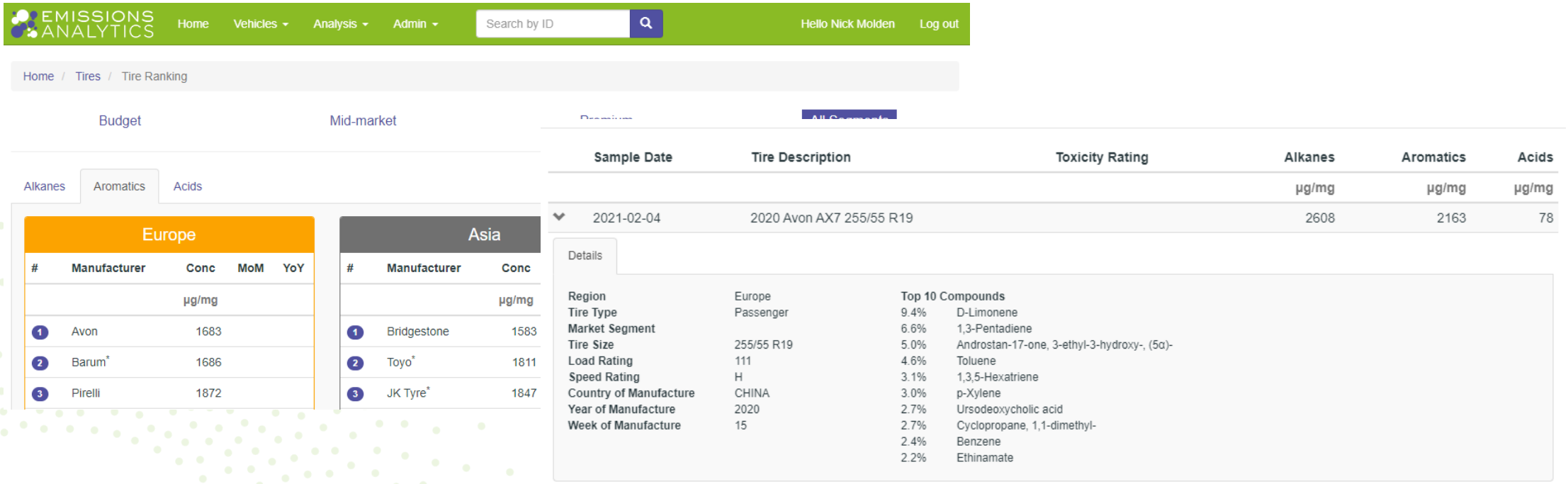
Summary

- Tyre wear emissions are all around and inside us
- Encompassing larger and smaller particles, but tyres also off-gas VOCs
- Aromatics and alkanes are on average much lower in American tyres
- Likely to be deliberate to match market preferences
- Heavy duty tyres are lower in aromatics
- Potential toxicity is similar overall
- Averages hide large variances between tyre models
- More compounds of concern are seen in European tyres

➢ Greater understanding is needed to form optimal policy

BTAS brake and tyres analysis system

Subscription database



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

Thank you.

Nick Molden

Chief Executive Officer

nick@emissionsanalytics.com

+44 (0)20 7193 0489

ASSURED | INDEPENDENT | RESPONSIVE

ASSURED | INDEPENDENT | RESPONSIVE

Assured
Emissions testing in real-world conditions brings challenges that experience anticipates and expertise overcomes. We deliver.

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.

EMISSIONS ANALYTICS