The chemistry and physics of tyre wear

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Setting the scene

- We study the holistic environmental impact of vehicles on the environment
- Through an on-going programme of independent tests
- Working with industry, authorities and academics
- To reconcile transportation with a sustainable environment


The issue
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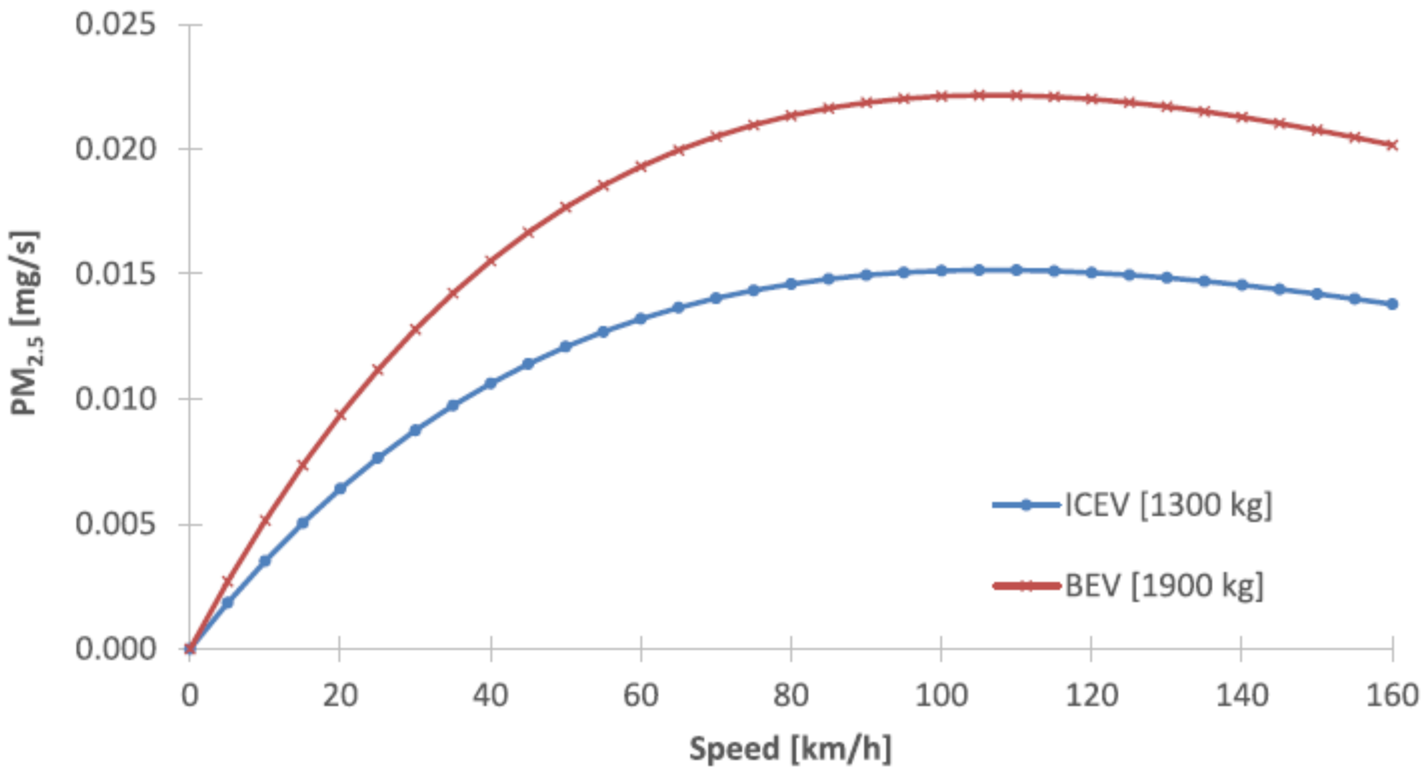
The tyre problem

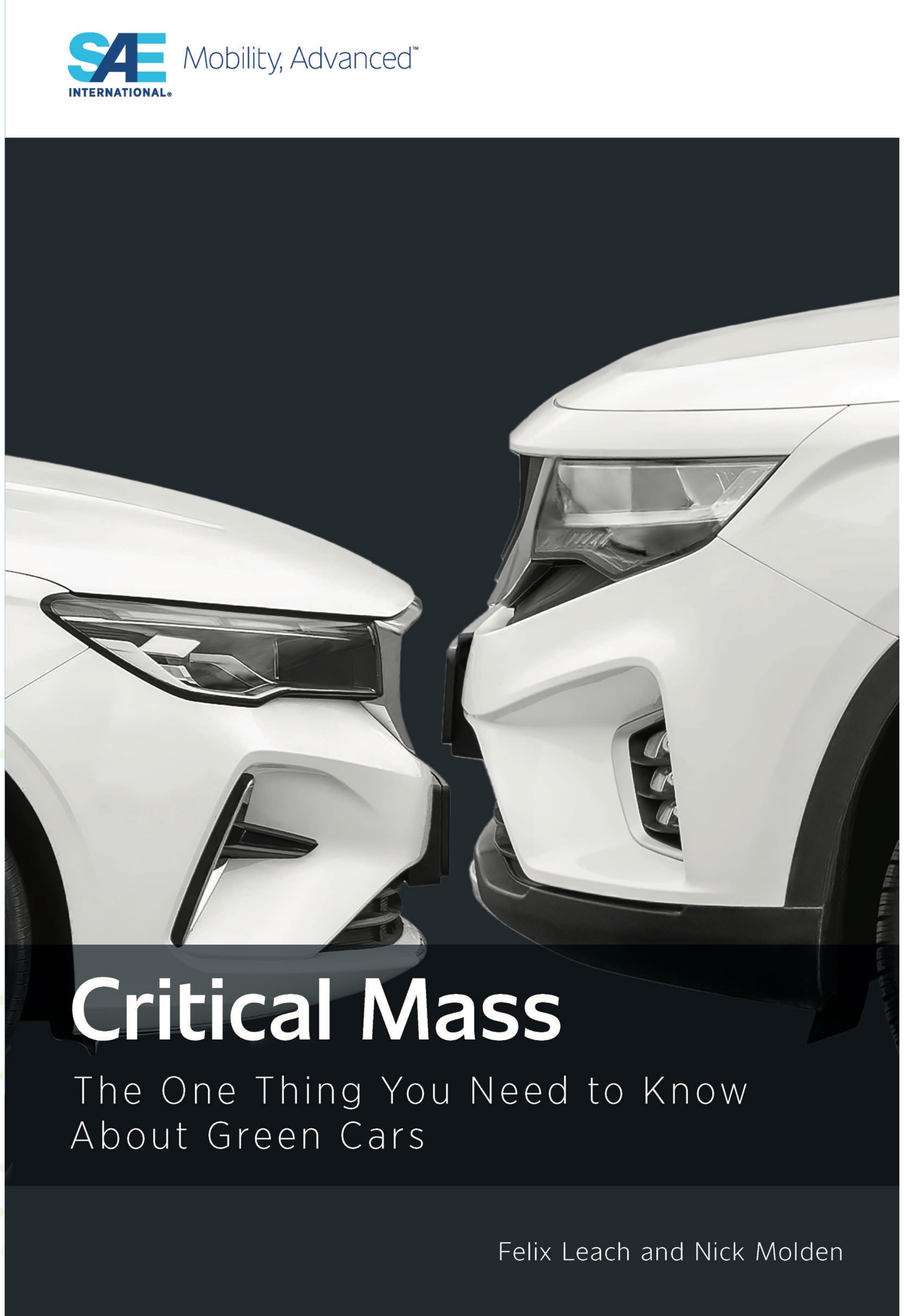
- Complex chemistry
- Complex physics
- Complex health effects
- Complex environmental effects
- Complex politics
- Complex economics

- COMPLEX EVERYTHING, plus…
- Significant information asymmetries
- Mixed regulatory track record is about to collide with this problem

Why tyres now?

- Dramatically reduced tailpipe emissions
- Research efforts and breakthroughs
- Heavier and battery electric vehicles
- Approximately 25% increase





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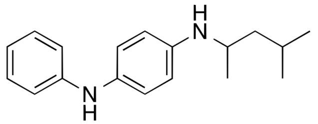
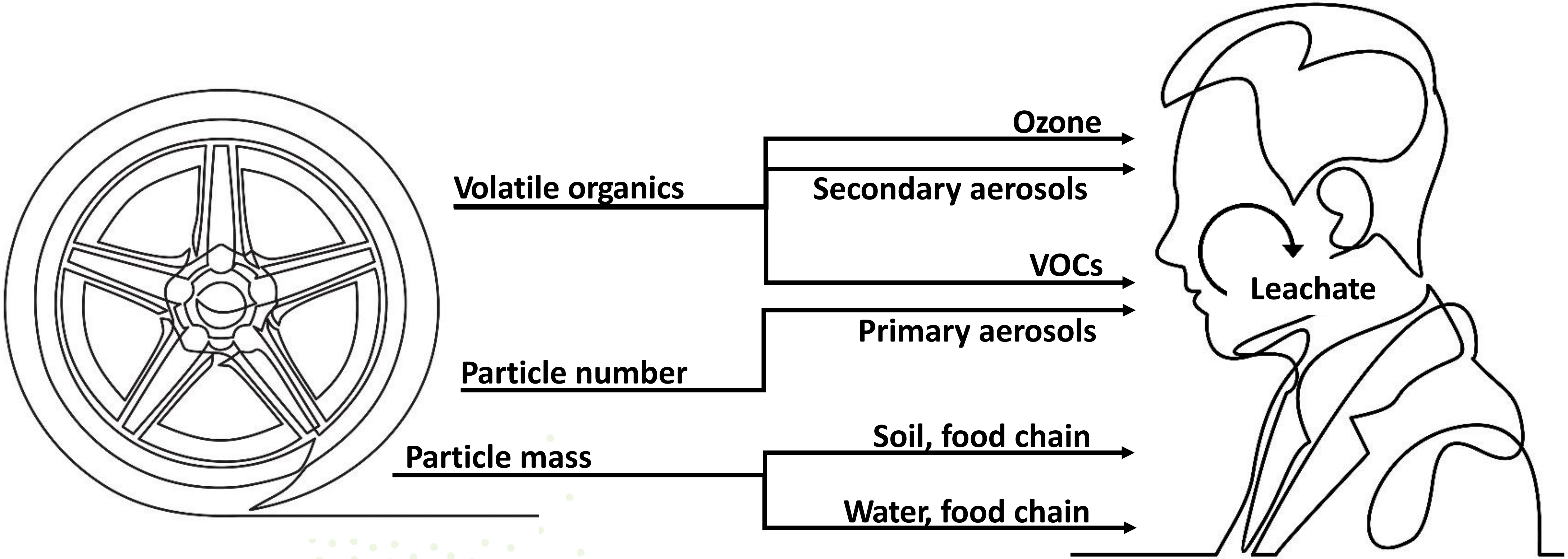
Multiple vectors

- 6 million tonnes of tyre wear globally per year
- 1-2 billion end-of-life tyres per year
- 7 thousand tonnes of 6PPD in the wear






Experimental approach
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Test programme

- 501 new tyres tested
- Split between US and Europe
- Sourced from retail and wholesale
- On-road mass loss
- Real-time size distribution
- Untargeted Pyrolysis-GCxGC-TOF-MS analysis undertaken of tread
- Untargeted TD-GCxGC-TOF-MS from off-gassing chamber of whole tyre
- Full organic compound identification and quantification

Market tyres

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Key observations

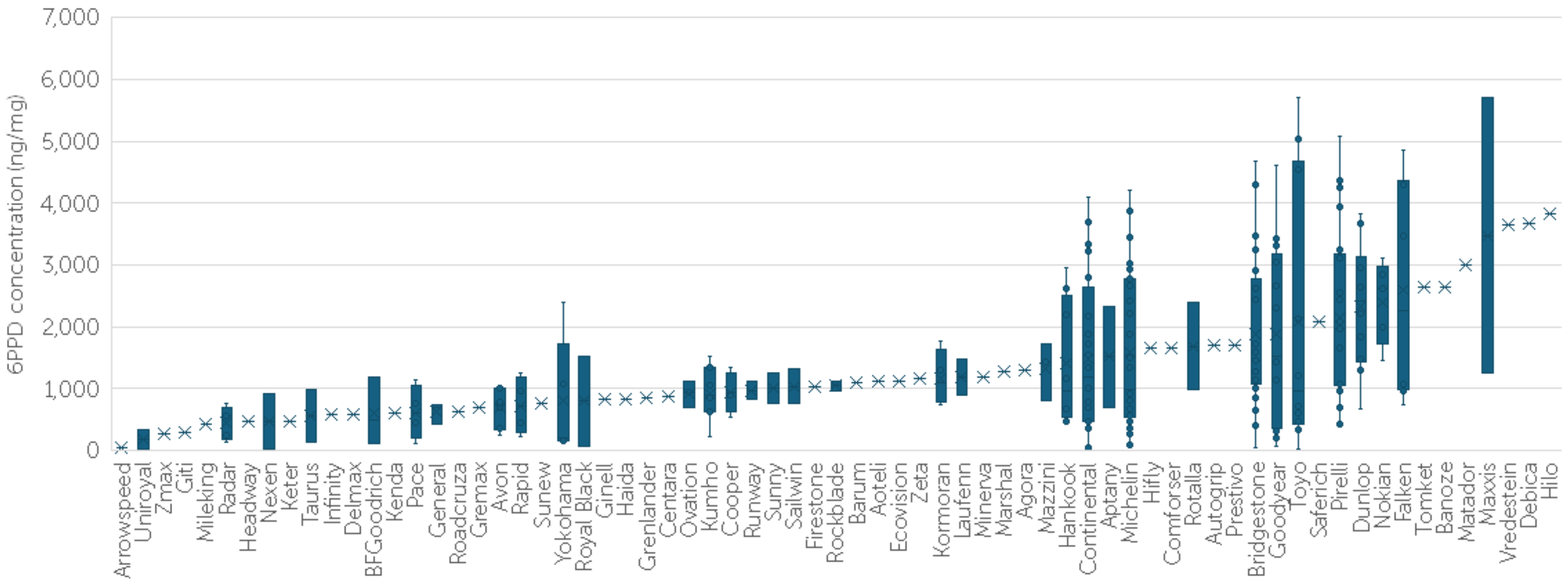
- Tyres are complex and heterogeneous for…
- Wear and chemical composition
- 410 organic compounds on average in a tyre
- 15,916 unique compounds (post-pyrolysis) across 501 tyres
- 6PPD in 100% of tyres – mean concentration 1.2 µg/mg, max 5.7 µg/mg (x4.8)
- Mass wear varies – mean 99 mg/km, max 246 mg/km (x2.5)

➢ More variation in the chemistry than the physics?

➢ Deliberately formulated, not random variation

Manufacturer rankings – EU car tyres

- Yokohama is a major manufacturer using less 6PPD
- Established European and US manufacturers clustering in 1,500-2,500 ng/mg range
- Large variability points towards using a limit value



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%)

Physics

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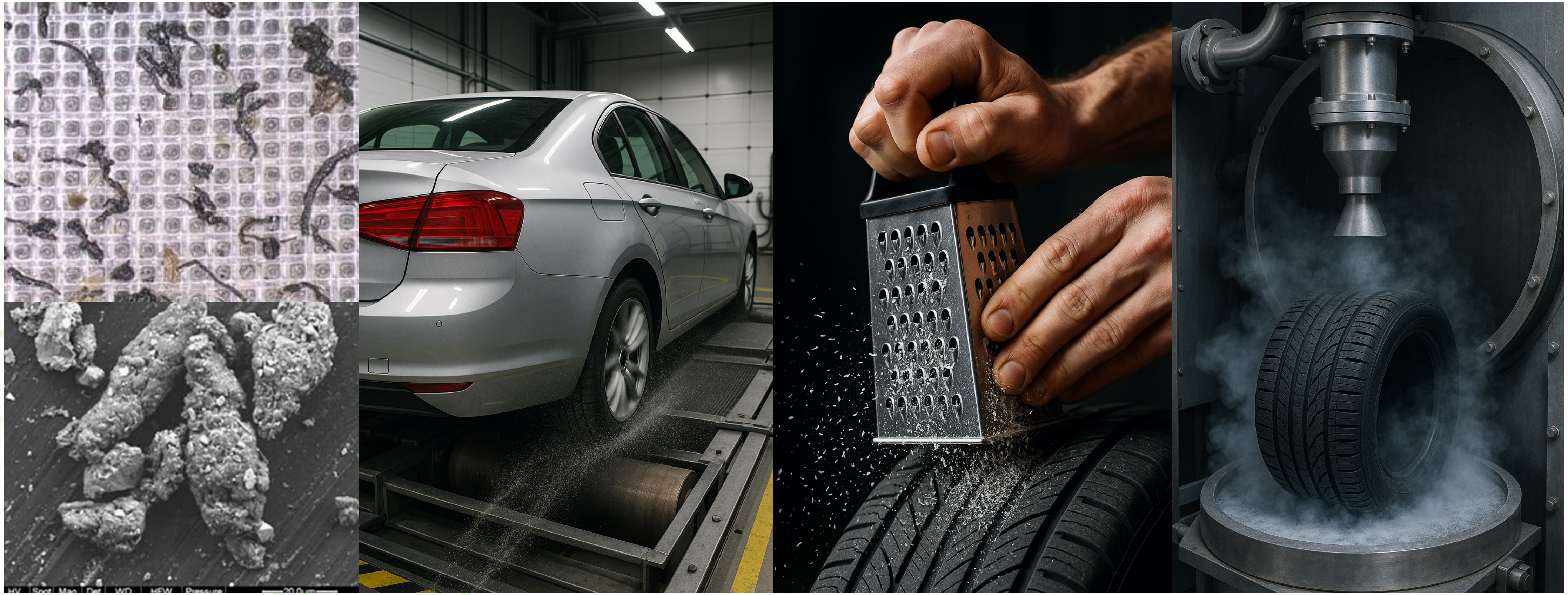
What are tyre particles? Definitions and artefacts…



TWP

TRWP

Dynamometer Grating Cryomilling

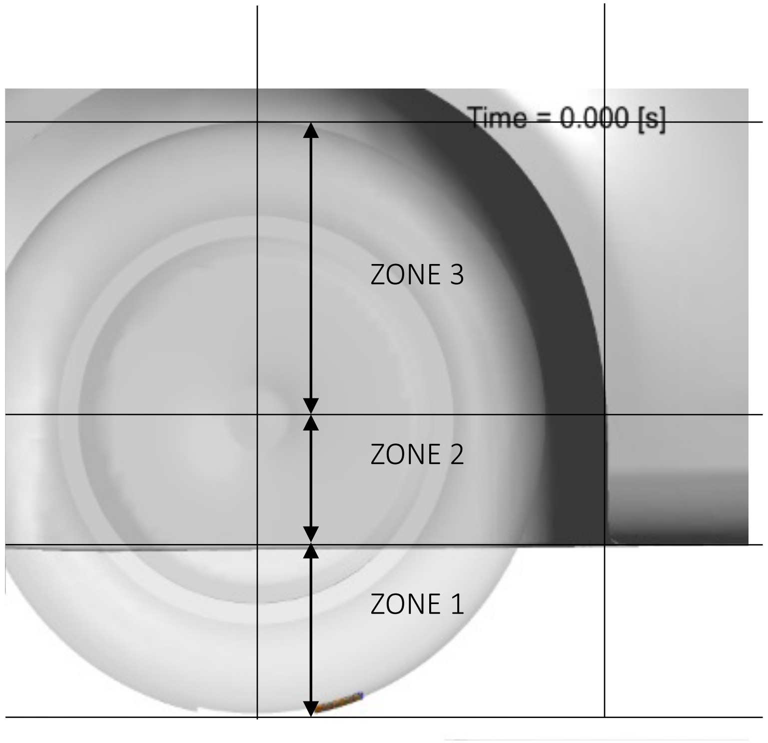
On-vehicle sampling – principles

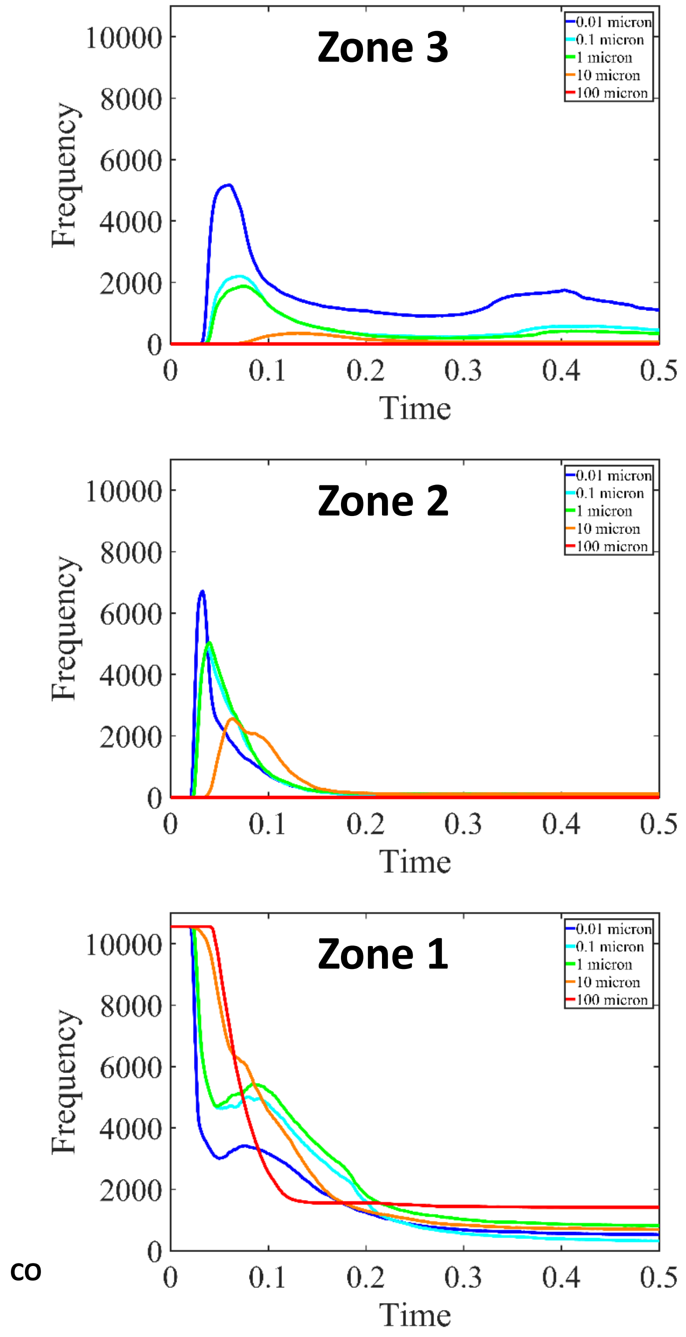
- Universal fitment across vehicles
- Fits to any and all wheels on a vehicle
- No vehicle modification required
- Articulates as the vehicle steers
- Safe and road-legal
- Can be coupled with any detector
- And collecting plates/receptacle
- Patent-pending

➢ Mass, number and physical collection

Sampling challenges

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





Transit distance – Colorado Rocky Mountains

- Wind-blown particles on dirty, high-elevation (2,865-3,690 m) snow
- Likely to contribute to melting of snow and ice as well as to warming the atmosphere

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JGR Atmospheres

RESEARCH ARTICLE

10.1029/2024JD041116

Special Collection:
Dust and dust storms: From physical processes to human health, safety, and welfare

Key Points:

- Light absorbing particles, as blackened microplastic matter from road-tire wear, occur in snow of the Colorado

Microplastic and Associated Black Particles From Road-Tire Wear: Implications for Radiative Effects Across the Cryosphere and in the Atmosphere

Richard L. Reynolds[1], Nick Molden[2,3], Raymond F. Kokaly[4], Heather Lowers[4], George N. Breit[4], Harland L. Goldstein[1], Elizabeth K. Williams[1], Corey R. Lawrence[1], and Jeff Derry[5]

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Abstract The environmental effects of airborne micro- and nano-size plastic particles are poorly understood. Microscopy and chemical analyses of atmospherically deposited particles on snow surfaces at high elevation (2,865–3,690 m) in the Upper Colorado River basin (UCRB; Colorado Rocky Mountains) revealed the presence of black substances intimately associated with microplastic fibers, particles interpreted to have originated as tire matter. Identical and similar particles occur in shredded tires and road-surface samples. The substance responsible for the black color of all tires is carbon black, a graphitic light-absorbing tire additive produced by hydrocarbon combustion that homogeneously permeates the mixture of tire polymers and other additives. Such black tire matter may thus exert radiative effects closely similar to those of black carbon. The presence in snow of many organic compound types common to tires, measured by two-dimensional gas chromatography, suggests that atmospherically deposited black road-tire-wear matter is among the light-absorbing particulates that advance the onset and rate of snow melt in the UCRB. The mass of road-tire-wear particles shed from vehicles may be estimated by multiplying measured amounts of eroded tire-per-distance traveled by vehicular distances. Under a combination of measurements and assumptions about the amounts and radiative properties of atmospheric tire-wear particles, the radiative effects of these particles might add about 10%–30% to those effects from black carbon, an estimate ripe for revision. On regional and global scales, the amounts and effects of emitted and deposited tire-wear matter likely vary by factors of geographic source, transport pathway, and depositional setting.

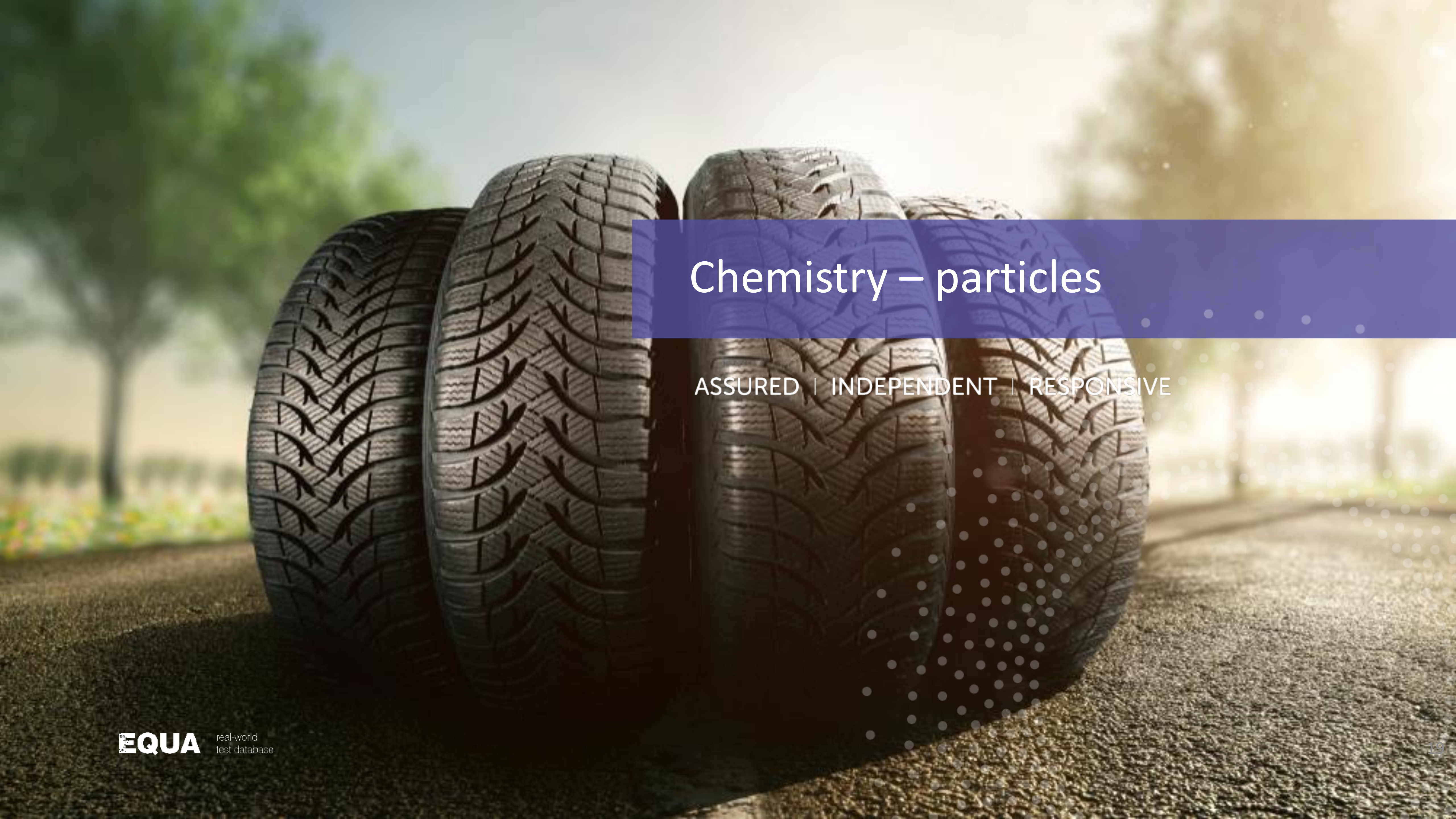
Results From Organic Compound, Spectral Reflectance, and Total Organic Carbon Analyses

Site	WY	OC number	OC sum%	Fluorene	1,3-Pentadiene	2,4-Dimethylstyrene	Biphenyl	Rtot	TOC
McClure Pass	14	396	53	64.2	440.0	1.6	11.4	0.3601	8.35
McClure Pass	16	369	49	77.9	269.3	14.6	11.9	0.3378	20.5
Wolf Creek Pass	15	402	47	54.6	0	0	15.2	0.3110	13.58
Wolf Creek Pass	16	377	48	29.9	0	8.5	9.3	0.2881	22.48
Berthoud Pass	16	386	56	0.2	1223.1	29.0	14.1	0.3282	12.44
Grand Mesa	16	405	49	49.3	1.2	1.3	12.0	0.3746	8.52

Note. WY, water year of sample collection. OC Number, numbers of specific organic compounds in a snow sample determined by the GCxGC method that are in the road-tire-composition database (Molden, 2023a, 2023b); OC SUM%, the proportion of the number of organic compounds detected in a snow sample also found in the road-tire-composition database to the number of all organic compounds in that sample; concentrations of the four listed organic compounds in ng mg^{-1}; Rtot, average spectral reflectance across 0.37–2.5 μm wavelengths; TOC, total organic carbon in weight %.

Citation:

Reynolds, R. L., Molden, N., Kokaly, R. F., Lowers, H., Breit, G. N., Goldstein, H. L., et al. (2024). Microplastic and associated black particles from road-tire



Chemistry – particles

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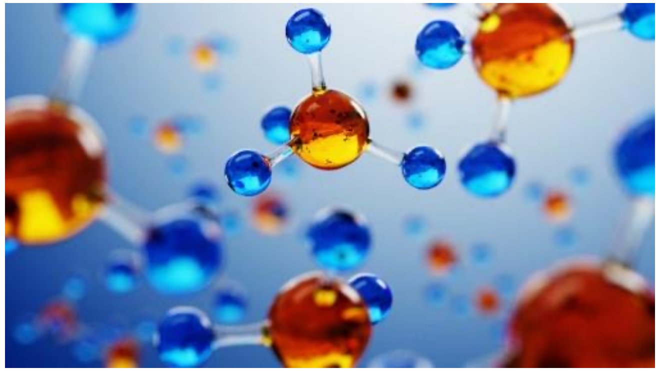
Reverse-engineering the tyre

- 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

Complexities of tyre analysis

Pyr-GCxGC-TOF-MS

Breakdown products



Potential toxicity

TD-GCxGC-TOF-MS

Reaction products

Organic composition

1. Naturally-derived chemicals
2. Synthetic polymer breakdown products
3. PAHs
4. Vulcanisation accelerators
5. Terpenoids from natural rubber
6. Benzothiazoles
7. PPD compounds

Functional group		Average concentration µg/mg
Allenes		**0.105**
Acyclic allenes	1	0.105
Benzenoids		**22.856**
Acenaphthylenes		0.084
Anthracenes	3	0.130
Benzene and substituted derivatives	2	19.956
Fluorenes		0.486
Naphthalenes		1.043
Phenalenes	3	0.055
Phenanthrenes and derivatives		0.281
Pyrenes		0.821
Hydrocarbons		**17.107**
Saturated hydrocarbons		0.002
Unsaturated hydrocarbons		17.105
Lipids and lipid-like molecules		**22.597**
Fatty Acyls	4 5	1.927
Prenol lipids		20.670
Organic acids and derivatives		**0.266**
Carboxylic acids and derivatives		0.266
Organic nitrogen compounds		**1.872**
Organonitrogen compounds		1.872
Organoheterocyclic compounds		**3.457**
Azolidines		0.940
Benzimidazoles		0.001
Benzothiazoles	6	0.918
Benzotriazoles		0.002
Oxepanes		1.410
Quinolines and derivatives	7	0.169
Triazines		0.017
Organometallic compounds		**0.034**
Organometalloid compounds		0.034

Known tyre additives

- 28 substances identified so far…

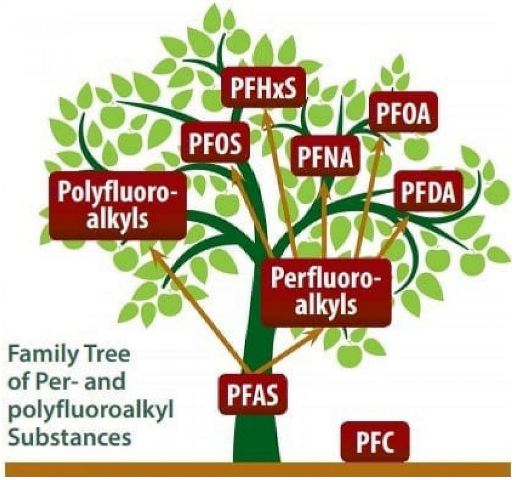
ng/mg	Number	Average concentration per tyre	Maximum concentration of any one compound
Antioxidant/antiozonant/heat protectant	12	2,567	5,717
Vulcanisation process	7	1,087	1,875
Silica or silane	4	34	18
Other	5	1,698	5,503
Total	**28**	**5,386**	**13,113**

Breakdown products

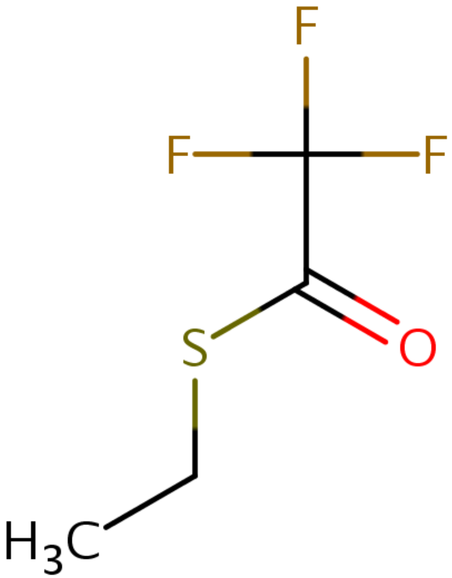
- Compounds derived from…

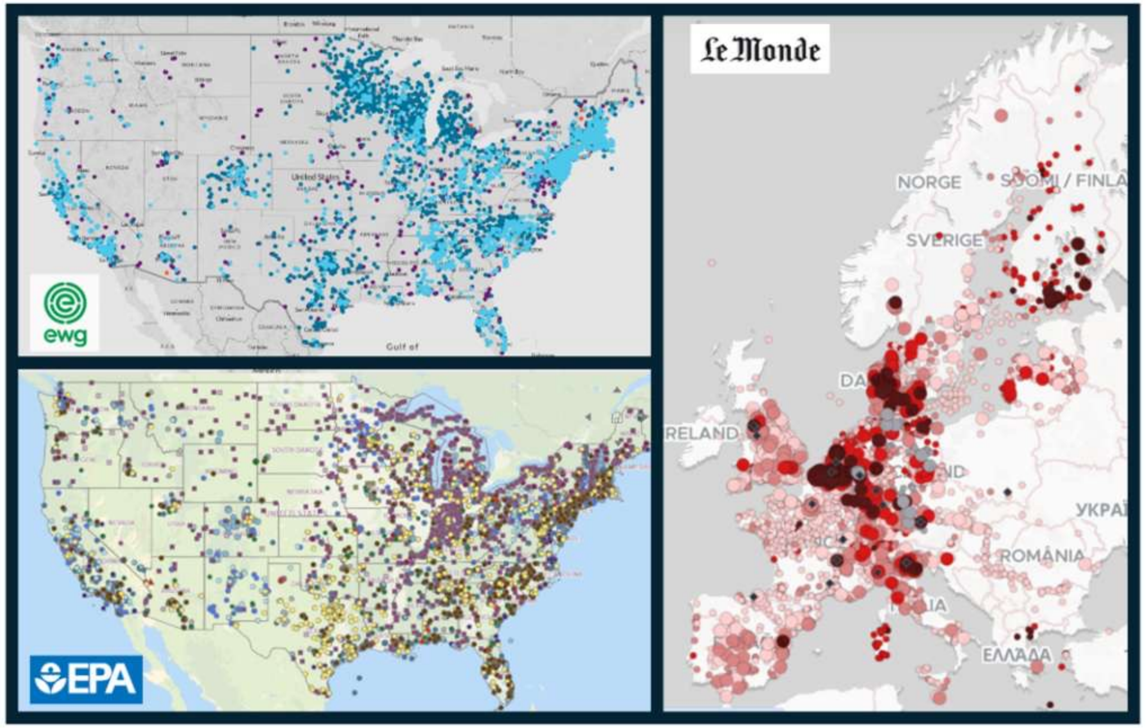
ng/mg	Number	Average concentration per tyre	Maximum concentration of any one compound
Natural rubber	10	32,008	96,707
Styrene-butadiene rubber	27	26,940	42,333
Extender oil	23	2,529	10,916
Other polymers	6	1,230	11,036
Antioxidants	5	30	112
Vulcanisation accelerator	4	171	652
Total	**75**	**62,908**	**96,707**

…And the opposite … forever chemicals



- Potentially infinite set of fluorinated compounds
- >10,000 codified
- For example, Ethanethioic acid, trifluoro-, S-ethyl ester
- $C_4H_5F_3OS$
- On the US EPA PFAS list





Insights from reverse-engineering

Headline	What we see in the numbers	Likely formulation reason
OE1 has the most PAHs	Highest mean aromatics+PAHs of any major make, ~30% above OE5 and ~60% above OE2.	Heavy use of aromatic extender oils and carbon black to hit OE1's high-speed, low-deformation targets.
OE2 skews towards aliphatics	Some of the lowest PAH totals.	Use of high-silica + aliphatic process oils to cut rolling resistance within EU PAH limits.
OE3 shows halogens	Only major brand with clear presence of halogens.	Brominated or chlorinated flame-retardant traces – potentially manufacturing process contamination
OE4 is chemically "middle-of-the-road"	Moderate across all organic groups; PAHs ~15% below OE1 and 5-10% above OE5.	OE4's silica-rich tread compounds reduce aromatic oils but keep a sizable hydrocarbon backbone for wear resistance.
OE5 vs OE6	Similar PAH levels but OE5 carries ~14% more aliphatics.	OE5 tends to favour higher molecular-weight softeners for grip.

Chemistry - gases

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Sampling system

- Accommodates whole tyre
- Clean, steel internal surface
- Insulated chamber
- Fan for even heat distribution
- Lamps as heat source
- Thermal desorption tube connection

Test results

- 100s of VOCs released in each chamber exposure
- Background VOCs in chamber were measured and subtracted from VOCs emitted from tyres
- Recurrent species in all samples

	Aniline	Methyl Isobutyl Ketone	Benzo-thiazole	Methyl-cyclo-hexane	Cyclo-hexane	1,3-dimethyl-benzene	*n*-hexane	Toluene	2-methyl-2-Propan-amine	*p*-xylene
New Tyre	1.73	3.01	1.23	-	0.33	-	0.17	1.00	1.59	2.79
Old Tyre	0.15	2.11	0.69	0.12	0.01	0.86	0.19	0.91	-	0.29
Small Tyre	1.92	1.51	0.99	1.45	0.67	0.84	0.54	0.64	0.35	0.01
Large Tyre	2.41	1.59	1.08	0.91	0.65	0.59	0.45	0.47	-	0.01

Emission rates at T = 25°C in 10^{-2} g h^{-1} per tyre

Box model results for Los Angeles (1)

Assumptions

Boundary layer height = 1 km

Air is completely well-mixed within the boundary layer

Temperature = 25 °C (mean temperature in June)

Number of vehicles = 2.3 million (LA city)

[OH] = 5×10^{6} molecules cm^{-3} (midday peak in LA)

Ozone (O_3) and Secondary Organic Aerosol (SOA) formation potentials from literature

Box model results for Los Angeles (2)

Compound	CAS #	molar mass / g/mo	chamber emission rate (ER) / mol	LA City ER / molec cm-2 s-	VOC m	O3 rate	O3 vmr / p	Y SOA yiel	SOA / ug/
p-Xylene	106-42-3	106.17	8.89E+19	1.05E+12	3.36E+07	5.84	76.95	0.123	3.18E+00
Benzene, 1,3-dimethyl-	108-38-3	106.17	4.20E+19	4.95E+11	9.82E+06	9.75	37.52	0.0865	6.53E-01
m-xylene	108-38-3	106.17	4.20E+19	4.95E+11	9.82E+06	9.75	37.52	0.0865	6.53E-01
Toluene	108-88-3	92.14	4.12E+19	4.86E+11	3.44E+07	4	53.86	0.03	7.93E-01
n-decane	124-18-5	142.28	1.00E+19	1.18E+11	6.46E+06	0.68	1.72	0.055	2.73E-01
Benzene	71-43-2	78.11	9.53E+18	1.12E+11	3.12E+07	0.72	8.80	0.02	4.80E-01
n-nonane	111-84-2	128.26	5.20E+18	6.14E+10	3.40E+06	0.78	1.04	0.03	7.85E-02
n-tetradecane	629-59-4	198.39	4.91E+18	5.79E+10	2.77E+06	0.51	0.55	0.52	1.11E+00
n-undecane	1120-21-4	156.31	4.60E+18	5.43E+10	2.84E+06	0.61	0.68	0.08	1.75E-01
1, 2, 4-Trimethylbenzene	95-63-6	120.19	4.22E+18	4.98E+10	7.95E+05	8.87	2.76	0.05	3.06E-02
Naphthalene	91-20-3	128.17	4.00E+18	4.72E+10	1.07E+06	3.34	1.40	0.473	3.90E-01
n-tridecane	629-50-5	184.36	3.95E+18	4.66E+10	3.23E+06	0.53	0.67	0.5	1.24E+00
Ethyltoluene	622-96-8	120.19	3.53E+18	4.16E+10	1.82E+06	4.44	3.16	0.035	4.89E-02
Ethylbenzene	100-41-4	106.17	2.03E+18	2.40E+10	1.57E+06	3.04	1.87	0.03	3.62E-02
o-xylene	95-47-6	106.17	9.02E+17	1.06E+10	3.59E+05	7.64	1.07	0.123	3.39E-02
n-Propylbenzene	103-65-1	120.19	6.75E+17	7.97E+09	7.13E+05	2.03	0.57	0.05	2.74E-02
Methylnaphthalene	90-12-0	142.2	6.25E+17	7.38E+09	1.11E+05	3.06	0.13	0.473	4.03E-02

Results

$[O_3]$ = 322 ppb (*cf*. max in summer 2024 = ~50 ppb)

SOA = 7.6 µg m^{-3} (*cf*. max in 2024 = ~30 µg m^{-3})

Conclusions

While most likely an overestimate due to model assumptions, these results indicate that tyre VOC emissions may represent a non-negligible (and so far, overlooked) source of secondary pollutants in urban environments

Conclusion

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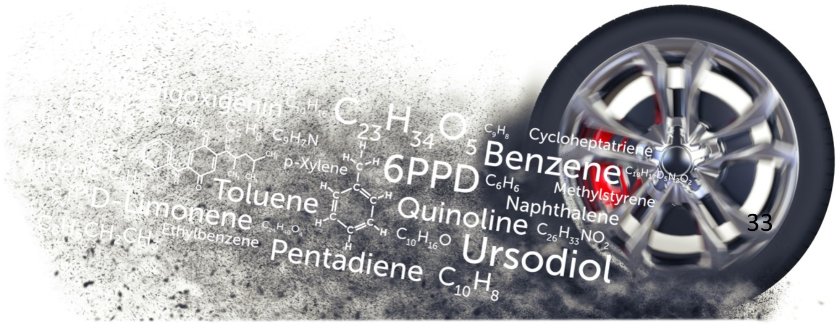
EQUA real-world test database

Key messages

- It's complex
- It's not going away
- There is much we don't understand
- But knowledge is progressing fast
- But we need to make sure we ask the right questions



Further insights

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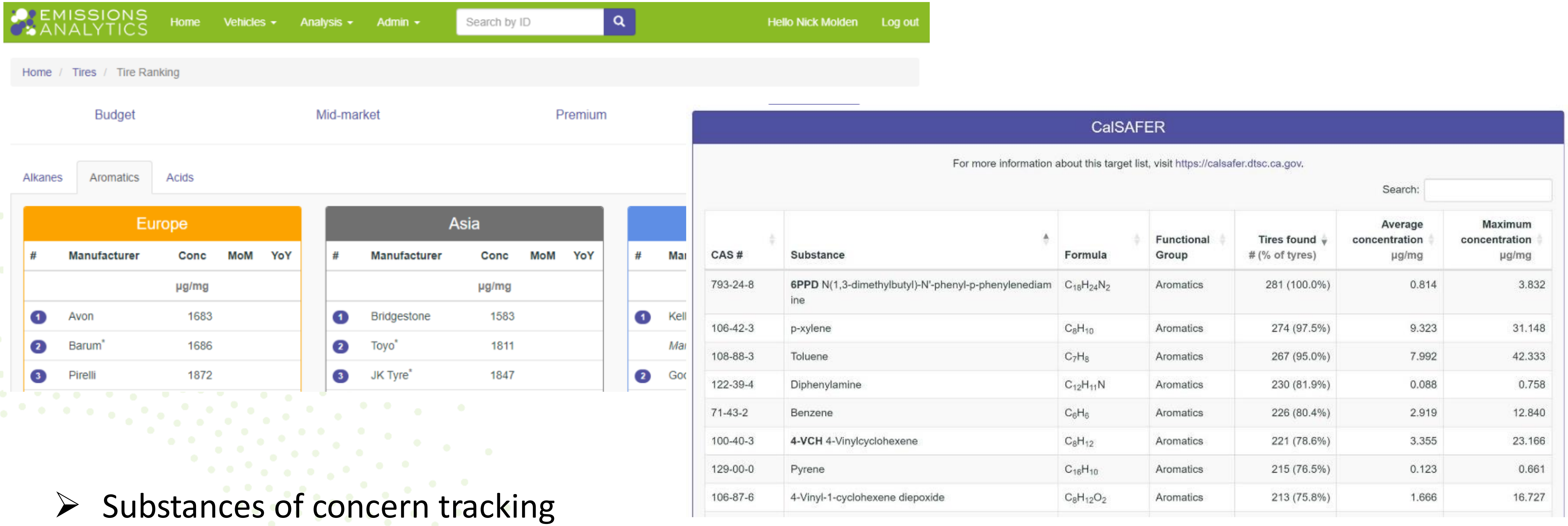
Tyre Emissions Research Consortium

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

Tyre chemical fingerprint database



Europe				
#	Manufacturer	Conc	MoM	YoY
		μg/mg		
1	Avon	1683		
2	Barum*	1686		
3	Pirelli	1872		

Asia				
#	Manufacturer	Conc	MoM	YoY
		μg/mg		
1	Bridgestone	1583		
2	Toyo*	1811		
3	JK Tyre*	1847		

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

Thank you.

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

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