

Characteristics of tyre dust in polluted air

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3 **CHARACTERISTICS OF TYRE DUST IN**
4 **POLLUTED AIR: STUDIES BY SINGLE PARTICLE**
5 **MASS SPECTROMETRY (ATOFMS)**
6

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1 **Abstract**

2 There is a paucity of quantitative knowledge on the contributions of non-exhaust (abrasion
3 and re-suspension) sources to traffic emissions. Abrasive emissions can be broadly
4 categorised as tyre wear, brake wear and road dust/road surface wear. Current research
5 often considers road dust and tyre dust as externally mixed particles, the former mainly
6 composed of mineral matter and the latter solely composed of mainly organic matter and
7 some trace elements. The aim of this work was to characterise tyre wear from both
8 laboratory and field studies by using Aerosol Time-Of-Flight Mass Spectrometry
9 (ATOFMS). Real-time single particle chemical composition was obtained from a set of
10 rubber tyres rotating on a metal surface. Bimodal particle number size distributions
11 peaking at 35 nm and 85 nm were obtained from SMPS/APS measurements over the
12 range 6-20,000 nm. ATOFMS mass spectra of tyre wear in the particle size range 200-
13 3000 nm diameter show peaks due to exo-sulphur compounds, nitrate, Zn and ions of high
14 molecular weight ($m/z > 100$) attributed to organic polymers. Two large ATOFMS datasets
15 collected from a number of outdoor studies were examined. The former was constituted of
16 48 road dust samples collected on the roads of London. The latter consisted of ATOFMS
17 ambient air field studies from Europe, overall composed of more than 2,000,000 single
18 particle mass spectra. The majority (95%) of tyre wear particles present in the road dust
19 samples and atmospheric samples are internally mixed with metals (Li, Na, Ca, Fe, Ti), as
20 well as phosphate. It is concluded that the interaction of tyres with the road surface
21 creates particles internally mixed from two sources: tyre rubber and road surface
22 materials. Measurements of the tyre rubber component alone may underestimate the
23 contribution of tyre wear to concentrations of airborne particulate matter. The results
24 presented are especially relevant for urban aerosol source apportionment and $PM_{2.5}$
25 exposure assessment.

26

1 Keywords: Tyre dust; road surface wear; non-exhaust emissions; road traffic; ATOFMS

2

3 **1. INTRODUCTION**

4 Air quality management is an essential aspect of environmental policy. In 2005, the
5 European Commission published its Thematic Strategy on Air Pollution under the 6th
6 Environmental Action Programme: The Clean Air For Europe (CAFE, 2005) programme,
7 aiming to establish a long-term policy strategy targeting the adverse effects of air pollution
8 on human health and environment. Vehicular traffic is known to be one of the major, if not
9 the largest, source of primary atmospheric particulate matter (PM) in the urban
10 environment (EEA, 2009).

11

12 Road traffic emissions comprise not only tailpipe exhaust emissions but also non-exhaust
13 emissions derived from the vehicle-induced resuspension of dust deposited on the road,
14 and from the direct emissions from vehicle wear (brakes, tyres, discs etc.). Road dust is
15 comprised of soil and materials that arise from mechanical abrasion including wear of
16 pavement, tyres, brakes and clutches, as well as corrosion of chassis, bodywork, and
17 other vehicle components; and corrosion of street signs, guiderails, and fencing (Luhana et
18 al., 2004). Road dust is a chemically complicated mixture with a multitude of sources,
19 including natural sources (e.g., soil, plant fragments and other biological materials) and
20 traffic-related sources.

21

22 Traffic related non-exhaust emissions are currently not subject to legislative controls, and
23 consequently these emissions are increasingly significant contributors to the
24 environmental burden of particles as exhaust particle emissions decrease (Denier van der

1 Gon et al., 2013). Following the recent review of Pant and Harrison (2013), the four
2 biggest components of non-exhaust particles are:

3

4 *Brake Wear*

5 Frictional contact between brake system components during forced deceleration is an
6 important source of particulate matter emissions from motor vehicles. Gietl et al. (2010)
7 found that barium comprises 1.1% of brake wear (PM₁₀) particles from the traffic fleet as a
8 whole, allowing its use as a quantitative tracer of brake wear emissions at other traffic
9 influenced sites. Dall'Osto et al. (2013) found that Fe-Cu can also be used as a tracer of
10 brake wear. These elements are typical traffic markers, as the abrasion of brakes
11 produces particles characterised by high concentrations of Cu, Ba, Zn and Fe (Sanders et
12 al., 2003; Johansson et al., 2008).

13

14 *Mineral Dust*

15 The composition of road dust has been found to be dominated by elements and
16 compounds typically associated with crustal material (Ca, Ti, and minor trace elements
17 such as La, Ce, Ga and Sr.). Road dusts and roadside soils often also contain significant
18 concentrations of a range of metals, including Pb, Cu, Cd, and Zn, indicative of
19 contamination by road vehicle emissions. The road dust consists primarily of soil derived
20 minerals (60%) with quartz averaging 40-50% and remainder being clay minerals such as
21 albite, microcline, chlorite and muscovite originating from surrounding soils. Organic matter
22 primarily originating from plant matter is also present (Gunawardana, 2012).

23

24 *Tyre Wear*

25 Tyre wear particles are produced from the interaction of tyres with the roadway surface.
26 Generally, tyres comprise a rubber compound reinforced with steel wires and textile. At

1 present, very few reliable estimates of tyre wear in the ambient air are available, primarily
2 due to limitations in the chemical markers used to quantify this type of PM. Previous
3 research has shown tyre dust particles to be elongated particles with mineral incrustations
4 from the road surface, which are quite different from tread particles produced by grinding
5 or abrading a tyre tread (Kreider et al., 2010).

6 7 *Road Surface Wear*

8 Particles abraded from the road surface also become suspended, either directly or as
9 resuspension from road surface dust. Their composition reflects that of the road surfacing
10 materials: typically minerals with a bitumen binder.

11
12 While the brake wear is directly generated from brake components, and road dust
13 comprises more general mineral components, the research on tyre dust has been less
14 exhaustive and far less is known of its characteristics (Pant and Harrison, 2013). Several
15 studies have been conducted to characterise tyre wear particles (Camatini et al., 2001;
16 Dahl et al., 2006; Gustafsson et al., 2008; Sjödin et al., 2010; Lee et al., 2013). As regards
17 the contribution to urban PM concentrations, results indicated that tyre concentrations in
18 the PM₁₀ fraction are low with averages ranging from 0.05 to 0.70 µg m⁻³, representing an
19 average PM₁₀ contribution of 0.84% (Panko et al., 2013). Kwak et al. (2013) also reported
20 a minor amount of tyre wear in urban dust, whereas the main proportion consisted of
21 crustal matter generated from road surface wear and road dust. This finding is consistent
22 with previous conclusions of Boulter (2005), who reported that less than 10% of car tyre
23 wear materials are emitted as PM₁₀ under 'typical' driving conditions and by Gehrig et al.
24 (2004), who concluded that tyre wear accounted for 7.5% of PM₁₀ at a kerbside site and
25 2% of PM₁₀ at an urban background site. Recently, Harrison et al. (2012a) reported
26 separate estimation of the contributions of brake dust, tyre dust, and resuspension to

1 particle mass in the range 0.9-11.5 μm aerodynamic diameter of 55%, 11% and 38%,
2 respectively. As regards the tyre dust chemical composition, automobile tyre rubber is
3 composed of 40-60% rubber polymers, 20-35% reinforcing agents/fillers such as carbon
4 black or silica, and 15-20% mineral oils such as extender oils/ softeners. The composition
5 of the rubber depends on where in the tyre the rubber is used. Zinc typically comprises
6 about 1% of tyre mass and Zn in road dust is often derived primarily from tyre wear
7 (Adachi and Tainosho, 2004), although many other sources of Zn exist in urban areas
8 (Pant and Harrison, 2013) and this element should not be regarded as a specific tyre wear
9 marker. The key tracer components of tyre wear include n-alkanes, n-alkanoic acids,
10 PAHs, benzothiazoles and trace metals. Overall, Pant and Harrison (2013) reported that
11 tyre dust may have significant difference in composition among different countries.

12

13 The objective of this study was to reduce the uncertainty regarding tyre wear contributions
14 in urban air. It used single particle mass spectrometry (SPMS), which gives direct insights
15 into the mixing state of aerosols. Single particle analysis, as in SPMS, allows
16 determination of whether a population of particles is “internally” (each single particle
17 belonging to the aerosol population presents the same chemical composition as the bulk
18 composition) or “externally” (single particles of different chemical compositions) mixed. In
19 order to do so:

- 20 • a tyre wear experiment was run in the laboratory with a rubber tyre moving on a metal
21 surface in order to evaluate the chemical composition of aerosolised tyre fragments;
- 22 • a large number of road dust samples were collected in order to estimate the tyre dust
23 content;
- 24 • tyre dust mass spectra were sought in data from a number of ambient field studies
25 carried out in different locations in which an Aerosol Time-of-Flight Mass Spectrometer
26 (ATOFMS) was used for acquisition of compositional data on individual particles.

1

2 One of the major problems in the analysis of non-exhaust PM using field data has been
3 the difficulty in distinguishing between wear and tear emissions and road dust since the
4 chemical composition is often very similar (Bukowiecki et al., 2010; Pant and Harrison,
5 2013). The ATOFMS cannot provide quantitative aerosol mass loading concentrations, but
6 its unique strength relies in the fact that it can monitor in real time variations in the single
7 particle composition. Previous single particle studies have identified rubber particles from
8 tyre wear experiments in the laboratory and found Zn using SEM-EDX (Scanning Electron
9 Microscope-Energy Dispersive X-ray Spectroscopy) analysis (Camatini et al., 2001).
10 Adachi and Tainosho (2004) found single particle tyre tread being associated with ZnO. In
11 this study we use single particle mass spectrometry which gives more statistically robust
12 results through characterisation of the many thousands of single particle mass spectra
13 obtained. Nevertheless, it is worth pointing out that a limitation of this study is that it is a
14 laboratory study which does not fully represents real world conditions. However, this
15 unique single particle study allows us to study the mixing state of tyre dust, a source of
16 urban aerosol not well characterised to date.

17

18 **2. METHODOLOGY**

19 **2.1 Instrumentation**

20 During the experiment instruments deployed were:

21

22 ATOFMS (Model 3800-100, TSI, Inc.) collects bipolar mass spectra of individual aerosol
23 particles. Ambient aerosol is focused into a narrow particle beam for sizes between 100
24 nm and 3 μm (vacuum aerodynamic diameter). Thus, a positive and a negative ion
25 spectrum of a single particle are obtained. The mass spectrum is qualitative in that the
26 intensities of the mass spectral peaks are not directly proportional to the component mass

1 but are dependent on the particle matrix, the coupling between the laser and the particle
2 and the shot to shot variability of the laser. However, the ATOFMS can provide
3 quantitative information on particle number as a function of composition; providing a
4 measure of all particle components and can be used to assess mixing state. During this
5 study, the ART-2a neural network algorithm was used for classifying the large number of
6 particles collected. The TSI ATOFMS datasets were imported into YAADA (Yet Another
7 ATOFMS Data Analyzer) and single particle mass spectra were grouped with Adaptive
8 Resonance Theory neural network, ART-2a (Song et al., 1999). The parameters used for
9 ART-2a in this experiment were: learning rate 0.05, vigilance factor 0.85, and iterations 20.
10 Further details of the parameters can be found elsewhere (Dall'Osto and Harrison, 2006).
11 An ART-2a area matrix (AM) of a particle cluster represents the average intensity for each
12 m/z for all particles within a group and therefore reflects the typical mass spectrum of the
13 particles within a group. The ART-2a algorithm generated a number of clusters used to
14 describe the dataset herein presented.

15

16 Aerodynamic Particle Sizer (APS TSI 3321, size range 523-20,000 nm, aerodynamic
17 diameter) and two Scanning Mobility Particle Sizer (SMPS TSI3071/CPC 3022A size
18 range 15 nm-800 nm, and SMPS TSI3085/CPC3025 size range 5 nm-160 nm, mobility
19 diameter) were used to provide the aerosol size distributions of the atmospheric dust
20 particles herein described.

21

22

23

24 **2.2 Laboratory Tyre Dust Experiment**

25 The tyre wear rig (Fig. 1) comprises a vehicle wheel and tyre pressed under load against a
26 large rotating metal wheel. Friction was generated by setting an angle between the vehicle

1 wheel and the metal wheel, simulating a cornering manoeuvre. The experiment was run
2 for a total number of 25 hours. The first part ran on 18th April 2011 from 11:30 till 20:00.
3 Experiments were run on different tyres (HOMO 88H 185/65/R15 and Michelin 185/70/14)
4 and blanks were obtained by sampling the background and also with the metal wheel
5 rotating with no wheel attached. During night-time the aerosol instruments were left
6 sampling the background air. The morning after, on 19th of April 2011, the experiment was
7 repeated again between 0900 and 1230. Figure 2 shows the data collected in the lab
8 experiment. The sampling inlets were placed at distance of about 15 cm from the
9 tyre/wheel interface and connected to the instruments via a 1 m long 1/4 inch conductive
10 plastic tubing.

11

12 It is important to stress that the limitation of this study is the flat metal surface used to run
13 the rubber tyre. This does not represent real world conditions, as road wear is generated
14 from the friction between the tyre and the road, which occurs far more easily on
15 asphalt/concrete roads than on a smooth metal surface. However, this gives a unique
16 opportunity to study the chemical composition of tyre dust and then to see if such particles
17 can be found under real world ambient conditions.

18

19 **2.3 Single Particle Measurements of Road Dust Samples**

20 A number of road dust samples were collected at four different locations within the city of
21 London during the REPARTEE experiment (Harrison et al., 2012b). Samples were
22 collected between 8th October and 30th October 2006 from four different locations around
23 London. The four sites were very different from each other, in particular in relation to their
24 volumes of traffic (see map of the four sites in Harrison et al., 2012b). The four sites were
25 within 1 km of each other:

1 *A: Marylebone Road site (MR)*. This road is spread on 6 lanes with frequent congestion,
2 with traffic flows of over 80,000 vehicles per day.

3 *B: BT tower (BT)*. A side road situated on the corner between Cleveland Street and Maple
4 Street, within the congestion charge zone of London.

5 *C: Inner Circle of Regents Park (RR)*. Road situated within Regent's Park, with leaves and
6 soil often seen on the ground.

7 *D: Footpath in Regents Park (RP)*. This little pathway is made of concrete/stones and no
8 cars are allowed, although bicycles are.

9

10 Road samples were taken by sweeping the road surface with a brush into a small plastic
11 bag. A different brush was used for each location, and the brush was washed before the
12 collection. Forty-eight samples (12 each monitoring site) were taken during the month of
13 October 2006. Mass spectra from each dust sample were obtained by placing each dust
14 sample into a flask in a sonicator to create a suspension of dust particles under filtered lab
15 air flow. The aerosol was then directed into the ATOFMS inlet for analysis and about 500
16 single-particle mass spectra were collected per sample (2791 particles in total).

17

18 **2.4 Field Studies**

19 A number of field studies have been run by the University of Birmingham in the last
20 decade. The ATOFMS can be used with two different inlets. The ATOFMS TSI model
21 3800-100 uses an aerodynamic lens to direct particles to the sizing region of the
22 instrument (Su et al. 2004). By contrast, the ATOFMS TSI Model 3800 utilizes a simple
23 nozzle/skimmer inlet (Gard et al. 1997). In terms of particle collection efficiency, the
24 aerodynamic lens provides a major improvement toward smaller particle sizes ($<1 \mu\text{m}$). In

1 the following studies, the aerodynamic lens ATOFMS TSI 3800-100 system (200-3000
2 nm), was used:

- 3 • A remote marine site in the coastal area of Mace Head, Ireland (Dall'Osto et al.,
4 2010a).
- 5 • A cruise in the Tropical Atlantic Ocean in 2006 (Dall'Osto et al., 2010b).
- 6 • A cruise in the North Atlantic Ocean during MAP (Decesari et al., 2012).
- 7 • A regional site in the Po Valley, Italy in 2009 (Decesari et al., 2013).
- 8 • A regional site in Harwell, England in 2010 (Giorio et al., 2012).
- 9 • A roadside site in Birmingham, UK in 2005.
- 10 • A roadside site on Marylebone Road, London, UK in 2009.
- 11 • A roadside site in Barcelona (Spain) during the SAPUSS field study (Dall'Osto et al.,
12 2013).

13

14 **3. RESULTS**

15 **3.1 Laboratory Tyre Dust Experiment**

16 **3.1.1 Size distributions of tyre dust**

17 Figure 2 shows the plot of aerosol size distributions (both SMPSs and APS) taken during
18 the day of the tyre experiment. When the mean aerosol size distributions are plotted (Fig.
19 3), it is clear that a bimodal particle distribution is seen below 100 nm with modes at about
20 35 nm and 85 nm. Unimodal (70-90 nm) and bimodal (<10 and 30-60 nm) number size
21 distributions in the nano size range have been reported for tyre particles under low and
22 high speed conditions respectively (Mathissen et al., 2011). Dahl et al. (2006) found an
23 enrichment of tyre particles between 15-50 nm using a road simulator. They identified two
24 types of particle: one comprising mineral oils from the softening filler, the other of soot-like
25 agglomerates from the carbon-reinforcing filler material. Our APS results showed little
26 enhancement of coarse particles above background across the whole size range during

1 experiments 1 and 2. In summary, few particles above 1 μm were detected, although those
2 may significantly contribute to mass.

3

4 Kreider et al. (2010) characterized the physical and chemical properties of particles
5 generated from the interaction of tyres and road surfaces. However, these particles were
6 distributed in the very large coarse mode, spanning from 4-6 μm to 265-280 μm with the
7 mode centred at approximately 50-75 μm .

8

9 **3.1.2 Chemical speciation of tyre dust**

10 Art-2a was run on the 25,000 ATOFMS single particle mass spectra detected during the
11 lab studies. A number of Art-2a clusters were detected, most of which were associated
12 with background conditions. One cluster was found to peak during the experiment when
13 the tyre was running on the metal surface. The spectrum obtained is shown in Figure 4,
14 and is the average of the two different tyres used. Given that the two tyres generated the
15 same single particle mass spectra, the results are presented as representing tyre dust as
16 generated in the laboratory. In the positive mass spectrum there is a main peak at m/z 39,
17 which could be due to potassium or an organic fragment. Other organic peaks can be seen
18 at m/z 41, 43 and 69. The peaks at m/z 69, 81 and 95 (particularly the strong peak at m/z
19 95) may represent the exo-sulphur aromatic series (sulphur attached to an aromatic ring)
20 (McLafferty, 1993). Sulphur is used as vulcaniser in the tyre, so S internally mixed with
21 organic compounds is expected in tyre dust. Zinc (Zn) is added to tyre tread as zinc oxide
22 and organozinc compounds to facilitate the vulcanization process. However, Zn is emitted
23 from brake wear, motor oil and other sources and cannot be used as a unique tracer for
24 tyre wear (Lough et al., 2005). Zn can be detected in ATOFMS single particle mass
25 spectra. For example, a Zn particle type detected in a steel industry study showed the
26 presence of ions at m/z 64, $[\text{Zn}]^+$; 97, $[\text{ZnCl}]^+$ and -169 , $[\text{ZnCl}_2]^-$ (Dall'Osto et al., 2008).

1 During this study Zn (query search m/z 64 without the presence of m/z 48 [Ti], Dall'Osto et
2 al., 2010b) was detected in about 16% of the particles. The negative mass spectrum
3 shows the presence of peaks due to CN (m/z -26, -42) as well as nitrate (m/z -46, -62)
4 which are not expected. Nitrogen compounds in tyre dust are usually not seen and the
5 mass spectra from the ATOFMS may be simply a representation of the extreme sensitivity
6 to K and nitrate of the instrument (Gross et al., 2000). A number of unique peaks can be
7 seen in the high molecular weight ($m/z > 100$) range. The peaks at m/z 140 and m/z -163
8 may be due to potassium nitrate ((K_2NO_3) and $(K(NO_3)_2$, respectively (McLafferty, 1993),
9 but also to unidentified organic compounds. Other unique peaks at m/z 173, m/z -127, m/z
10 -146 can be seen. These are not characterised and are likely due to rubber copolymer
11 components.

12

13 **3.2 Single Particle Experiment with Road Dust Samples**

14 The ATOFMS spectrum obtained from the tyre experiment above was compared with the
15 48 road dust samples using YAADA. Only few single particle mass spectra (< 10) identical
16 with the laboratory generated tyre dust were found. Overall, less than 0.1% of the road
17 dust mass spectra matched the tyre road dust sample. This implies that tyre dust was not
18 found in the same form that was generated in the laboratory. However, by searching the
19 unique peaks associated with the tyre material (m/z 140, m/z 173, m/z -163), it was found
20 that about 4% of the particles were associated with such unique markers. This implies that
21 the mixing state of the particles found in the real world is different from the laboratory
22 study. An average spectrum of the particles containing specific tyre dust m/z peaks is
23 shown in Fig. 5. It is clear other peaks are present. Fig. 6 shows the difference, taken as:
24 Difference (Fig. 6) = real world road dust with tyre markers (Fig. 5) minus laboratory tyre
25 dust (Fig. 4), and scaled relative to the two biggest peaks (m/z 39 and m/z -62).

26

1 The difference comprises mainly ions due to crustal elements (particularly Li, Na, Al, Fe
2 and Si). The positive mass spectrum clearly shows the peaks associated with Ca (m/z 40)
3 and Fe (m/z 56). Additionally minor peaks are Al (m/z 27), and this is confirmed clearly by
4 the negative peak at m/z -43 (AlO). Peaks with m/z of 48 and 64 are due to Ti and TiO,
5 another common marker seen in dust, and at m/z 7 is attributed to Li. The negative peaks
6 include -26 (organic peak), EC (-48) and phosphate (-63, -79). The presence of the
7 phosphate may be due to lubricating oil - a marker that the ATOFMS is sensitive to
8 (Spencer et al., 2006). The signal at m/z 64 could be due to Zn, but the signal could also
9 be associated with titanium oxide (TiO, m/z 64).

10

11 The results suggest that the tyre, when rotating on a real road surface, creates particles
12 internally mixed with the minerals contained in road surface materials. Hence, the tyre is
13 degrading the road surface, creating a particle internally mixed between tyre material and
14 road surface material. This is not a new observation, as a number of studies have already
15 pointed out this mechanism (Kreider et al., 2010). However, this study shows for the first
16 time that most, if not all, tyre dust particles are internally mixed with minerals coming from
17 the abrasion of the road surface. Additionally, whilst the study of Kreider et al. (2010)
18 focused on particles in the size range 4-280 μm , our study mainly characterise PM smaller
19 than 3 μm and more relevant to $\text{PM}_{2.5}$ exposures.

20

21 **3.3 Field Studies**

22 To provide further evidence, ATOFMS road dust markers (sum of m/z 140, m/z 173 and
23 m/z -163, peak area >100) were sought in a number of ambient field studies run in the
24 past. This very large ATOFMS dataset is an ensemble of field studies carried out by the
25 University of Birmingham (UK) in more than a decade, spanning from very remote open
26 ocean areas to heavily trafficked road sites (please see references reported in section 2.4 for

1 further details). Table 1 clearly shows that tyre related dust was not found at sites away
2 from urban agglomerates. Furthermore, it can be seen that the highest percentages were
3 found at roadside sites (London, Birmingham and Barcelona - about 2%) and in the road
4 dust samples collected (4%). Whilst Table 1 may appear simple, it comprises more than
5 2,000,000 single particle mass spectra collected across the European Continent.

6

7 **4. DISCUSSION AND CONCLUSION**

8 Road dust, of which crustal dust is a key component, consists primarily of coarse-sized
9 particles derived from different sources such as traffic, industrial emissions, mineralogical
10 dust etc. The composition of road dust shows spatial as well as temporal variation and it is
11 often difficult to classify dust unequivocally into crustal/re-suspended/direct emission etc.
12 Very few reliable estimates of tyre wear in the ambient air are available, primarily due to
13 limitations in the elemental markers which have been used to quantify this type of PM.

14

15 This study suggests that pure tyre wear particles are not often found in real world road
16 dust samples and ambient aerosol. By contrast, most of them are found internally mixed
17 with minerals and other substances, possibly including contributions from lubricating oil
18 and vegetative debris. It is important to note that, within the road dust samples, all the tyre
19 road dust particles were found in the samples taken on the roads (Marylebone Road and
20 the road next the BT tower), whereas no tyre dust-like spectra were found in the Inner
21 Circle of Regent's Park (RR) or in the Footpath in Regent's Park (RP) in the city of
22 London. This gives confidence in our ATOFMS markers and the results herein presented.
23 Our results are quantitatively very consistent with those of Kreider et al. (2010) and
24 quantitatively broadly consistent with those of Panko et al. (2013) in showing an
25 association of tyre rubber with mineral material.

26

1 The ATOFMS cannot provide quantitative measurements without appropriate scaling
2 factors (Dall'Osto et al., 2006). However, when looking at the particles containing
3 ATOFMS tyre wear markers (4% by number), we find that most of them by volume were
4 distributed in the size range 1-3 μm .

5
6 There is clearly a discrepancy in the size distributions of tyre particles measured in the
7 laboratory (mainly sub-100 nm) and those in the field studies (1-3 μm). If present in the
8 atmospheric samples, the sub-100 nm particles would not be detected by the ATOFMS.
9 The particle counting instruments showed only modest production of 1-3 μm particles in
10 the laboratory study, although sufficient to be detected by the ATOFMS, suggesting that
11 the mechanism of particle generation in the laboratory from friction between the tyre and a
12 smooth metal surface may be different from that on the road where the surface is rough.
13 However, earlier studies using rougher surfaces have also shown a predominance of
14 nano-sized particles (Dahl et al., 2006; Mathissen et al., 2011).

15
16 One consequence of our findings is that tyre wear obtained by abrading a tyre, e.g. by
17 using a coarse stainless steel file at between two and four different locations on each tyre
18 (Sadiktsis et al. 2012) may not be appropriate for toxicological studies. Our study shows
19 that the large majority of tyre dust particles in urban air are internally mixed with minerals.
20 This implies that field studies using chemical tracers for tyre wear and resuspension
21 particles may under-estimate those arising from tyre-road interaction and over-estimate
22 the resuspension component.

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1 **TABLE LEGEND**

2 **Table 1.** Percentages of tyre particles in ambient field studies run with the ATOFMS.
3 Twelve field studies were examined, with a total of more than 2 millions
4 particle mass spectra.
5

6 **FIGURE LEGENDS**

7
8 **Figure 1.** Photo of the tyre rig at the University of Birmingham. The arrow points
9 towards the point of contact between the tyre (on the left) and the metal wheel
10 (to the right).
11

12 **Figure 2.** The tyre dust lab experiment. Top chart shows the Art-2a ATOFMS particle
13 type associated to tyre dust (ATOFS counts/hour), middle charts show
14 aerosol size distributions (APS, SMPS, nano-SMPS) and bottom chart shows
15 the experimental mode used.
16

17 **Figure 3.** SMPS size distributions of the tyre experiment (and relative background). The
18 difference (average of diff exp 1 and diff exp 2) shows an enhancement of
19 particles at 35 and 85 nm.
20

21 **Figure 4.** ATOFMS art2a cluster associated to tyre dust in the laboratory.

22 **Figure 5.** Average spectra of road dust single particles containing tyre dust key m/z
23 peaks.
24

25 **Figure 6.** Difference between tyre dust (from lab study) and road dust with tyre markers.
26
27

1 **Table 1.** Percentages of tyre particles in ambient field studies run with the ATOFMS.
2 Twelve field studies were examined, with a total of more than 2 millions particle mass
3 spectra.
4

Monitoring site	Characteristic	% of tyre dust (by number of particles)
Mace Head	Marine	0%
North Atlantic	Marine	0%
Tropical Atlantic	Marine	0%
Po Valley	Regional background	0.5%
Harwell	Regional background	0.5%
Marylebone road	Roadside	2.5%
SAPUSS Barcelona	Roadside	2%
London streets	Road dust samples	4%

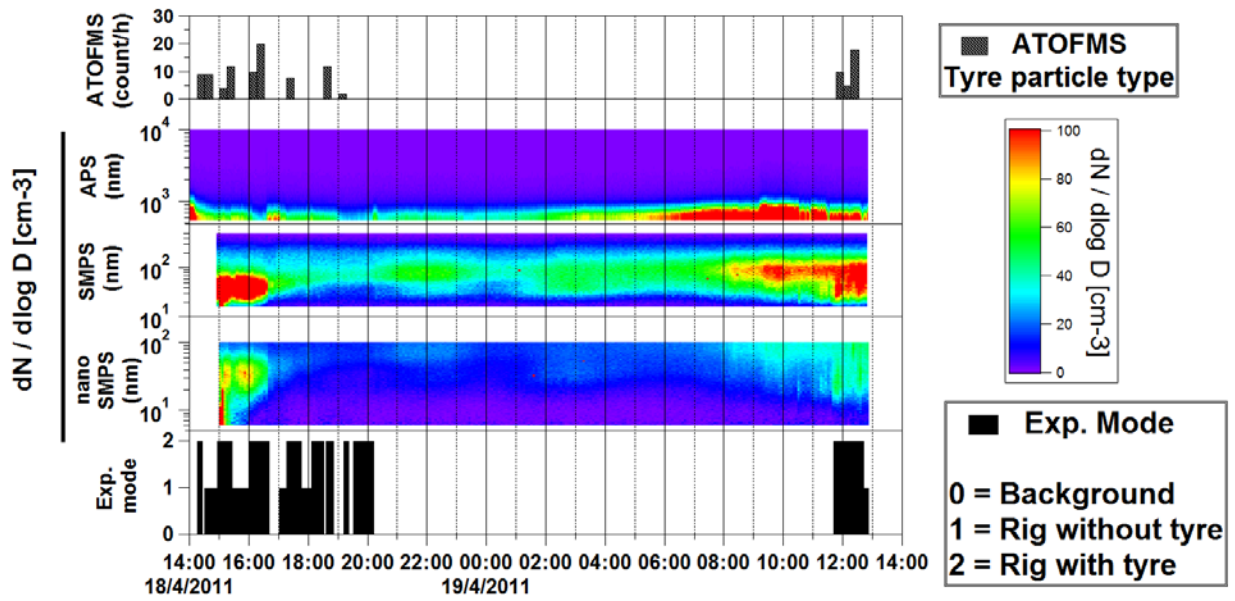
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Figure 1. Photo of the tyre rig at the University of Birmingham. The arrow points towards the point of contact between the tyre (on the left) and the metal wheel (to the right).

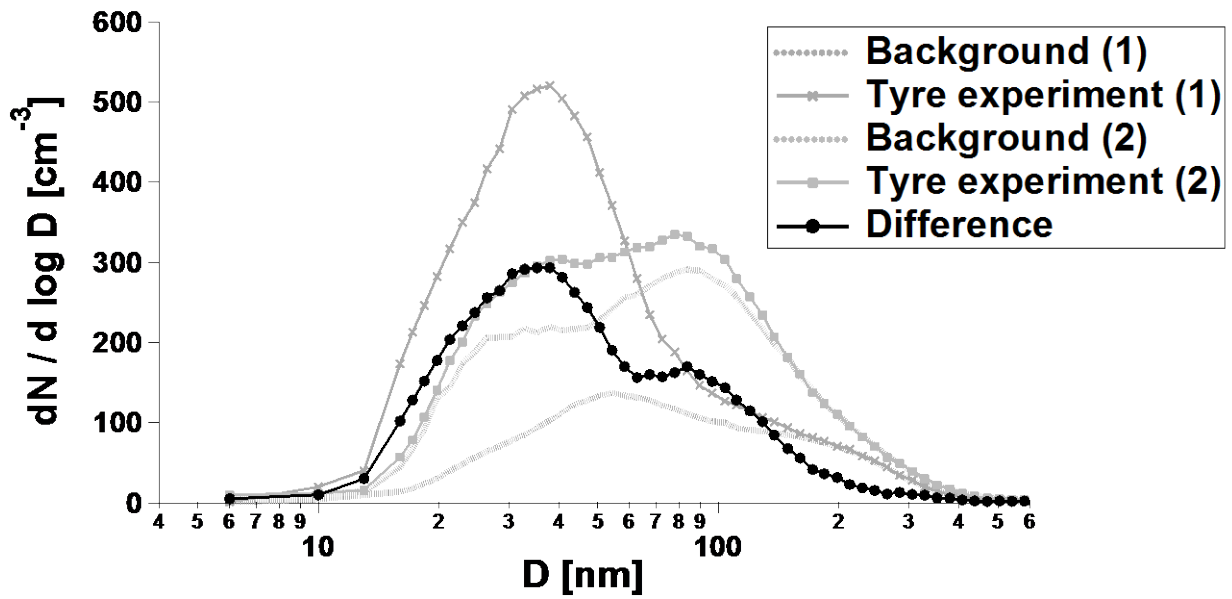
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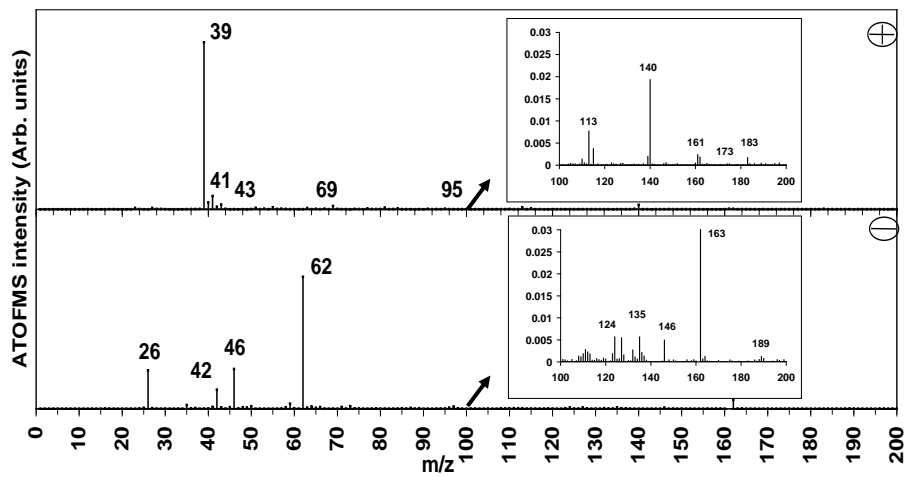
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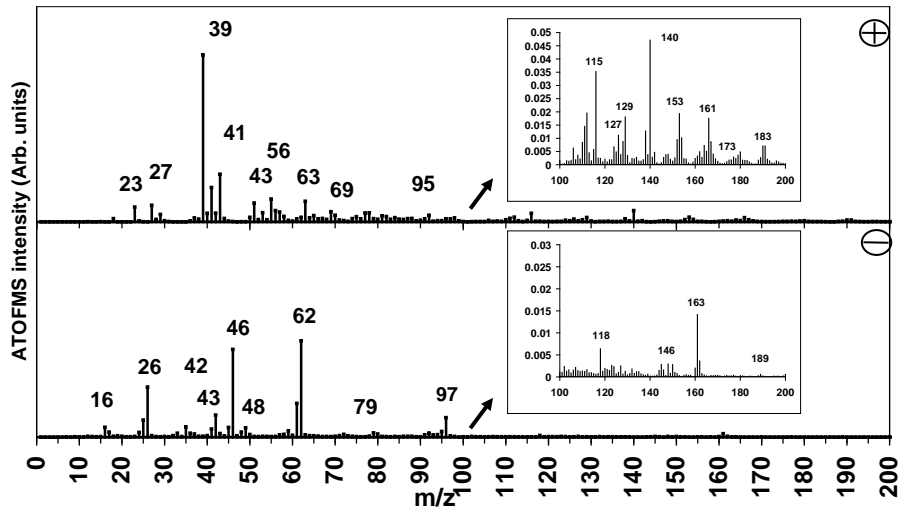
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8 **Figure 4.** ATOFMS art2a cluster associated with tyre dust in the laboratory.



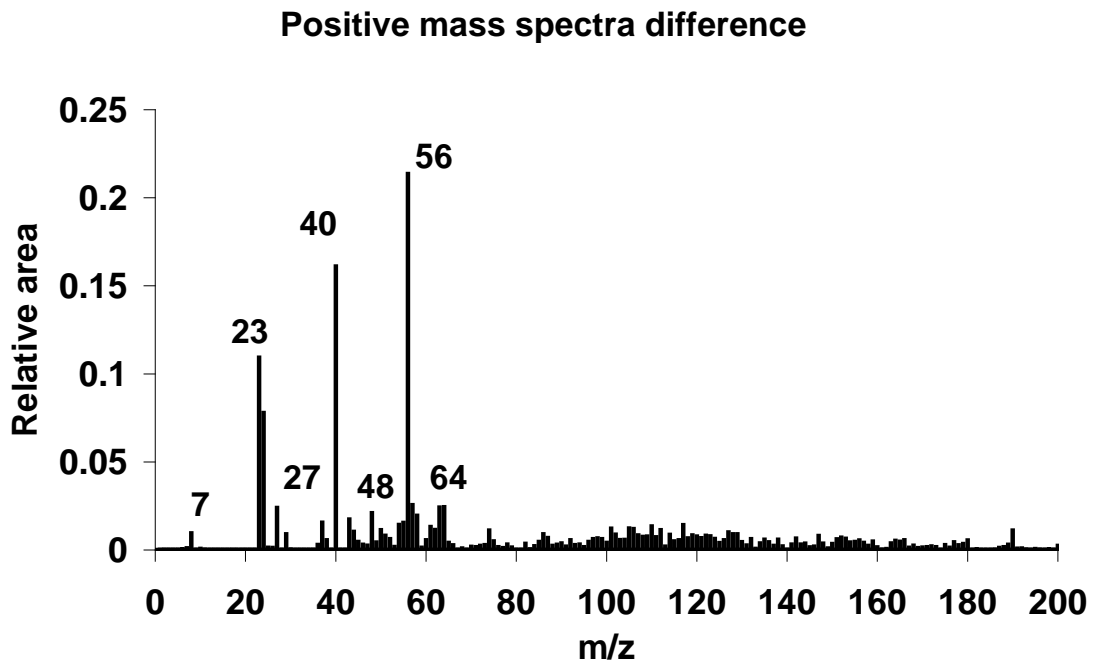
Tyre dust on road samples

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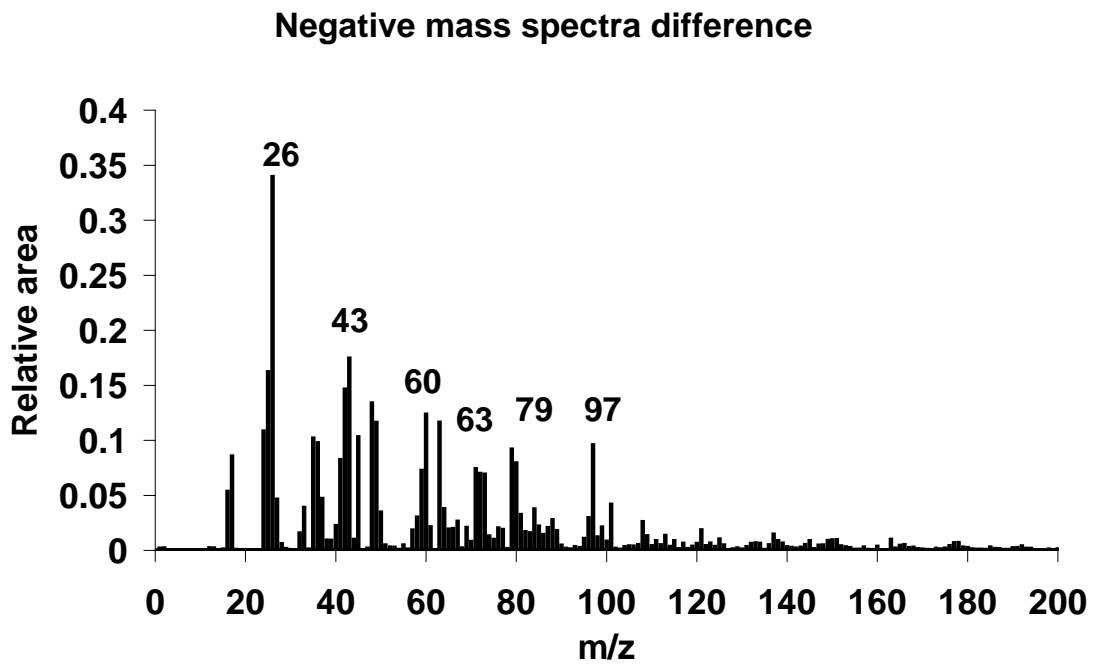
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